



HAL
open science

Spectroscopie de très haute sensibilité avec des molécules et métrologie des fréquences

Christophe Daussy

► **To cite this version:**

Christophe Daussy. Spectroscopie de très haute sensibilité avec des molécules et métrologie des fréquences. Optique [physics.optics]. Université Paris-Nord - Paris XIII, 2008. tel-00764983

HAL Id: tel-00764983

<https://theses.hal.science/tel-00764983>

Submitted on 13 Dec 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

UNIVERSITÉ PARIS XIII

laboratoire de physique des lasers
UMR 7538 CNRS

dossier de synthèse

présenté par

Christophe DAUSSY

pour obtenir

L'habilitation à diriger des recherches

*Spectroscopie de très haute sensibilité avec
des molécules et métrologie des fréquences*

Travaux présentés le 20/11/2008 devant le jury composé de:

Monsieur	Christian J. Bordé	
Monsieur	Azzedine Boudrioua	
Monsieur	Christian Chardonnet	
Monsieur	Jean-Marie Flaud	rapporteur
Monsieur	Marc Himbert	rapporteur
Monsieur	Terry Quinn	rapporteur
Monsieur	Trond Saue	président du jury

Remerciements

Le travail présenté dans ce mémoire a été mené au Laboratoire de Physique des Lasers de l'Université Paris XIII, dans l'équipe HOTES «horloges optiques et tests fondamentaux par spectroscopie et interférométrie atomique et moléculaire», dirigée conjointement par Christian J. Bordé et Christian Chardonnet. Mes remerciements vont d'abord à Messieurs Marc Himbert, Christian Chardonnet et Charles Desfrancois, qui se sont succédés à la direction du Laboratoire au cours de cette période.

Christian Chardonnet a encadré mes premiers pas dans la recherche. Je tiens à lui exprimer ma profonde reconnaissance pour son dynamisme, son enthousiasme et son engagement personnel tout au long de ce travail. Son rôle a été déterminant dans la réussite de cette aventure. Ses conseils et ses explications, tant sur le plan expérimental que sur la compréhension de la physique m'ont beaucoup apporté.

Christian J. Bordé s'est intéressé de très près au problème de la recherche de l'effet de non conservation de la parité dans les années 80. La perspective de franchir une nouvelle étape dans cette histoire l'a donc passionné. En proposant une approche originale pour la mesure de la constante de Boltzmann, il est à l'origine du projet que je développe actuellement dans l'équipe. Sa vision très large de la métrologie et de la spectroscopie a été déterminante pour guider le développement de cette expérience.

Je souhaite profondément remercier l'ensemble de l'équipe HOTES, Anne Amy-Klein, Benoît Darquié, Frédéric Du Burck, Olivier Lopez et Thanh Nguyen pour leur aide et leur disponibilité. Les années que j'ai passées en leur compagnie ont été à la fois très agréables et très enrichissantes scientifiquement et humainement. C'est en grande partie grâce à la qualité de leur travail que nous avons pu mener à bien les travaux présentés dans ce manuscrit.

J'ai une pensée toute particulière pour les thésards avec lesquels j'ai travaillé: Vincent Bernard, Thibaut Marrel, Michael Ziskind, Mickaël Guinet, Khélifa Djerroud et Cyril Lemarchand. Je remercie également les visiteurs, R.J. Butcher, A. Shelkownikov, qui m'ont fait bénéficier de toute leur expérience.

Le développement des différentes expériences n'a pu être menée à bien que grâce à la compétence des personnels techniques du laboratoire. Je remercie Jean-Yves Chauvet, Julien De Lapeyre De Bellair, Germaine Simon, Fabrice Wiotte pour la partie électronique de ce travail et pour leurs conseils sur les asservissements. Je remercie également Gérard Baqué, Jean Berry, Michel Fosse et Albert Kaladjian pour l'ensemble des réalisations mécaniques. Enfin, je remercie Thierry Billeton pour la partie optique, essentielle dans notre expérience ainsi que ainsi que Marc Barbier et Dejan Kocic de l'atelier d'informatique.

J'exprime mes vifs remerciements à M. Trond Saue, spécialiste des calculs de chimie quantique, notamment appliqués à l'évaluation de l'effet de la non conservation de la parité dans les molécules et qui a bien voulu présider le jury de soutenance.

Je suis très reconnaissant envers Messieurs Azzedine Boudrioua, Jean-Marie Flaud, Marc Himbert et Terry Quinn pour l'intérêt qu'ils ont manifesté à ce travail en acceptant de participer au Jury.

Enfin, je voudrais saisir cette occasion pour remercier l'équipe administrative du laboratoire, Martine Alster, Sabine Barbut, Solange Dousset, Nathalie Froger et Antonia Wilk. J'ai particulièrement apprécié leur grande disponibilité et l'efficacité de leur travail.

Table des matières

<i>Remerciements</i>	3
<i>Curriculum Vitae</i>	7
<i>Publications et communications</i>	13
<i>Introduction</i>	33
CHAPITRE I. Étude de la non conservation de la parité moléculaire	35
Introduction	35
I. L'effet NCP en chimie quantique	37
II. Expériences en cellules	38
A. Première expérience à très haute résolution	38
B. Deuxième test	43
C. Limites de l'expérience en cellule	45
III. Vers une mesure NCP en jet moléculaire	48
A. Le projet NCPMOL (ANR-05-BLAN-0091)	48
B. Résultats préliminaires	49
a) Spectroscopie de la molécule CHFCl	49
b) Spectroscopie des complexes de rhénium	50
c) Spectroscopie de l'uréthane	52
Conclusion	54
CHAPITRE II. Transfert de fréquence par fibre optique et application à la métrologie des fréquences	57
Introduction	57
I. Transfert de fréquence par liaison optique	60
A. Liaison par transfert d'une référence à 100 MHz	60
B. Liaison par transfert d'une référence à 1 GHz	63

II. Mesure de fréquences par laser femtoseconde	66
Introduction	66
A. Mesure de l'étalon CO ₂ /OsO ₄ à 10 μm	67
B. Mesure avec l'acide formique	70
C. Mesure de raies de l'iode autour de 500 nm	70
Conclusion	70
CHAPITRE III. Mesure de la constante de Boltzmann par spectroscopie laser	73
Introduction	73
I. La mesure de la constante de Boltzmann	74
A. La thermométrie acoustique	74
B. La mesure de la constante diélectrique	75
C. Principe de notre expérience	76
II. Première mesure optique de la constante de Boltzmann	77
A. Présentation du spectromètre	77
B. Premiers résultats	81
C. Forme de raie et analyse des données	83
a) La forme de la raie d'absorption	83
b) Nouvelle procédure d'analyse des données	84
III. Vers une mesure au niveau du ppm	86
A. L'expérience de deuxième génération	86
B. Derniers résultats et développements en cours	88
Conclusion	91
Conclusion et perspectives	93
Annexe : principales publications	99
Références	175

Curriculum Vitae

DAUSSY Christophe

Né le 16 mai 1972

Université Paris XIII, Institut Galilée, Laboratoire de physique des lasers (UMR 7538)

99 avenue J.-B. Clément 93430 Villetaneuse

Tel.: 01 49 40 33 73

Email : christophe.daussy@univ-paris13.fr

Depuis le 1^{er} septembre 1999 : **Maître de Conférences** (30^{ème} section) à l'Université Paris 13

- 6 mois de Congés pour Recherche ou Conversion Thématique (septembre 2003 – février 2004) pour le développement d'une liaison par fibre optique, appliquée à un transfert de fréquence entre le Laboratoire de Physique des Lasers et le BNM-SYRTE - Observatoire de Paris.
- 18 mois d'accueil en Délégation CNRS (février 2004 – septembre 2005) pour l'application de la liaison optique à la comparaison des étalons de fréquence de nos deux laboratoires via un laser femtoseconde.

Formation

1999 **-Stage Post-doctoral** au Laboratoire Primaire du Temps et des Fréquences, Observatoire de Paris.

Lasers / Etalon de temps / Chaîne de fréquence

1995-1999 **-Doctorat de physique** au laboratoire de physique des lasers
Sujet : « Premier test de très haute précision de violation de la parité dans le spectre de la molécule chirale CHFCIBr »
Thèse soutenue le 29/01/99 à l'Université Paris XIII, Mention très honorable avec félicitations

Directeur de thèse : Christian Chardonnet

Jury : Mme M.A. Bouchiat (présidente), M. J.M. Flaud (rapporteur), M. J.B. Robert (rapporteur), M. J. Baudon, M. Ch. J. Bordé, M. Ch. Chardonnet, M. P. Glorieux, M. M. Quack

Lasers / Asservissement / Traitement du signal / Optique et spectroscopie non linéaire / Technique du vide

- 1995 -*Stage de DEA - 6mois* (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique)
Interactions molécule-surface / Adsorption / Rayonnement synchrotron/ Spectroscopie de temps de vol / Spectromètre de masse
- 1995 -*Diplôme d'Etudes Approfondies* : Physique Expérimentale des Atomes et des Molécules et Applications, (Paris VI), Mention Très Bien

Activités d'enseignement

J'ai débuté mes activités d'enseignement au niveau du Deug 1^{ère} année dans les différentes mentions SM, STPI et MIAS au cours des deux premières années puis je suis ensuite intervenu dans un plus grand nombre de formations (Deug 2^{ème} année, Licence d'Ingénierie Electrique, Licence de Sciences Physiques, Formation Ingénieurs Télécom, Licence Science et Communication, Master laser et nanosciences).

Matières enseignées :

Optique Géométrique / Optique de Fourier / Electromagnétisme / Optique et Laser / Propagation Guidée / Lignes-Guides-Fibres / Propriétés Electriques de Milieux Continus – Optique / Image et Vision / Initiation à l'électronique / Electronique Analogique / Traitement du Signal et Modulation / Signaux et Systèmes / Interface et Simulation (LabView) / Mécanique / Thermodynamique / Méthodologie au Travail Universitaire

Responsabilités

- Agent Chargé de la Mise en Œuvre des règles de prévention et de sécurité (ACMO) au Laboratoire de Physique des Lasers depuis 2004,
- Membre de la Commission de Spécialistes 30^{ème} section de l'Institut Galilée - Université Paris 13 de 2002 à 2008,
- Responsable pédagogique de la 1^{ère} année de la formation d'Ingénieur Sup Galilée, Spécialité Télécom et Réseaux de l'Institut Galilée - Université Paris 13 depuis septembre 2005,

- Responsable de l'Enquête Industrielle en formation d'Ingénieur Sup Galilée, Spécialité Télécom et Réseaux (1^{ère} année) de l'Institut Galilée - Université Paris 13 à partir de septembre 2008,
- Membre d'un groupe de travail « Liaison Enseignement Secondaire – Enseignement Supérieur » en partenariat avec des enseignants du secondaire et le Rectorat de l'Académie de Créteil depuis 2004,
- Membre élu du bureau PAMO depuis 2007 et membre du comité scientifique de la conférence PAMO-JSM 2008.

Activité de diffusion de la science

- Présentation de mini conférences lors de la manifestation Savante Banlieue / Fête de la Science à l'Institut Galilée (depuis 2004)
- Consultant Scientifique pour la « Fondation 93 » dans le cadre du projet « EUREKA » à destination des collèges et lycées de Seine-Saint-Denis. Projet mené en partenariat avec la Cité des Sciences et de l'Industrie depuis 2004 (~20h/an)
- Intervenant au cours de l'année scolaire 2007/2008 auprès d'une classe de CM2 du Blanc-Mesnil pour un Projet mêlant approche artistique et scientifique autour du thème de la lumière « Chercheur d'Art et de Sciences » (~20h/an)
- Consultant « La main à la pâte »
- Intervenant « Atelier Science » au Lycée Feyder d'Epinay-sur-Seine à destination des élèves de 2^{nde} et première à la rentrée 2008 (~20h/an)

Encadrement :

Doctorants :

- T. Marrel (sout. 15 décembre 2000) : le spectre à très haute résolution de la molécule chirale CHFClBr à 9,3 μm : test de violation de la parité et étude de la structure hyperfine (participation à l'encadrement 30 %)
- M. Ziskind (sout. 21 décembre 2001) : test de l'effet de violation de la parité dans la molécule chirale CHFClBr et test du principe de Pauli dans OsO₄ et SF₆ (participation à l'encadrement 70 %)
- M. Guinet (sout. 23 novembre 2006) : première détermination de la constante de Boltzmann par une méthode optique (participation à l'encadrement 50 %)

- K. Djerroud (sout. prévue fin 2008) : mesure directe de la constante de Boltzmann par voie optique : vers une redéfinition du Kelvin (participation à l'encadrement 80%)
- C. Lemarchand (à partir de septembre 2008) : vers une mesure de la constante de Boltzmann au niveau du ppm

Stagiaires :

Diplôme ou statut	Etudiant	participation à l'encadrement	Année (durée stage)
Sc. du contingent	O. Phavorin	100%	1998 (6 mois)
Ater	A. Gauguet	100%	2007/2008 (1 an)
Ater	F. Kwabia Tchana	100%	2005/2006 (1 an)
Master 2	C. Lemarchand	100%	2008 (4 mois)
DEA	M. Bahriz	100%	2004 (4 mois)
DEA	M. Ziskind	100%	1998 (4 mois)
DEA	J. Barthes	100%	1999 (4 mois)
DEA	M. Khelifi	100%	2002 (4 mois)
DEA	M. Ardjouné	100%	2005 (4 mois)
DEA	G. Emiliyanov	50%	2001 (4 mois)
Doctorant	R. Viglione	100%	2001 (1 mois)
Master 1	Y. Vibol	80%	2008 (4 mois)
Master 1	C. Stoeffler	100%	2006 (2 mois)
Maîtrise de Physique	S. De Rossi	60%	2000 (2 mois)
2 ^{ème} année X	B. Corbin	100%	2004 (4 mois)
Licence de Sc. Physiques	A. Zerrouki	100%	2002 (1 mois)
Licence de Sc. Physiques	Z. Abdelhadi	100%	2002 (3 mois)
DEUST	N. Truong Trung	100%	1997 (2 mois)
BTS Optique 1 ^{ère} année	G. Kovacs	100%	2004 (3 mois)
BTS Optique 1 ^{ère} année	N. LAUER	100%	1998 (2 mois)
BTS Optique 1 ^{ère} année	I. Héron	100%	1998 (2 mois)

Activités de recherche

J'ai mené mon travail de recherche depuis 1995 au sein de l'équipe HOTES «*horloges optiques et tests fondamentaux par spectroscopie et interférométrie atomique et moléculaire*» dirigée conjointement par Ch. J. Bordé et Ch. Chardonnet.

Sujets de recherche :

- Développement d'un spectromètre basé sur un étalon de fréquence ultra stable à 10 μm
- Recherche d'un effet de violation de la parité dans le spectre de la molécule chirale CHFCIBr et étude de la structure hyperfine de la molécule CHFCIBr
- Transport avec contrôle des propriétés spectrales d'un étalon de fréquence par fibre optique sur 43 km et application à la comparaison des étalons de fréquence du Laboratoire de Physique des Lasers et du LNE-SYRTE - Observatoire de Paris
- Réalisation, à l'aide d'un laser Ti:Sa femtoseconde, des premières mesures de fréquences des différents étalons de l'équipe HOTES du LPL directement par raccordement à l'étalon primaire du SYRTE via une liaison par fibre optique entre les deux laboratoires
- Première mesure directe de la constante de Boltzmann par méthode optique (collaboration LNE INM/Cnam)

Membres de l'équipe

Responsables : Ch. Chardonnet et Ch. J. Bordé (Directeurs de Recherche, CNRS)

Membres permanents :

C.T. Nguyen (Ingénieur de Recherche, CNRS, jusqu'en février 2002)

M. Himbert (jusqu'en 2004) (Pr. chaire de métrologie CNAM)

A. Amy-Klein, F. Du Burck (Professeurs)

C. Daussy (Maître de Conférences),

O. Lopez (Ingénieur d'études, CNRS depuis 2000)

B. Darquié (CR2 CNRS, depuis octobre 2007)

Collaborations :

Réseau Européen portant sur « New Generation of Frequency Standards in the Spectral Regions of 30 and 60 THz ». Janvier 1995-Décembre 1997

collaborations internationales :

- Lebedev Institute, Troitsk, Russie (A. Shelkovnikov), Cavendish Laboratory,

Cambridge, UK (R.J. Butcher) – franges de Ramsey, variation des constantes fondamentales

- Laser Physics Institute, Novosibirsk, Russie (A. Goncharov, Mikhail Skvortsov Alexander Shilov étudiant en thèse) – nouvelles sources lasers visible – spectroscopie de l'iode
- Physikalische Technische Bundesanstalt - Braunschweig Allemagne (G. Kramer)
- Instituto Politecnico di Metrologia "G. Colonetti" - Turin - Italie (M.P. Sassi)
- Institut für Angewandte Physik - Bonn D (W. Urban)
- Université d'Auckland, Nouvelle-Zélande (P. Schwerdtfeger) – Violation de la parité moléculaire
- Université de Bath (P. Knight) – laser femtoseconde et mesures de fréquences
- University of Western Australia (M.E. Tobar, A.N. Luiten) – lien optique
- PTB, Berlin, Allemagne (J. Fischer), Seconde Université de Naples, Italie (Livio Gianfrani) – mesure de la constante de Boltzmann (Eranet IMERA)

Collaborations nationales :

- Laboratoire de Spectroscopie Hertzienne - Lille (F. Herlemont, J. Legrand)
- Laboratoire de Physique Moléculaire et Applications - Paris (A. Valentin)
- LNE-SYRTE (A. Clairon, A. Landragin, N. Dimarcq, G. Santarelli, M. Lours, F. Narbonne, P. Lemonde, S. Bize, A. Clairon), LKB (F. Biraben, Ch. Salomon) – PPF lien optique
- Laboratoire de Chimie Quantique et Modélisation Moléculaire, STRASBOURG (Trond Saue, Radovan Bast) STIM-ENS Lyon (L. Guy), Laboratoire de Stéréochimie et Interactions Moléculaires - Ecole Normale Supérieure de Lyon (A. Collet) Sciences chimiques de Rennes (J. Crassous), PhLAM-Lille (D. Petitprez, T. Huet), LADIR-Paris 6 (P. Asselin, P. Soulard) Institut d'Astrophysique Spatiale (A. Léger) – violation de la parité moléculaire
- LKB/Université d'Evry (L. Hilico) – métrologie des fréquences optiques
- LNE-INM (G. Bonnier, S. Briaudeau, L. Pitre, Y. Hermier) – mesure de la constante de Boltzmann

Publications et communications

Le travail de recherche que j'ai mené au LPL a donné lieu de depuis 1995 à 25 publications dans des revues à comité de lecture, 3 chapitres d'ouvrages, 42 communications orales (dont 19 conférences invitées) et 44 présentations par poster.

Articles dans des revues avec comité de lecture

Nationales

- [1] M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, Ch.J. Bordé and C. Chardonnet, *Premiers résultats de mesure optique de la constante de Boltzmann par métrologie des fréquences*, J. Phys. IV France 135, 181-182 (2006)
- [2] M. Guinet, A. Amy-Klein, A. Goncharov, A. Shelkownikov, C. Daussy, O. Lopez, C. Chardonnet, *Mesure de la fréquence absolue d'une raie à deux photons de SF6 en utilisant un peigne femtoseconde*, J. Phys. IV France 135, 183-184 (2006)
- [3] C. Daussy, C. J. Bordé, C. Chardonnet, *La constante de Boltzmann mesurée par spectroscopie laser*, Les Images de la Physique 2006, 80-85, (2007)
- [4] K. Djerroud, C. Daussy, O. Lopez, A. Amy-Klein, S. Briaudeau, Y. Hermier and C. Chardonnet, *Towards an optical measurement of the Boltzmann constant at the 10^{-5} level*, Annales de Physique 32, 175 (2007)
- [5] O. Lopez, C. Daussy, C. Chardonnet, G. Santarelli, and A. Amy-Klein, *Frequency dissemination with a 86-km optical fibre for fundamental tests of physics*, Annales de Physique 32, 187 (2007)

Internationales

- [1] Ch. Chardonnet, V. Bernard, Ch. Daussy, A. Gicquel, and E. Anger, *Polarization properties of thin films of diamond*, Appl. Optics **35**, 6692-6697 (1996) (Travaux ayant conduit au dépôt d'un brevet)
- [2] V. Bernard, Ch. Daussy, G. Nogues, L.F. Constantin, P.E. Durand, A. Amy-Klein, A. Van Lerberghe and Ch. Chardonnet, *CO₂ laser stabilisation to 0.1-Hz level using external electrooptic modulation*, IEEE J. Quantum Electron. **33**, 1282-1287 (1997)
- [3] V. Bernard, G. Nogues, Ch. Daussy, L.F. Constantin and Ch. Chardonnet, *CO₂ laser stabilized on narrow saturated absorption resonances of CO₂: improved absolute frequency measurements*, Metrologia **34**, 313-318 (1997)
- [4] B. Frech, L.F. Constantin, A. Amy-Klein, O. Phavorin, Ch. Daussy, Ch. Chardonnet, M. Mürtz, *Frequency measurements of saturated-fluorescence-stabilized CO₂ laser lines : comparison with an OsO₄-stabilized CO₂ laser standard*, Appl. Phys. B **67**, 217-221 (1998)
- [5] Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, Ch. J. Bordé and Ch. Chardonnet, *Limit on the Parity Nonconserving Energy Difference between the Enantiomers of a Chiral Molecule by Laser Spectroscopy*, Phys. Rev. Lett. **83**, 1554-1557 (1999)
- [6] A. Amy-Klein, L.F. Constantin, R.J. Butcher, Ch. Daussy, P.E. Durand, G. Nogues et Ch. Chardonnet, *Slow molecule detection or Ramsey fringes in two-photon spectroscopy : which is better for high resolution spectroscopy and metrology ?*, Opt. Express **4**, 67-76 (1999)
- [7] Ch. Daussy, F. Ducos, G.D. Rovera, O. Acef, *Performance of OsO₄ stabilized CO₂ lasers as optical frequency standards near 29 THz*, IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control **47(2)**, 518-521 (2000)
- [8] T. Marrel, M. Ziskind, C. Daussy and Ch. Chardonnet, *High precision rovibrational and hyperfine analysis of the $\nu_4=1$ level of bromochlorofluoromethane*, Journal of Molecular Structure **599**, 195-209 (2001)

- [9] C. Chardonnet, M. Ziskind, T. Marrel, C. Daussy, Ch. J. Bordé, C. Grain, L.F. Constantin, C.T. Nguyen, A. Shelkovnikov, R. J. Butcher, A. Amy-Klein, *Search for a frequency difference in the spectrum of the enantiomers of chiral molecules: how to reach a sensitivity better than 10^{-14}* , Proceedings of the SPIE conference: Laser Frequency Stabilization, Standards, Measurement, and Applications, édité par Jun Ye and John L. Hall 4269, 8-17, (2001)
- [10] M. Ziskind, T. Marrel, C. Daussy and Ch. Chardonnet, *Improved sensitivity in the search for a parity-violating energy difference in the vibrational spectrum of the enantiomers of CHFClBr*, Euro. Phys. J. D 20, 219-225 (2002)
- [11] J. Crassous, F. Monier, J.-P. Dutasta, M. Ziskind, C. Daussy, C. Grain, C. Chardonnet, *Search for resolution of chiral fluorohalogenomethanes and parity violation effects at the molecular level*, ChemPhysChem 4, 541-548 (2003)
- [12] A. Amy-Klein, A. Goncharov, C. Daussy, C. Grain, O. Lopez, G. Santarelli, C. Chardonnet, *Absolute frequency measurement in the 28 THz spectral region with a femtosecond laser comb and a long-distance optical link to a primary standard*, Appl. Phys. B 78, 25-30 (2004)
- [13] F. du Burck, C. Daussy, A. Amy-Klein, A. N. Goncharov, O. Lopez, C. Chardonnet, J.-P. Wallerand, *Frequency measurement of the Ar⁺ laser stabilized on narrow lines of molecular Iodine at 501.7 nm*, IEEE Trans. on Instr. and Meas, 54, 754-758 (2005)
- [14] C. Daussy, O. Lopez, A. Amy-Klein, A. Goncharov, M. Guinet, C. Chardonnet, F. Narbonneau, M. Lours, D. Chambon, S. Bize, A. Clairon, G. Santarelli, M.E. Tobar, A.N. Luiten, *Long-distance frequency dissemination with a resolution of 10^{-17}* , Physical Review Letters 94, 203904 (2005) également paru dans Virtual Journal of ultrafast Science 4 Issue 6, "Ultrafast Methods and Measurement Techniques", published by American Physical Society and American Institute of Physics <http://www.vjulfast.org> (2005)
- [15] A. Amy-Klein, A. Goncharov, M. Guinet, C. Daussy, O. Lopez, A. Shelkovnikov, C. Chardonnet, *Absolute frequency measurement of an SF₆ two-photon line using a femtosecond optical comb and sum-frequency generation*, Optics letters 30, 3320 (2005)

- [16] C. Chardonnet, C. Daussy, O. Lopez, A. Amy-Klein, *Toward a first observation of molecular parity violation by laser spectroscopy*, Lecture Series on Computer and Computational Sciences (2005)
- [17] F. Narbonneau, M. Lours, S. Bize, A. Clairon, G. Santarelli, O. Lopez, C. Daussy, A. Amy-Klein and C. Chardonnet, *High Resolution Frequency Standard Dissemination via Optical Fibre Metropolitan Network*, Review of Scientific Instruments 77, 064701 (2006)
- [18] C. Daussy, M. Guinet, A. Amy-Klein, K. Djerroud, Y. Hermier, S. Briaudeau, Ch.J. Bordé, and C. Chardonnet, *First direct determination of the Boltzmann constant by an optical method*, Phys. Rev. Lett. 98, 250801 (2007)
- [19] F. Bielsa, K. Djerroud, A. Goncharov, A. Douillet, T. Valenzuela, C. Daussy, L. Hilico and A. Amy-Klein, *HCOOH High resolution spectroscopy in the 9.18 μ m region*, Journal of Molecular Spectroscopy 247, 41–46, (2008)
- [20] O. Lopez, A. Amy-Klein, C. Daussy, Ch. Chardonnet, F. Narbonneau, M. Lours, and G. Santarelli, *90-km optical link with a resolution of 2×10^{-18} for RF frequency transfer*, Eur. Phys. J. D 48, 35–41 (2008)

Articles dans des revues sans comité de lecture

- [1] V. Bernard, Ch. Daussy, G. Nogues, P.E. Durand, L. Constantin, A. Amy-Klein and Ch. Chardonnet, *Sub-hertz stabilisation of CO₂ lasers in the 30 THz spectral region*, Proceedings of 11th european frequency and time forum, 112-116 (1997)
- [2] Ch. Daussy, T. Marrel, O. Phavorin, A. Amy-Klein, C.T. Nguyen, Ch. J. Bordé et Ch. Chardonnet, *Stabilisation en fréquence d'un laser à CO₂ au niveau de 3×10^{-15} et recherche d'un effet de violation de la parité dans les molécules chirales*, Ann. Phys. Fr. 23, 225-226 (1998)

-
- [3] F. Ducos, G.D. Rovera, Ch. Daussy and O. Acef, *Performances of OsO₄ stabilized CO₂ lasers as optical frequency standards near 29 THz*, Proceedings of 13th european frequency and time forum and 1999 IEEE international frequency control symposium 2 714-717 (1999)
- [4] M. Ziskind, T. Marrel, C Daussy, C. J. Bordé and C. Chardonnet, *Parity violation test in chiral molecules by laser spectroscopy at 10⁻¹³ level*, Conference Digest, Proceedings of IQEC, IEEE (2000)
- [5] Chardonnet, T. Marrel, M. Ziskind, Ch. Daussy, A. Amy-Klein and Ch. J. Bordé, *Spectroscopie de molécules chirales : recherche d'un effet de violation de la parité*, J. Phys IV Pr. 10, 45-54 (2000)
- [6] P. Bordé, G. Perrin, T. Nguyen, A. Amy-Klein, C. Daussy, P.-I. Raynal, A. Léger, and G. Mazé, *10-micron wavefront spatial filtering : first results with chalcogenide fibers*, Proc. SPIE 4838, *Interferometry for Optical Astronomy II* (2002)
- [7] P. Bordé, G. Perrin, A. Amy-Klein, C. Daussy, and G. Mazé, *Updated results on prototype chalcogenide fibers for 10 μm wavefront spatial filtering*, Proceedings of the conference "Toward Other Earths, Darwin/TPF and the search for extrasolar terrestrial planets", Heidelberg, Germany, , ESA SP-539 (2003)
- [8] F. Narbonneau, M. Lours, C. Daussy, O. Lopez, A. Clairon and G. Santarelli, *Ultra-Stable Optical Links for Metrological Applications*, Proceedings of the 2003 IFCS and 17th EFTF, 1041-1047 (2003)
- [9] C. Daussy, O. Lopez, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli, *Transmission of an optical frequency standard utilizing an 85 km fiber optic link*, Europhysics Conference Abstracts Vo. 27E EF-04-MON (2003)
- [10] A. Amy-Klein, C. Grain, R.J. Butcher, A. Shelkownikov, C. Daussy, O. Lopez, M. Guinet, A. Goncharov and C. Chardonnet, *Absolute frequency measurement around 30 THz with a femtosecond laser comb*, Proceedings of 18th european frequency and time forum (2004)

-
- [11] C. Daussy, O. Lopez, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Frequency standard transfer over a 43-km optical fiber*, Proceedings of 18th european frequency and time forum (2004)
- [12] F. Du Burck , J.P. Wallerand, A. Goncharov, O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, *Narrow lines in molecular iodine near the dissociation limit*, Proceedings of 18th european frequency and time forum (2004)
- [13] F. du Burck, C. Daussy, A. Amy-Klein, A. N. Goncharov, O. Lopez, *Frequency measurement of the iodine-stabilized Ar⁺ laser at 501.7 nm*, Proceedings of CPEM (2004)
- [14] C. Daussy, M. Guinet, A. Amy-Klein, A. Shelkovnikov, A. Goncharov, R.J. Butcher, C. Grain , O. Lopez, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Long-distance optical link to primary standard and absolute frequency measurement in the 28-THz spectral region*, Proceedings of CPEM (2004)
- [15] A. Amy-Klein, A. Goncharoc, F. Du Burck, A. Shelkovnikov, R. J. Butcher, C. Grain, C. Daussy, O. Lopez, C. Chardonnet, *Mesures absolues de fréquences optiques avec un laser femtoseconde*, J. Phys. IV France 119, 3-8 (2004)
- [16] C. Daussy, O. Lopez, A. Amy-klein, M. Guinet, C. Chardonnet, F. Narbonneau, M. Lours, A. Clairon and G. Santarelli, *Transmission par fibre optique sur une distance de 43 km d'une référence de temps-fréquence avec une résolution de 10^{-18}* , Proceedings of OPTRO 2005 (2005)
- [17] M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, C.J. Bordé and C. Chardonnet, *Mesure directe de la constante de Boltzmann par une méthode de métrologie des fréquences*, Proceedings of OPTRO 2005 (2005)
- [18] O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Fibre frequency dissemination with resolution below 10^{-17}* , Proceedings of 20th european frequency and time forum (2006)

- [19] O. Lopez, C. Daussy, A. Amy-klein, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli, *Fiber frequency dissemination with resolution in the 10^{-18} range*, Proceedings of 2006 IEEE International Frequency Control Symposium (2006)

Ouvrages ou chapitre d'ouvrage scientifique

- [1] Ch. Chardonnet, Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen et Ch. J. Bordé, *Parity violation test in chiral molecules by laser spectroscopy*, paru dans "*Parity Violation in atomic Physics and Electron Scattering*", World Scientific, ed. B. Frois and M.A. Bouchiat, 325-355 (1999)
- [2] Amy-Klein A., Constantin L.F., Grain C., Ziskind M., Marrel T., Shelkovnikov A., Butcher R.J., Nguyen C.T., Daussy C., Chardonnet Ch., *Ultra-high resolution infrared spectroscopy : state-of-the-art and applications*, Proceedings de 26th Intern. Conf. on Infrared and Millimeter Waves IRMMW, ed. O. Portugall et J. Léotin, ISBN 2-87649-035-8, 232-238 (2003)
- [3] C. Daussy, S. Briaudeau, M. Guinet, A. Amy-Klein, Y. Hermier, Ch. J. Bordé and C. Chardonnet, *Spectroscopic determination of the Boltzmann constant: first results*, Laser Spectroscopy, World Scientific Publishing Co. Pte. Ltd., edited by Prof Ed Hinds, Prof Allister Ferguson and Dr Erling Riis (2005)

Conférences invitées

- [1] Ch. Chardonnet, Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen et Ch. J. Bordé, *Laser spectroscopy test of parity violation in chiral molecules*, PAVI/97 (Parity Violation in Electron-hadron electroweak interactions), Paris, France (27-31 octobre 1997)
- [2] Ch. Chardonnet, Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen et Ch. J. Bordé, *Test of Parity violation in the spectrum of chiral molecules*, ICONO'98, Moscou, Russie (29 juin-3 juillet 1998)

- [3] Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, Ch. Bordé et Ch. Chardonnet, *Recherche d'un effet de violation de la parité dans le spectre de molécules chirales*, 3^{èmes} Journées de Spectroscopie Moléculaire, Reims, France (7-8 juillet 1998)
- [4] Ch. Chardonnet, Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen et Ch. J. Bordé, *Laser spectroscopy test of parity violation in chiral molecules*, Quantum Optics, Castelvechio Pascoli, Italie (29 septembre-3 Octobre 1998)
- [5] C. Chardonnet, C. Daussy, T. Marrel, M. Ziskind, A. Amy-Klein and Ch.J. Bordé, *New search for parity violating effects in chiral molecules*, ICOLS'99, 14th International Conference on Laser Spectroscopy, Innsbruck, Autriche, (7-11 juin 1999)
- [6] T. Marrel, Ch. Daussy, M. Ziskind, C.T. Nguyen, A. Amy-Klein, Ch. J. Bordé, Ch. Chardonnet, *High precision test of parity violation in the spectrum of the chiral molecule CHFClBr*, Microsymposium at IUPAC congress, Berlin, Allemagne (15 and 16 août 1999)
- [7] C. Chardonnet, T. Marrel, M. Ziskind, C. Daussy, A. Amy-Klein and Ch.J. Bordé, *Spectroscopie de molécules chirales : recherche d'un effet de violation de la parité*, COLOQ'6, 6^{ème} colloque sur les Lasers et l'Optique Quantique, Bordeaux, France (7-9 septembre 1999)
- [8] C. Chardonnet, M. Ziskind, T. Marrel, C. Daussy and Ch.J. Bordé, *Parity violation test in chiral molecules by laser spectroscopy at 10^{-13} level*, IQEC 2000, Nice, France (10-15 septembre 2000)
- [9] C. Chardonnet, M. Ziskind, T. Marrel, C. Daussy and Ch.J. Bordé, *Towards an observation of a parity violation effect in the spectrum of chiral molecules*, ISCD 12, Chirality 2000, Chamonix, France (24-28 septembre 2000)
- [10] C. Chardonnet, M. Ziskind, T. Marrel, C. Daussy, Ch.J. Bordé, C. Grain, L.F. Constantin, C.T. Nguyen, A. Shelkovnikov, R. J. Butcher and A. Amy-Klein, *Search for a frequency difference in the spectrum of the enantiomers of chiral molecules: how to reach a sensitivity better than 10^{-14}* , SPIE San José, USA (Janvier 2001)

- [11] A. Amy-Klein, L.F. Constantin, C. Grain, M. Ziskind, A. Shelkovnikov, C.T. Nguyen, C. Daussy and C. Chardonnet, *Ultra-high resolution infrared spectroscopy : state-of-the-art and applications*, 26th International Conference on Infrared and Millimeter Waves IRMMW, Toulouse, France, (10-14 septembre 2001)
- [12] A. Amy-Klein, A. Goncharov, C. Grain, A. Shelkovnikov, C. Daussy, O. Lopez, R.J. Butcher, F. Du Burck, and C. Chardonnet, *Ultra-precise optical frequency measurements: application to tests of variation of fundamental constants and parity violation in molecules*, LO'2003, St Petersburg, Russie (30juin-4juillet 2003)
- [13] Amy-Klein, A. Goncharov, C. Grain, A. Shelkovnikov, C. Daussy, O. Lopez, R.J. Butcher, F. Du Burck, and C. Chardonnet, *Absolute frequency measurements of molecular transitions at ultra-high precision: towards new tests of time variations of the fundamental constants*, 16th International Conference on Laser Spectroscopy (ICOLS03), Palm Cove, Australie (13-18 juillet 2003)
- [14] A. Amy-Klein, A. Goncharov, F. Du Burck, A. Shelkovnikov, R.J. Butcher, C. Grain, C. Daussy, O. Lopez, C. Chardonnet, *Mesures absolues de fréquences optiques avec un laser femtoseconde*, COLOQ8, Toulouse, France (3-5 septembre 2003)
- [15] A. Amy-Klein, A. Shelkovnikov, R.J. Butcher, C. Grain, C. Daussy, O. Lopez, A. Goncharov, C. Chardonnet, *Développements récents en spectroscopie à ultra-haute résolution et application à la mise en évidence de la violation de la parité*, Journées de Physique Moléculaire, Université du Littoral, Dunkerque, France (1-3 juin 2004)
- [16] A. Amy-Klein, A. Goncharov, C. Grain, R.J. Butcher, A. Shelkovnikov, C. Daussy, O. Lopez, F. du Burck, M. Guinet, C. Chardonnet, *Absolute Frequency Measurement of Molecular Transitions with a Femtosecond Laser Comb*, PAMO 04, Rennes, France (7 juillet 2004)
- [17] C. Chardonnet, C. Bordé , C. Daussy , A. Amy-Klein, M. Guinet, O. Lopez, *Application of high precision optical frequency measurement to a new determination of the Boltzmann Constant by Doppler spectroscopy*, ICONO'2005 : Saint-Pétersbourg, Russie (11-15 mai 2005)

- [18] C. Daussy, A. Amy-Klein, C. Chardonnet, *Search for a frequency difference in the spectrum of the enantiomers of chiral molecules: towards a first observation of a parity violation effect in molecules*, 19th HRMS, Salamanque, Espagne (11-16 septembre 2005)
- [19] C. Chardonnet, A. Amy-Klein, C. Daussy, O. Lopez, C. Grain, A. Shelkovnikov, B. Butcher, A. Clairon, G. Santarelli, M. Lours, F. Narbonneau, *Parity violation in molecules: towards a first observation*, PAVI06, Ile de Milos, Grèce (16-20 mai 2006)
- [20] C. Daussy, A. Amy-Klein, C. Chardonnet, *Search for a frequency difference in the spectrum of the enantiomers of chiral molecules: towards a first observation of a parity violation effect in molecules*, 3^{ème} rencontre franco-chinoise, Lille, France (18-20 septembre 2006)
- [21] O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Long distance frequency dissemination at 10^{-18} level*, International Workshop on "advances in precision tests and experimental gravitation in space", Firenze, Italie (September 28-30 2006)
- [22] C. Chardonnet, C. Daussy, O. Lopez, A. Amy-Klein, *Towards a first observation of molecular parity violation by laser spectroscopy*, ICCMSE, Chania, Grèce (30 octobre- 1 novembre 2006)
- [23] O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Precise Long-Distance frequency transfer and Applications*, Optical Frequency & Time Measurement and Generation, IEEE LEOS Summer Topicals 2007, Portland , USA (23-25 juillet 2007)

Communications avec actes**Nationales****Oral**

- [1] C. Chardonnet, A. Amy-Klein, Ch.J. Bordé, R. J. Butcher, L.F. Constantin, C. Daussy, A. Goncharov, C. Grain, T. Marrel, A. Shelkovnikov, M. Ziskind, *Mesures de haute précision et applications à la physique moléculaire*, journée thématique « métrologie et physique fondamentale » Université Paris 6, Paris, France (7 mai 2002)
- [2] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch. J. Bordé et Ch. Chardonnet, *Toward an optical measurement of the Boltzmann constant at the 10^{-15} level*, Doctoriales de la métrologie française, Conservatoire National des Arts et Métiers, Dijon, France (11 décembre 2007)

Poster

- [1] V. Bernard, Ch. Daussy, P.E. Durand, T. George, H. W. Nicolaisen, A. Amy-Klein et Ch. Chardonnet, *Stabilisation en fréquence de lasers à CO_2 au niveau du hertz*, COLOQ4, Palaiseau, France (6-8 novembre 1995)
- [2] Ch Daussy, T. Marrel, O. Phavorin, A. Amy-Klein, C.T. Nguyen Ch. J. Bordé et Ch. Chardonnet, *Stabilisation en fréquence d'un laser à CO_2 au niveau de 3.10^{-15} et recherche d'un effet de violation de la parité dans les molécules chirales*, COLOQ5, Strasbourg, France (8-10 septembre 1997)
- [3] A. Amy-Klein, A. Goncharov, F. Du Burck, A. Shelkovnikov, R.J. Butcher, C. Grain, C. Daussy, O. Lopez, C. Chardonnet, *Mesures de fréquences moléculaires et test de variation des constantes fondamentales avec un laser femtoseconde*, Congrès général de la SFP, Lyon, France (7-10 juillet 2003)

-
- [4] S. Chénais, C. Daussy, T. Billeton et J.-C. Keller, *Une première approche de l'optique en 1er cycle universitaire par la colorimétrie : T.P. « synthèse des couleurs »*, COLOQ9, Dijon, France (7-9 septembre 2005)
- [5] M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, C.J. Bordé and C. Chardonnet, *Premiers résultats de mesure optique de la constante de Boltzmann par métrologie des fréquences*, COLOQ9, Dijon, France (7-9 septembre 2005)
- [6] M. Guinet, A. Amy-Klein, A. Goncharov, A. Shelkownikov, C. Daussy, O. Lopez, C. Chardonnet, *Mesure de la fréquence absolue d'une raie à deux photons de SF₆ en utilisant un peigne femtoseconde*, COLOQ9, Dijon, France (7-9 septembre 2005)
- [7] M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, C.J. Bordé and C. Chardonnet, *Mesure directe de la constante de Boltzmann par une méthode de métrologie des fréquences*, International Symposium OPTRO 2005, Paris, France (9-12 mai 2005)
- [8] M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, C.J. Bordé and C. Chardonnet, *Vers une mesure optique de la constante de Boltzmann : premiers résultats*, 12ème Congrès International de Métrologie, Lyon, France (20-23 juin 2005)
- [9] F. Kwabia Tchana, K. Djerroud, M. Guinet, C. Daussy, S. Briaudeau, A. Amy-Klein, Y. Hermier, Ch. J. Bordé et C. Chardonnet, *Première mesure optique de la constante de Boltzmann par métrologie des fréquences*, JSM Lyon, France (3-5 juillet 2006)
- [10] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch.J. Bordé and C. Chardonnet, *Détermination de la constante de Boltzmann par méthode spectroscopique*, COLOQ 10th conference on lasers and quantum optics, Grenoble, France (2-5 juillet 2007)
- [11] A. Amy-Klein, O. Lopez, C. Daussy, C. Chardonnet, G. Santarelli, *Transfert d'une référence de fréquence par fibre optique avec une résolution meilleure que 10⁻¹⁷*, COLOQ 10th conference on lasers and quantum optics, Grenoble, France, (2-5 juillet 2007)

- [12] F. Bielsa, K. Djerroud, A. Goncharov, A. Douillet, T. Valenzuela, C. Daussy, L. Hilico et A. Amy-Klein, *Mesure de fréquences absolues dans la bande ν_6 de l'acide formique : références de fréquence à $9,2 \mu\text{m}$* , COLOQ 10th conference on lasers and quantum optics, Grenoble, France, (2-5 juillet 2007)
- [13] C. Daussy, O. Lopez, C. Chardonnet, G. Santarelli, A. Amy-Klein, *Transfert d'une référence de fréquence par fibre optique avec une résolution meilleure que 10^{-17}* , Congrès général de la SFP 2007, 9-13 juillet 2007, Grenoble, France
- [14] C. Daussy, K. Djerroud, A. Amy-Klein, Y. Hermier, S. Briaudeau, Ch.J. Bordé and C. Chardonnet, *Détermination de la constante de Boltzmann par méthode spectroscopique*, Congrès général de la SFP 2007, Grenoble, France (9-13 juillet 2007)
- [15] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch. J. Bordé et Ch. Chardonnet, *Toward an optical measurement of the Boltzmann constant at the 10^{-15} level*, Doctoriales de la métrologie française, Conservatoire National des Arts et Métiers, Dijon, France (11 décembre 2007)
- [16] K. Djerroud, A. Gauguet, C. Lemarchand, C. Daussy, O. Lopez, A. Amy-Klein, Ch.J. Bordé and C. Chardonnet, *Vers une détermination de la constante de Boltzmann par méthode spectroscopique à un niveau de 10 ppm*, PAMO 2008, Lille, France (7-10 juillet 2008)
- [17] C. Stoeffler, B. Darquié, A. Shelkovnikov, C. Daussy, O. Lopez, A. Amy-Klein et C. Chardonnet *Vers une première observation de violation de la parité dans les molécules, par spectroscopie laser*, PAMO 2008, Lille, France (7-10 juillet 2008)

Internationales

Oral

- [1] V. Bernard, Ch. Daussy, G. Nogues, P.E. Durand, L. Constantin, A. Amy-Klein and Ch. Chardonnet, *Sub-hertz stabilization of CO_2 lasers in the 30 THz spectral region*, 11th european frequency and time forum, Neuchâtel (4-7 mars 1997)

-
- [2] T. Marrel, Ch. Daussy, Ch. Bordé et Ch. Chardonnet, *Test of parity violation in the spectrum of chiral molecules*, EQEC'98, Glasgow (14-18 septembre 1998) (Postdeadline)
- [3] F. Ducos, G.D. Rovera, Ch. Daussy and O. Acef, *Performances of OsO₄ stabilized CO₂ lasers as optical frequency standards near 29 THz*, 13th european frequency and time forum and 1999 IEEE international frequency control symposium, Besançon, France (13-16 avril 1999)
- [4] A. Amy-Klein, A. Goncharov, C. Daussy, C. Grain, O. Lopez, C. Chardonnet and G. Santarelli, *Absolute frequency measurements of the OsO₄ stabilized CO₂ frequency standard and of 9 μm CO₂ laser lines with a femtosecond laser comb*, IQEC 2002, Moscou, Russie (22-28 juin 2002) (Postdeadline)
- [5] P. Bordé, G. Perrin, T. Nguyen, A. Amy-Klein, C. Daussy, P.-I. Raynal, A. Léger, and G. Mazé, *10-micron wavefront spatial filtering: first results with chalcogenide fibers*, Interferometry for Optical Astronomy II, Waikoloa, Hawaï (22-28 août 2002)
- [6] C. Daussy, O. Lopez, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli, *Frequency standard transfer over 43-km optical fiber*, 18th european frequency and time forum, Guildford, UK (5-7 avril 2004)
- [7] A. Amy-Klein, R.J. Butcher, A. Shelkovnikov, C. Daussy, O. Lopez, C. Grain, M. Guinet, A. Goncharov and C. Chardonnet, *Two-photon Ramsey fringes at 30 THz referenced to a Cs fountain via an optical frequency comb*, 18th european frequency and time forum, Guildford, UK (5-7 avril 2004)
- [8] C. Daussy, O. Lopez, A. Amy-Klein, R.J. Butcher, M. Guinet, A. Shelkovnikov, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli and A. Clairon, *Long-distance optical link to primary standard and absolute frequency measurement in the 28-THz spectral region*, CPEM 2004, Londres, UK (27 juin-2 juillet 2004)
- [9] F. du Burck, C. Daussy, A. Amy-Klein, A. N. Goncharov, O. Lopez, *Frequency measurement of the Iodine-stabilized Ar⁺ laser at 501 nm*, CPEM 2004, Londres, UK (27 juin-2 juillet 2004)

- [10] M. Guinet, A. Amy-Klein, C. Daussy, O. Lopez, F. Du Burck, C. Chardonnet, *Two photon Ramsey fringes at 30 THz referenced to a cryogenic Sapphire oscillator/Cs fountain via an optical frequency comb*, RFLPW-YS, S^t Petersburg, Russie (3-9 Juillet 2004)
- [11] F. Narbonneau, M. Lours, C. Daussy, O. Lopez, A. Amy-Klein, C. Chardonnet, S. Bize, A. Clairon, G. Santarelli, *Current status of fibre frequency dissemination for metrology applications*, 19th european frequency and time forum, Besançon, France (21-24 mars 2005)
- [12] C. Daussy, O. Lopez, A. Amy-klein, M. Guinet, C. Chardonnet, F. Narbonneau, M. Lours, A. Clairon and G. Santarelli, *Transmission par fibre optique sur une distance de 43 km d'une référence de temps-fréquence avec une résolution de 10^{-18}* , International Symposium OPTRO 2005, Paris, France (9-12 mai 2005)
- [13] C. Chardonnet, C. Daussy, S. Briaudeau, A. Amy-Klein, O. Lopez, Y. Hermier, G. Bonnier, A. Richard, E. Rénaot and C. Bordé, *Determination of the Boltzmann constante by Doppler broadening measurements in equilibrium gas cell: feasibility*, Euromet project, Workshop on methods for new determinations of the Boltzmann constant, Berlin, Allemagne (20-21 janvier 2005)
- [14] O. Lopez, C. Daussy, A. Amy-klein, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli, *Fiber frequency dissemination with resolution in the 10^{-18} range*, 2006 IEEE International Frequency Control Symposium, Miami, Florida, USA (5-7 Juin 2006)
- [15] K. Djerroud, C. Daussy , A. Amy-Klein, M. Guinet, S. Briaudeau, Y. Hermier, C. Chardonnet and C. Bordé , *Optical Measurement of the Boltzmann Constant*, RFWYS'06, Les Houches, France (3-6 octobre 2006)
- [16] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch. J. Bordé et Ch. Chardonnet, *Toward an optical measurement of the Boltzmann constant at the 10^{-15} level*, Colloque franco-indien organise par le centre franco-indien pour la promotion de la recherche avancée, Gif-sur-Yvette, France (29 octobre – 2 novembre 2007)

- [17] K. Djerroud, C. Daussy, O. Lopez, A. Amy-Klein, S. Briaudeau, Y. Hermier, C. Chardonnet and Ch. J. Bordé, *Optical measurement of the Boltzmann constant at the 10^{-5} level*, 3rd Workshop on Progress in determining the Boltzmann Constant, La-Plaine-St-Denis, France (7 avril 2008)

Posters

- [1] G. Comtet, G. Dujardin, L. Hellner, A. Mayne and Ch. Daussy, *Site dependence of the photofragmentation of molecular oxygen on Si(111)7X7*, Eur. Reas. Conference, fundamental aspects of surface science, semi-conducteur surface, Blankenberge, Belgique (1996)
- [2] Ch. Daussy, V. Bernard, G. Nogues, P.E. Durand, L. Constantin, A. Amy-Klein, T. Nguyen and Ch. Chardonnet, *Frequency stabilisation of CO₂ laser below 10^{-14} Allan variance*, Metrology and fundamental physical constants, Les Houches, France (3-7 juin 1996)
- [3] T. Marrel, Ch. Daussy, Ch. Bordé et Ch. Chardonnet, *Test of parity violation in the spectrum of chiral molecules*, Quantum Optics, Castelvecchio Pascoli, Italie (29 septembre-3 Octobre 1998)
- [4] T. Marrel, Ch. Daussy, M. Ziskind, Ch. J. Bordé and Ch. Chardonnet, *High precision test of parity violation in the spectrum of the chiral molecule CHFClBr*, Relativistic effects in heavy-element chemistry and physics, Acquafredda di Maratea, Italie (10-15 avril 1999)
- [5] Ch. Chardonnet, Ch. Daussy, T. Marrel, M. Ziskind, A. Amy-Klein, Ch. Bordé, *New search for parity violating effects in chiral molecules*, Sixteenth Colloquium on High Resolution Molecular Spectroscopy, HRMS 99, Dijon, France (6-10 septembre 1999)
- [6] M. Ziskind, T. Marrel, C. Daussy, A. Amy-Klein, C.T. Nguyen, Ch.J. Bordé, C. Chardonnet, *Search for a frequency difference in the spectrum of the enantiomers of chiral molecules*, HRMS'01, Nijmegen, Pays-Bas, (9-13 septembre 2001)

- [7] M. Ziskind, C. Daussy, Ch.J. Bordé, C. Chardonnet, *Search for violation of the symmetrization postulate in the rovibrational spectra of OsO₄ and SF₆*, HRMS'01, Nijmegen, Pays-Bas, (9-13 septembre 2001)
- [8] A. Amy-Klein, A. Goncharov, C. Daussy, C. Grain, O. Lopez, C. Chardonnet and G. Santarelli, *Absolute frequency measurements of the CO₂/OsO₄ frequency standard and of 9 μm CO₂ laser lines with a femtosecond laser comb*, CPEM02, Ottawa, Canada (16-21 juin 2002)
- [9] A. Amy-Klein, A. Goncharov, C. Daussy, C. Grain, O. Lopez, C. Chardonnet and G. Santarelli, *Absolute frequency measurements of the OsO₄ stabilized CO₂ frequency standard and of 9 μm CO₂ laser lines with a femtosecond laser comb*, IQEC, Moscou, Russie (22-28 juin 2002)
- [10] A. Amy-Klein, R.J. Butcher, C. Chardonnet, C. Daussy, A. Goncharov, C. Grain, O. Lopez, A. Shelkovnikov and H. Vigué, *High-precision frequency measurement and fundamental physics with molecules*, HYPER, Paris, France, (4-6 novembre 2002)
- [11] P. Bordé, G. Perrin, A. Amy-Klein, C. Daussy, and G. Mazé, *Updated results on prototype chalcogenide fibers for 10 μm wavefront spatial filtering*, Conference "Toward Other Earths, Darwin/TPF and the search for extrasolar terrestrial planets", Heidelberg, Allemagne (22-25 avril 2003)
- [12] A. Amy-Klein, A. Goncharov, C. Grain, A. Shelkovnikov, C. Daussy, O. Lopez, R.J. Butcher, F. Du Burck, and C. Chardonnet, *Interest of precision molecular spectroscopy for a test of variation of fundamental constants*, ACFC, Bad Honnef, Allemagne (16-18 juin 2003)
- [13] C. Daussy, O. Lopez, A. Amy-Klein, A. Goncharov, C. Grain, R.J. Butcher, A. Shelkovnikov, F. Du Burck, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli, *Transmission of an optical frequency standard utilizing an 85 km fiber optic link: metrological applications*, EQEC 2003, Munich, Allemagne (22-27 juin 2003)

- [14] F. Narbonneau, M. Lours, C. Daussy, O. Lopez, Clairon and G. Santarelli, *Ultra-stable ground frequency dissemination via optical fibres*, 18th european frequency and time forum, Guildford, UK (5-7 avril 2004)
- [15] F. Du Burck, J.P. Wallerand, A. Goncharov, O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, *Narrow lines in molecular iodine near the dissociation limit*, 18th EFTF, Guildford, UK (5-7 avril 2004)
- [16] C. Daussy, O. Lopez, A. Amy-Klein, A. Goncharov, M. Guinet, C. Chardonnet, F. Narbonneau, M. Lours, S. Bize, D. Chambon, A. Clairon, G. Santarelli, Syrte, M.E Tobar, A.N. Luiten, *Long-distance frequency dissemination with a resolution of 10^{-17}* , 17th ICOLS, Cairngorms, Ecosse (19-24 juin 2005)
- [17] A. Amy-Klein, A. Goncharov, A. Shelkovnikov, M. Guinet, C. Daussy, O. Lopez, C. Chardonnet, *Simplified version of a frequency measurement at 30 THz using an optical frequency comb*, 17th ICOLS, Cairngorms, Ecosse (19-24 juin 2005)
- [18] C. Daussy, S. Briaudeau, M. Guinet, A. Amy-Klein, Y. Hermier, C.J. Bordé and C. Chardonnet, *Optical Determination of the Boltzmann constant: first results*, 17th ICOLS, Cairngorms, Ecosse (19-24 juin 2005)
- [19] C. Daussy, M. Guinet, S. Briaudeau, A. Amy-Klein, Y. Hermier, C.J. Borde and C. Chardonnet, *Optical determination of the Boltzmann constant : first results*, HIRMS 2005, Salamanque, Espagne (11-16 septembre 2005)
- [20] O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Fibre frequency dissemination with resolution below 10^{-17}* , 20th european frequency and time forum, Braunschweig, Allemagne (27-30 mars 2006)
- [21] O. Lopez, C. Daussy, A. Amy-Klein, C. Chardonnet, F. Narbonneau, M. Lours, G. Santarelli, *Fibre frequency dissemination with a resolution below 10^{-17}* , RFWYS'06, Les Houches, France (3-6 octobre 2006)

-
- [22] A. Amy-Klein, A. Shelkovnikov, R.J. Butcher, A. Goncharov, O. Lopez, C. Daussy, C. Chardonnet, *Electron to proton mass ratio time variation test with rovibrational molecular spectroscopy*, EFTF 2007, Genève, Suisse (29 mai-1 juin 2007)
- [23] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch.J. Bordé and C. Chardonnet, *First direct determination of the Boltzmann constant by an optical method*, HRMS 2007, Dijon, France (3-7 septembre 2007)
- [24] C. Daussy, K. Djerroud, A. Amy-Klein, Y. Hermier, S. Briaudeau, Ch.J. Bordé and C. Chardonnet, *First direct determination of the Boltzmann constant by an optical method*, International school « Quantum metrology and fundamental constants, Les Houches, France (1-12 octobre 2007)
- [25] K. Djerroud, C. Daussy, A. Amy-Klein, S. Briaudeau, Y. Hermier, Ch. J. Bordé et Ch. Chardonnet, *Toward an optical measurement of the Boltzmann constant at the 10^{-15} level*, Colloque franco-indien organise par le centre franco-indien pour la promotion de la recherche avancée, Gif-sur-Yvette, France (29 octobre – 2 novembre 2007)
- [26] K. Djerroud, A. Gauguet, C. Lemarchand, C. Daussy, O. Lopez, A. Amy-Klein, Ch.J. Bordé and C. Chardonnet, *Optical measurement of the Boltzmann constant at the 10^{-5} level*, HRMS 2008, Prague, République Tchèque (2-6 septembre 2008)
- [27] C. Stoeffler, B. Darquié, A. Shelkovnikov, C. Daussy, O. Lopez, A. Amy-Klein, and C. Chardonnet, *Towards a first observation of parity nonconservation in molecules by laser spectroscopy*, HRMS 2008, Prague, République Tchèque (2-6 septembre 2008)

Introduction

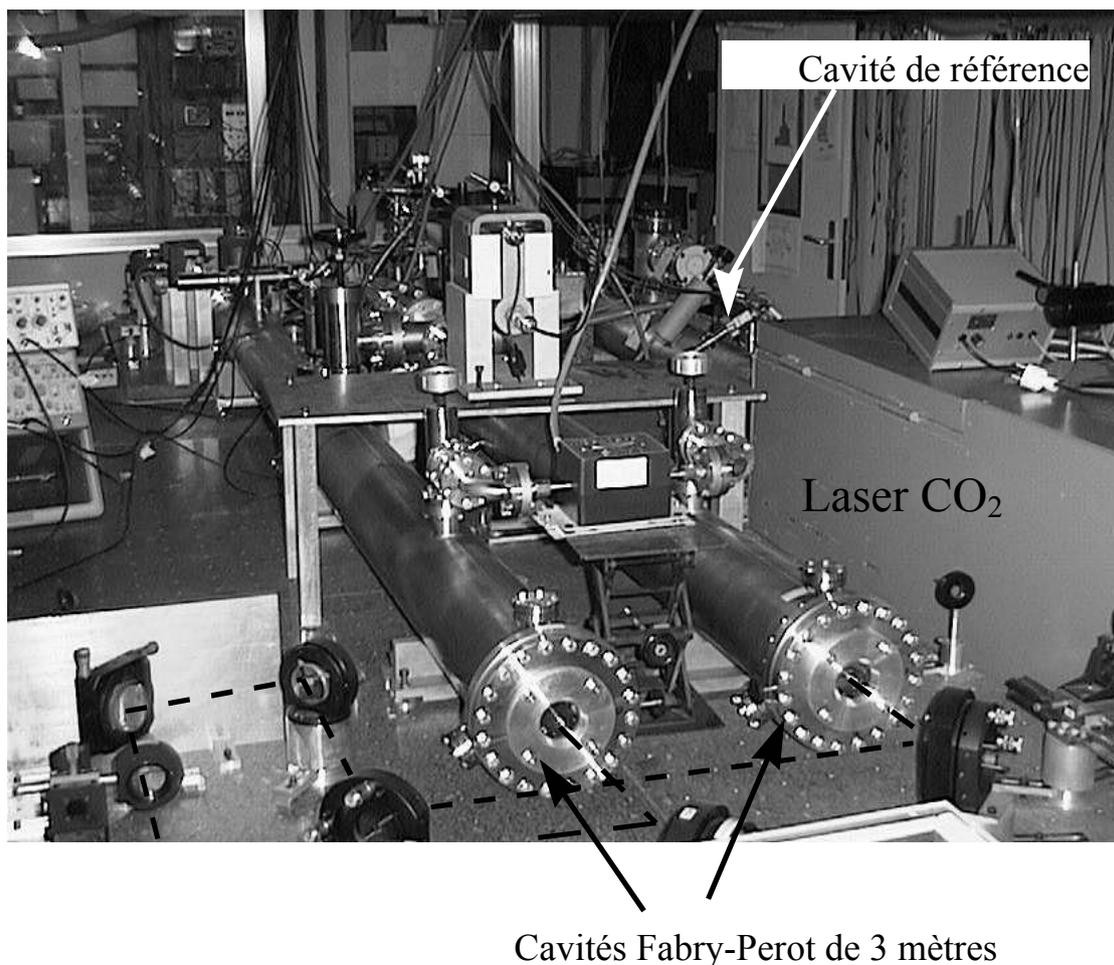
Mes activités de recherche au Laboratoire de Physique des Lasers ont débuté par mon travail de thèse de septembre 1995 à janvier 1999. Durant cette période, j'ai développé une première expérience de spectroscopie à ultra haute résolution pour la mise en évidence d'un effet de non conservation de la parité (NCP) dans le spectre de molécules chirales. Après l'obtention de mon doctorat, j'ai effectué un stage post-doctoral de 6 mois au LPTF (devenu depuis SYRTE) à Paris sur l'amélioration des performances de l'étalon de fréquence basé sur le laser à CO₂ à 10 μm. J'ai ensuite été recruté en tant que Maître de Conférences à l'Institut Galilée - Université Paris 13. Depuis je développe mes activités de recherche au Laboratoire de Physique de Lasers au sein de l'équipe IRCO₂ (Brisures de symétrie des molécules, horloges optiques et générations d'ondes atomiques cohérentes) devenue depuis l'équipe HOTES (Horloges optiques et tests fondamentaux par spectroscopie et interférométrie atomique et moléculaire), dirigée conjointement par Ch.J. Bordé et Ch. Chardonnet (Directeurs de Recherche, CNRS). La philosophie générale de l'équipe est de développer des expériences de très haute précision en spectroscopie moléculaire appliquées à des problèmes originaux de physique fondamentale.

De 1999 à 2002 nous avons poussé l'expérience de recherche d'un effet NCP à ses limites et conclu à la nécessité de passer à une expérience en jet moléculaire pour aboutir à l'observation de l'effet. Cette nouvelle expérience est en cours de développement depuis 2007 et s'appuie sur le dispositif de jet supersonique moléculaire développé et optimisé dans l'équipe depuis plus de 10 ans pour des applications métrologiques. La sensibilité requise pour l'observation d'un effet NCP nécessite par ailleurs des sources lasers très bien contrôlées en terme de stabilité de fréquence et de reproductibilité. A partir de 2003, j'ai donc participé aux premières étapes du développement d'un lien optique entre le Laboratoire de Physique des Lasers (LPL) et le SYRTE (Paris) pour le transfert longue distance d'une fréquence d'horloge. Nous avons ensuite appliqué ce transfert à des expériences de métrologie au LPL au cours desquelles nous avons notamment démontré une amélioration significative du

contrôle en fréquence de nos lasers à CO₂. Enfin depuis 2004, je développe une nouvelle expérience de spectroscopie moléculaire avec pour objectif la première mesure de la constante de Boltzmann par spectroscopie laser à un niveau de quelques ppm. Le travail mené depuis 4 ans sur ce projet devrait prochainement nous permettre d'atteindre notre objectif. Cette nouvelle thématique nous conduit également à nous intéresser à des problèmes très fondamentaux sur les profils de raies en absorption linéaire.

Dans ce manuscrit je présente un résumé des mes activités de recherche dans l'équipe HOTES depuis 1999.

CHAPITRE I. Étude de la non conservation de la parité moléculaire



Introduction

La non-conservation de la parité (NCP) dans les molécules a été suggérée pour la première fois par Rein en 1974 [1]. Cette NCP qui trouve son origine dans l'interaction faible dont la portée est l'échelle nucléaire a été observé dans des expériences de physique atomique et des hautes énergies, mais jamais dans des molécules. Letokhov a proposé sa mise en évidence en recherchant une différence de fréquence dans le spectre d'absorption infrarouge des énantiomères de la molécule chirale CHFCIBr dès 1975 [2]. Plus de trente ans plus tard,

aucune expérience n'a permis d'observer la violation de la parité dans les molécules. La raison essentielle est la petitesse de l'effet recherché. Malgré l'absence d'observation expérimentale, la NCP moléculaire a suscité un véritable engouement au sein de la communauté scientifique. En effet, depuis les suggestions de Rein et Letokhov, la production scientifique sur le sujet a été particulièrement riche et abondante. Certains auteurs ont en effet émis l'hypothèse que la petite différence d'énergie provoquée par l'interaction faible entre les molécules gauches et droites pouvait être la cause de la brisure de symétrie gauche-droite observée dans les molécules biologiques et plus largement dans les systèmes vivants [3]. Des modèles crédibles ont été développés qui rendent compte de l'amplification possible de l'excès énantiomérique d'une espèce sur l'autre, accréditant la thèse que la nature aurait privilégié une orientation par rapport à l'autre de façon déterministe [4]. Il s'agit là d'une hypothèse très controversée face à des approches non déterministes : le débat n'est toujours pas tranché. Parallèlement, de nombreux calculs de chimie quantique ont été menés sur diverses molécules biologiques pour déterminer cette différence d'énergie gauche-droite. Les programmes de calculs ont eux-mêmes été très sensiblement améliorés au cours des vingt dernières années [5, 6]. Sur le plan expérimental, en 1976 Letokhov et al. ont enregistré des spectres en absorption saturée [7] d'un mélange racémique de la molécule chirale CHFCIBr à une résolution de l'ordre de 1 MHz [8]. Aucun effet de dédoublement de la raie n'a été observé. Au cours des années 1977-1978, ces expériences ont été répétées au LPL à plus haute résolution (typiquement 50 à 100 kHz) sur les molécules CHFCIBr et CHFCII, aboutissant à la même conclusion. Une expérience sur le camphre a ensuite été tentée avec une sensibilité de 10^{-8} en 1977 [9], l'effet calculé ayant été estimé à 10^{-19} en 2004 [10]! La très grande sensibilité requise et la non disponibilité des énantiomères séparés des molécules chirales favorables auront été un frein très fort malgré l'engouement du sujet dont témoigne l'impressionnante bibliographie théorique qui s'y rapporte.

Il existe très peu de propositions alternatives : citons la spectroscopie RMN [11], une méthode consistant à créer une molécule chirale dans une superposition cohérente d'états propres gauches et droits et à étudier l'oscillation temporelle entre ces deux états [12] ou encore l'étude de la polarisation de la lumière traversant un milieu chiral dont la barrière tunnel entre états gauche et droit soit comparable à la différence d'énergie NCP [13]. Terminons enfin ce panorama en citant un article paru en 2000 [14] où un effet NCP a été annoncé dans une expérience de spectroscopie Mössbauer en phase solide mais le signe de

l'effet observé est en contradiction avec les calculs théoriques, contradiction qui n'a toujours pas été levée.

I. L'effet NCP en chimie quantique

La description théorique de la chimie offerte par la mécanique quantique conventionnelle ne tient compte que des interactions électromagnétiques. Ces forces conservent la parité, ce qui implique qu'une molécule chirale et son image dans un miroir sont dégénérées en énergie. L'hamiltonien de la chimie quantique électrofaible, d'autre part, contient une composante H^{NCP} qui ne conserve pas la parité et qui, par conséquent, induit une petite différence d'énergie entre deux énantiomères. Dans le cadre de la théorie quantique des champs, toute interaction est véhiculée par des bosons virtuels. La contribution principale à la différence d'énergie entre énantiomères provient de l'échange du boson Z^0 entre les électrons et les noyaux. Contrairement aux photons, échangés dans l'interaction électromagnétique, ces bosons sont massifs, ce qui limite drastiquement la portée de l'interaction.

L'introduction dans l'hamiltonien moléculaire des termes qui violent la parité δ_{NCP} , i.e. qui ne commutent pas avec l'opérateur parité conduit à une matrice hamiltonienne non diagonale dans la base des états de parités opposées. Les états de parités opposées ne sont alors plus stationnaires et la matrice peut être diagonalisée dans la base des états de chiralités opposées. La dégénérescence en énergie des niveaux moléculaires des deux énantiomères de la molécule est alors levée :

$$H_{\pm} = \begin{pmatrix} E_0 & \delta_{NCP} \\ \delta_{NCP} & E_0 \end{pmatrix} \quad H_{G,D} = \begin{pmatrix} E_0 + |\delta_{NCP}| & 0 \\ 0 & E_0 - |\delta_{NCP}| \end{pmatrix}$$

L'hamiltonien NCP correspondant est exprimé comme une somme sur des contributions atomiques : $H^{NCP} = \frac{G_F}{2\sqrt{2}} \sum \gamma_5 Q_{W;A} \rho^A$.

La charge faible $Q_{W;A}$, [$Q_{W;A} = Z_A (1 - 4 \sin^2 \theta_w) - N_A$ avec $\sin^2 \theta_w = 0.2319$] du centre A est déterminée par son nombre de protons et de neutrons, respectivement Z_A et N_A . La présence de la densité de nucléons normalisée ρ^A montre que l'interaction est effectivement limitée au volume nucléaire. La constante de couplage de Fermi G_F montre

dans laquelle la mesure de l'interaction est faible. La matrice 4×4 γ_5 couple les composantes des 4-spinneurs de Dirac de spins opposés et montre que l'interaction est nulle au premier ordre. C'est l'interaction spin-orbite d'origine relativiste qui, couplée à H^{NCP} , sera la cause principale de la levée de dégénérescence gauche-droite, δ_{NCP} . Cette différence d'énergie entre énantiomères croît en Z^5 ce qui suggère que les molécules candidates doivent contenir au moins un atome lourd.

II. Expériences en cellules

A. Première expérience à très haute résolution

Ce projet a été réinitié dans l'équipe HOTES en 1995 lorsque j'ai débuté ma thèse. A cette époque, deux éléments ont conduit l'équipe à s'engager dans cette voie : les progrès accomplis dans le contrôle en fréquence des sources lasers CO_2 et la possible disponibilité des échantillons séparés de CHFClBr , qui s'est concrétisée en décembre 1996 [15, 16]. En effet, le groupe d'A. Collet et J. Crassous – ENS Lyon venait de réussir la résolution efficace des énantiomères de cette molécule et a pu nous fournir des échantillons en vue de notre expérience.

Au cours de ma thèse, nous avons développé un nouveau système d'asservissement en fréquence des sources laser à CO_2 (à $10\mu\text{m}$). Nous avons obtenu une stabilité au niveau de 0,1 Hz sur 100 s, soit une stabilité relative de 3×10^{-15} [17, 18] (voir Figure 2).

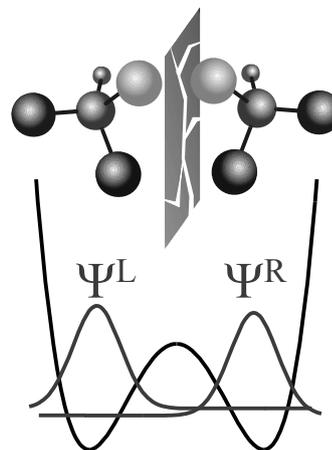


Figure 1 : la brisure de symétrie dans les molécules chirales

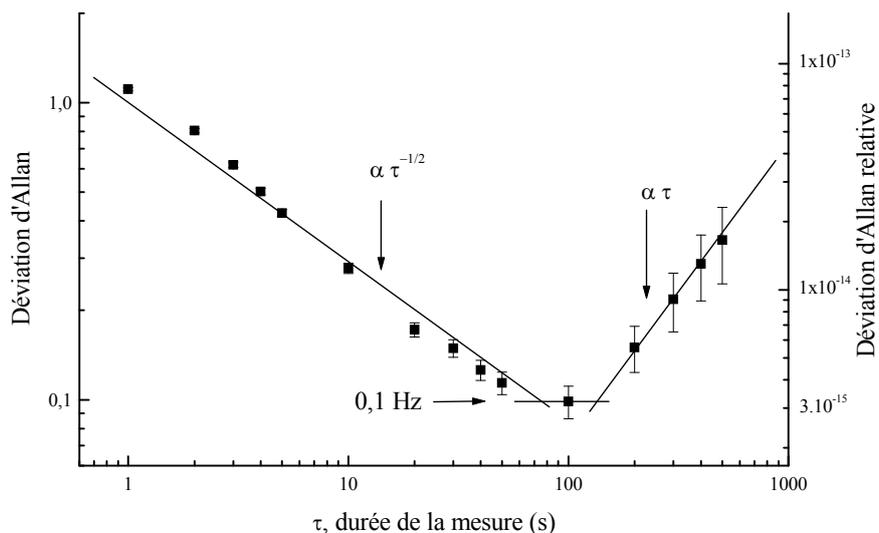


Figure 2 : déviation d'Allan du battement de deux lasers asservis sur la même raie d'absorption saturée P(46) d'OsO₄

Un modulateur électro-optique micro-onde très large bande (8-18 GHz) a ensuite été implanté sur l'expérience afin d'obtenir un rayonnement laser largement accordable en fréquence entre 9 et 12 μm , utilisable pour des expériences de spectroscopie à ultra haute résolution. Les premières expériences NCP ont alors débuté au cours de l'année 1998.

L'expérience consiste à comparer les fréquences vibrationnelles des énantiomères gauche et droit d'une molécule chirale. Les spectres sont enregistrés simultanément, avec le même laser, dans deux cavités Fabry-Perot jumelles de 3 mètres de long construites pour la mesure (voir Figure 3). La mise en évidence d'une différence de fréquences serait la signature d'un effet de violation de parité liée à l'interaction faible.

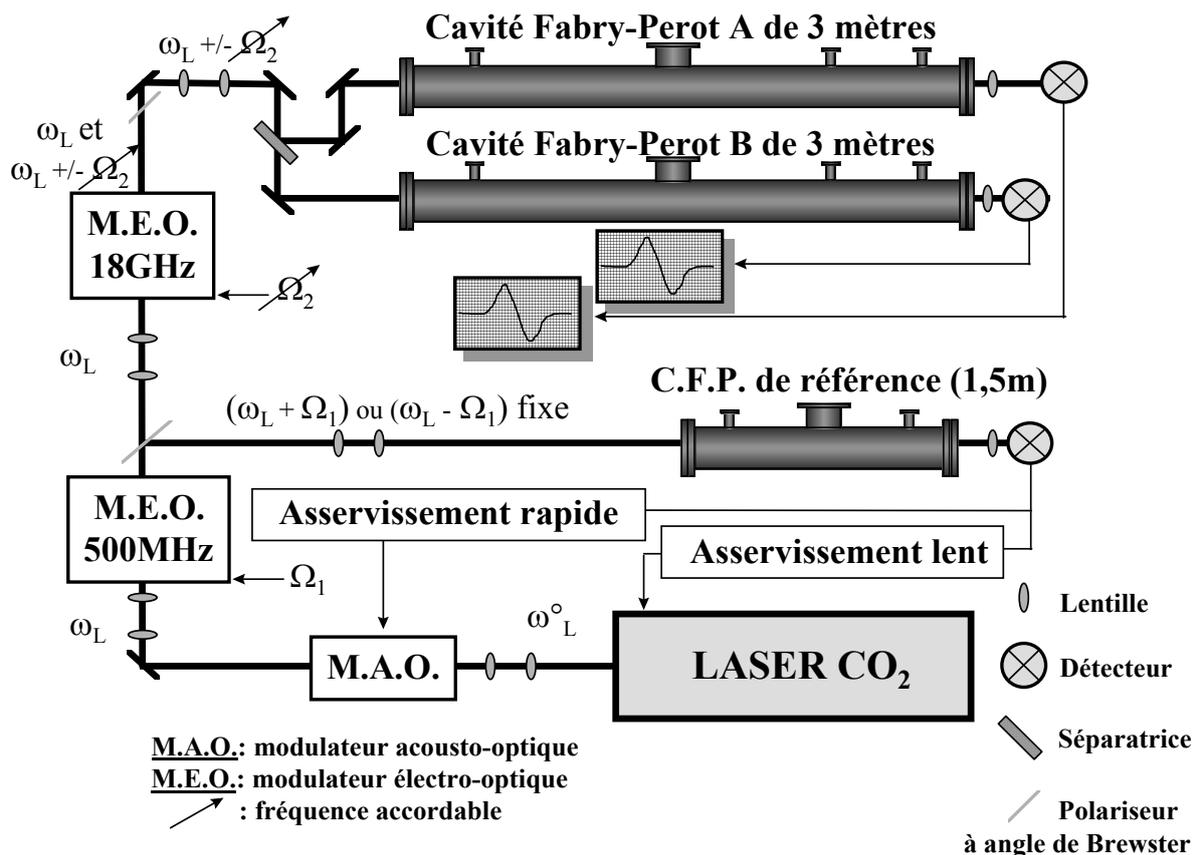


Figure 3 : spectromètre infrarouge développé pour l'expérience NCP

Une composante hyperfine particulière a été sélectionnée pour la réalisation du test. Ce choix a été le fruit d'études préliminaires lourdes comme la Figure 4 permet de l'imaginer. En effet, la connaissance du spectre de vibration-rotation (spectre supérieur – A. Valentin Paris 6) et son analyse complète réalisée par A. Bauder et al – Zurich (et publiée en 1997) [19] ont été des conditions sine qua none pour mener cette étude. Cette composante hyperfine appartenant à la transition $(40,7,34) \leftarrow (40,8,33)$ possède une structure non résolue, par ailleurs observée grâce à notre grande cuve à absorption qui ne permet pas, quant à elle, de mener cette comparaison avec la meilleure sensibilité.

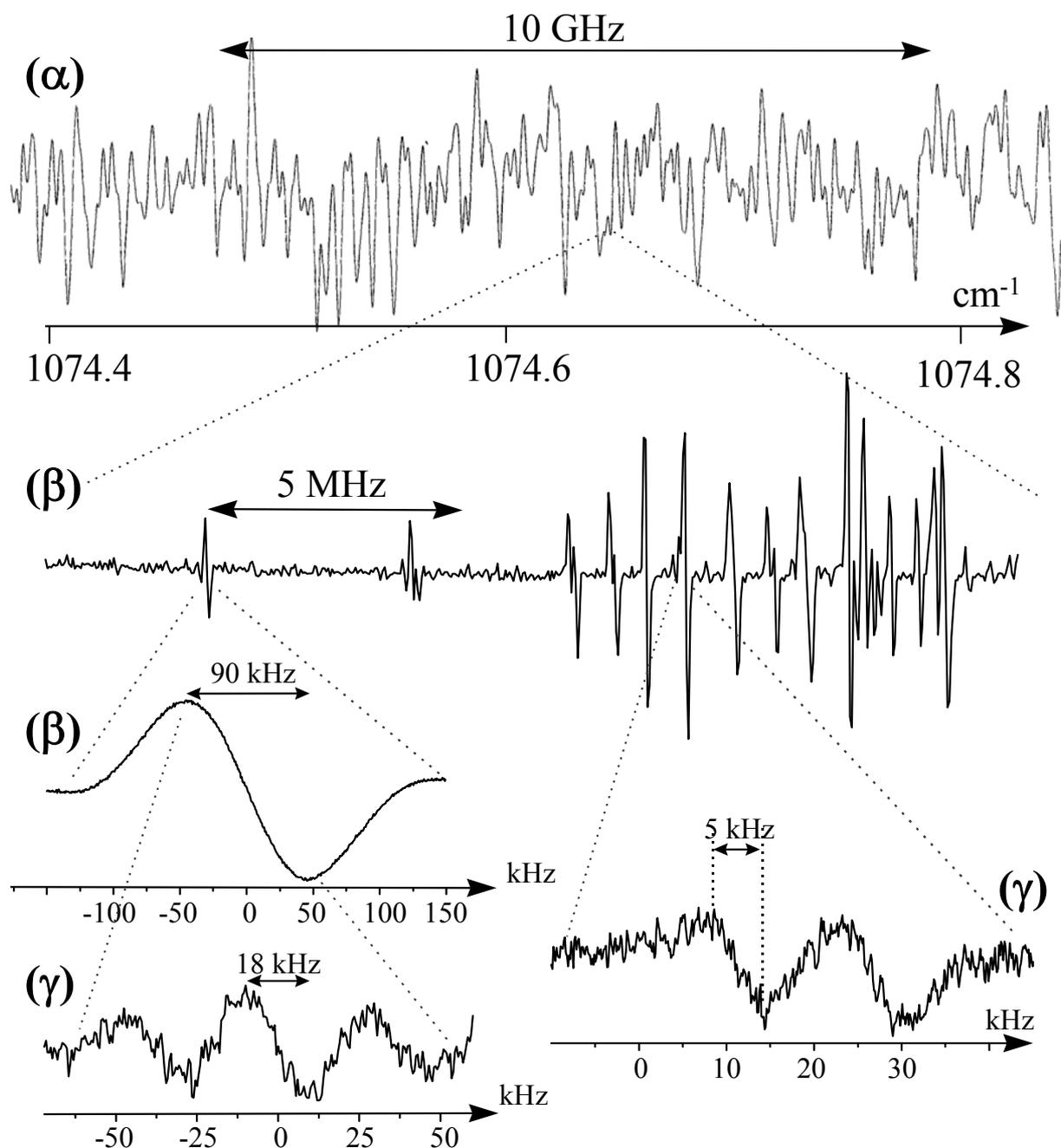


Figure 4 : structure hyperfine de la raie $(40,7,34) \leftarrow (40,8,33)$ enregistrée par spectroscopie à transformée de Fourier au L.P.M.A. (α), dans nos cavités Fabry-Perot jumelles(β) et dans notre grande cuve d'absorption de 18 mètres (γ)

Une difficulté majeure de l'expérience consiste à s'affranchir des effets systématiques. C'est pourquoi un soin particulier a été apporté pour créer des conditions expérimentales identiques aux deux espèces : un seul laser avec les mêmes conditions de modulation, la possibilité d'alterner le remplissage des cavités par l'un puis l'autre énantiomère. Grâce à ce

soin particulier et notamment par une compensation des effets liés aux cavités (voir Figure 5), nous avons ainsi obtenu après 580 mesures une incertitude statistique de 2 Hz et une sensibilité de 5 Hz limitée par les erreurs systématiques résiduelles estimées sur la mesure de l'écart à rapprocher de la largeur de raie de 90kHz. En tenant compte du fait que l'excès énantiomérique des échantillons était loin de 100% (22% et 56,5%), on en déduit une différence de fréquences entre les deux énantiomères de :

$$\nu(R-) - \nu(S+) = 9,4 \pm 5,1 \pm 12,7 \text{ Hz}$$

L'écart inférieur à 13 Hz mesuré entre les fréquences de transition des deux énantiomères de la molécule CHFClBr représente un écart relatif inférieur à 4×10^{-13} [20]. Ce résultat, obtenu en 1999, a représenté un gain de près de 5 ordres de grandeur, par rapport à l'expérience réalisée sur le camphre en 1977.

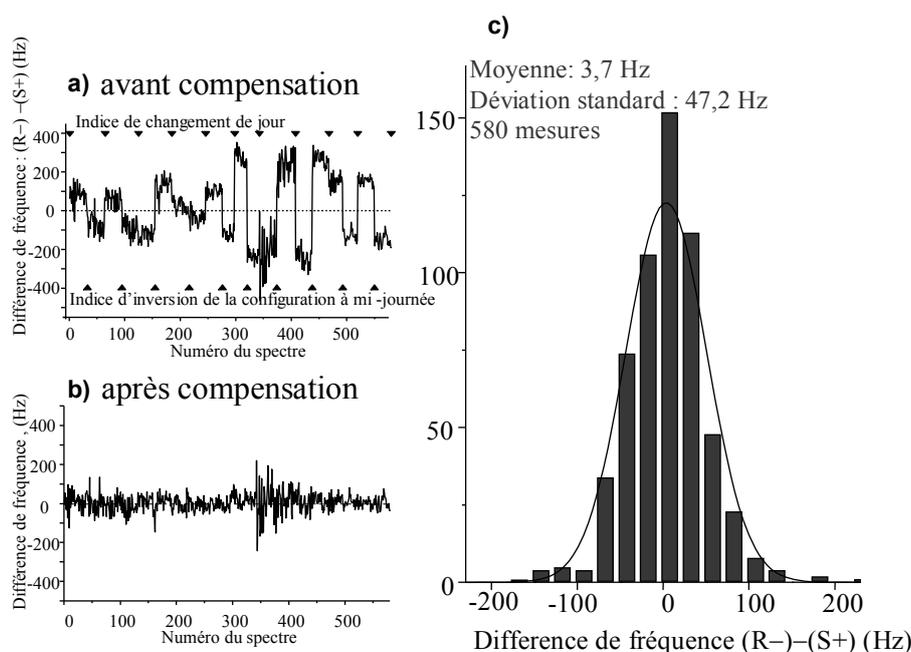


Figure 5 : a) mesures brutes de l'écart de fréquences entre énantiomères (R-) - (S+) ; b) mesures après compensation des effets de cavités ; c) histogramme de ces mesures corrigées

Suite à ce travail de thèse, j'ai intégré l'équipe HOTES en septembre 1999 après un bref séjour postdoctoral au SYRTE. Mon travail de recherche sur ce sujet a eu pour principaux objectifs, l'amélioration de la sensibilité du test et l'analyse des limites ultimes d'une telle expérience.

B. Deuxième test

Nous avons entrepris l'étude à très haute résolution du spectre hyperfin de la molécule test CHFCIBr . De nombreuses structures hyperfines ont été enregistrées, et l'étude des interactions quadrupolaires de cette molécule dans son état vibrationnel $\nu_4=1$ a été entreprise. Les tenseurs quadrupolaires des noyaux de brome et de chlore ont ainsi été complètement déterminés dans ce niveau pour les quatre espèces isotopiques d'abondance naturelle [21]. Ceci permet désormais la prédiction des structures hyperfines des transitions rovibrationnelles avec une précision de quelques kHz. Nous avons pu ainsi prédire la position d'une transition dont la structure hyperfine très compacte conduit à un meilleur rapport signal sur bruit en vue d'un nouveau test de violation de la parité.

Nous avons également apporté un certain nombre d'améliorations à l'expérience afin d'accroître encore la sensibilité du test:

- changement des miroirs des cavités Fabry-Perot pour en accroître la finesse,
- stabilisation du laser sur une transition de CO_2 pour améliorer la stabilité en fréquence à long terme,
- modification de la cavité laser pour obtenir une source plus puissante et réellement monomode,
- développement d'un asservissement en intensité,
- par ailleurs, nous avons pu obtenir des chimistes des échantillons mieux séparés.

Un nouveau test a alors été réalisé en 2000 [22]. Les fréquences de résonance des deux énantiomères ont été comparées à un niveau de 5×10^{-14} . Ces résultats sont comparés aux premières mesures sur la Figure 6.

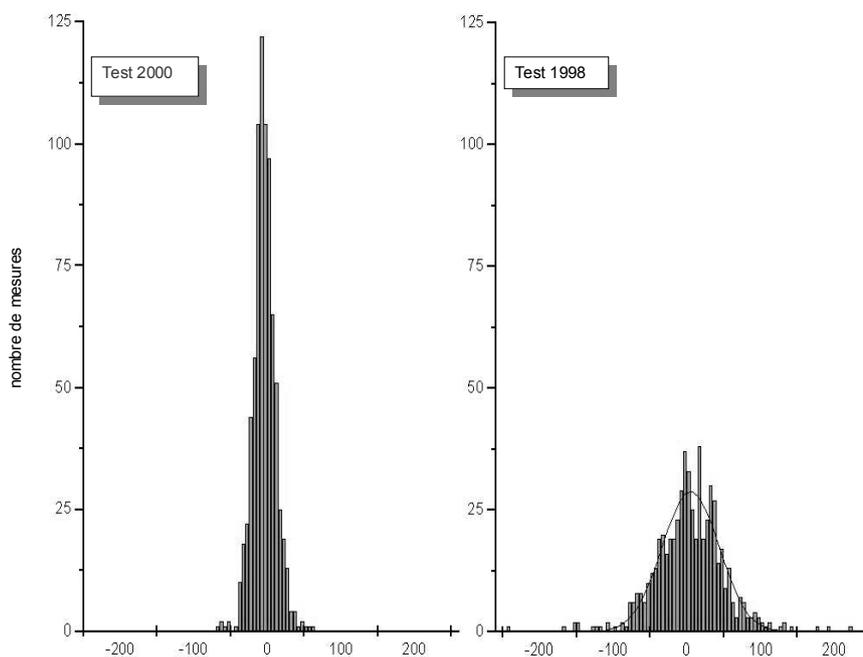
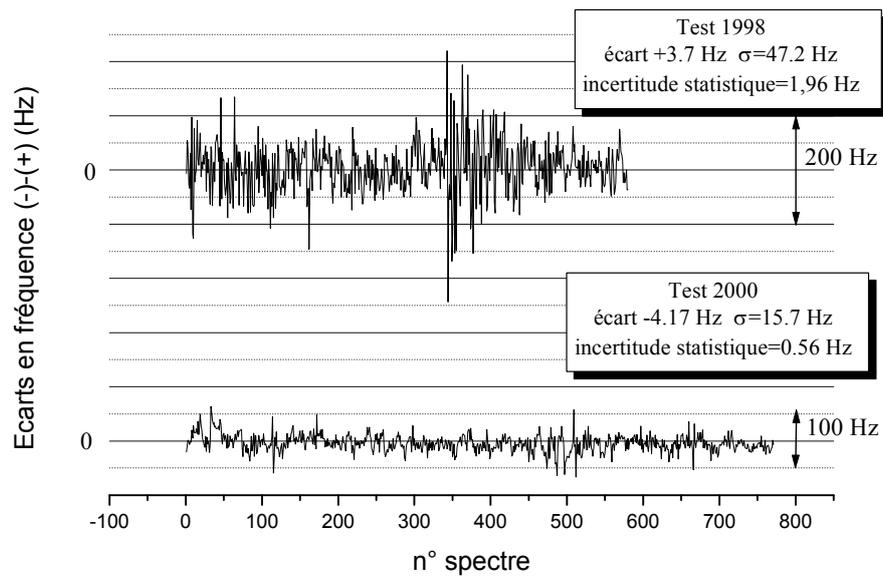


Figure 6 : comparaison des évolutions chronologiques (en haut) et histogrammes (en bas) de différence de fréquence $R(-)-S(+)$ après compensation des effets systématiques quotidiens des test 98 et 2000

A ce niveau de sensibilité, nous avons mis en évidence un écart de fréquence significatif proportionnel à la pression (voir Figure 7). Cette différence traduit non pas un effet de violation de la parité qui est essentiellement constant avec la pression mais un effet lié aux impuretés résiduelles des échantillons, inhérent à toute expérience en cellule. Cette seconde série d'expériences, même si elle ne nous a pas conduit à améliorer la sensibilité du test, nous a permis d'en identifier clairement les limites.

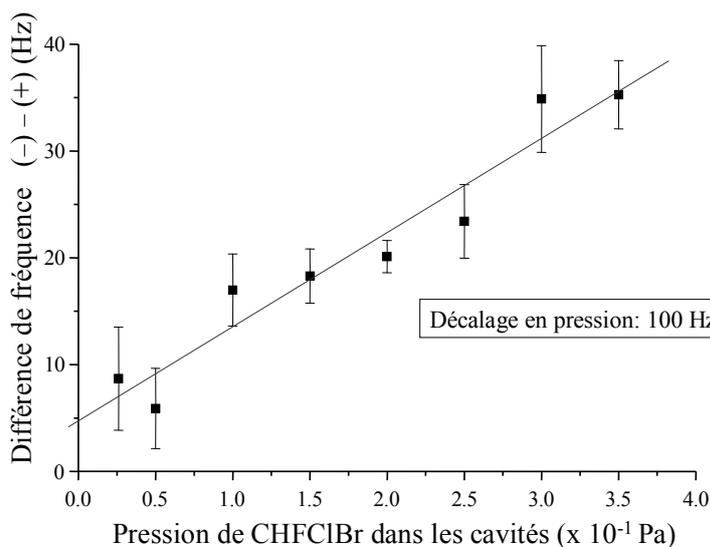


Figure 7 : mise en évidence de la dépendance en pression de l'écart de fréquence mesuré avec les échantillons délivrés en 1998

C. Limites de l'expérience en cellule

L'effet NCP attendu, de l'ordre du Hertz, est une petite fraction de la largeur de raie, c'est également environ quelques 10^{-14} de la fréquence laser. Il est donc impératif d'être très vigilant aux effets systématiques. Avant nos expériences NCP, aucun calcul de déplacement de fréquence de vibration n'était disponible et seuls des arguments qualitatifs permettaient de prévoir l'effet entre 10^{-16} et 10^{-13} . Nos résultats ont stimulé de nombreux travaux théoriques et plusieurs groupes ont ainsi pu calculer par des méthodes différentes l'effet NCP attendu sur la transition vibrationnelle de CHFCIBr étudiée expérimentalement (Lazzeretti-Modène [23], Quack-Zurich [24], Schwerdtfeger-Auckland [5]). Les trois résultats, obtenus par trois méthodes différentes dont l'une relativiste (développée par P. Schwerdtfeger) sont

concordants et situent l'effet à 2 mHz, soit une sensibilité relative de l'expérience nécessaire de 5×10^{-17} [25, 26]!

A l'issue de ces travaux, deux conclusions se sont imposées [27]:

- La nécessité de trouver une molécule test plus favorable que CHFCIBr . P. Schwerdtfeger a montré en 2002 qu'un écart de 2×10^{-15} pouvait être espéré à la même longueur d'onde (fréquence de vibration de la liaison C-F) sur la molécule de CHFBrI [26] et un effet de 7×10^{-15} pour la liaison C-F de ClHgCHFCl [28].
- La nécessité de revoir le dispositif expérimental qui reposait sur une expérience d'absorption saturée en cellule pour laquelle les effets collisionnels, même avec des précautions particulières, masqueraient tout effet NCP inférieur au Hertz soit 3×10^{-14} dans le domaine infrarouge exploré. Seule une expérience sur jet moléculaire où les effets collisionnels et liés aux impuretés du gaz sont considérablement réduits pourra donner lieu à une sensibilité supérieure.

Parallèlement, dans notre équipe, une expérience sur jet supersonique de SF_6 a permis d'observer des franges de Ramsey à deux photons avec une résolution inégalée de 100Hz [29] (100 kHz dans la 1^{ère} expérience NCP) (voir Figure 8).

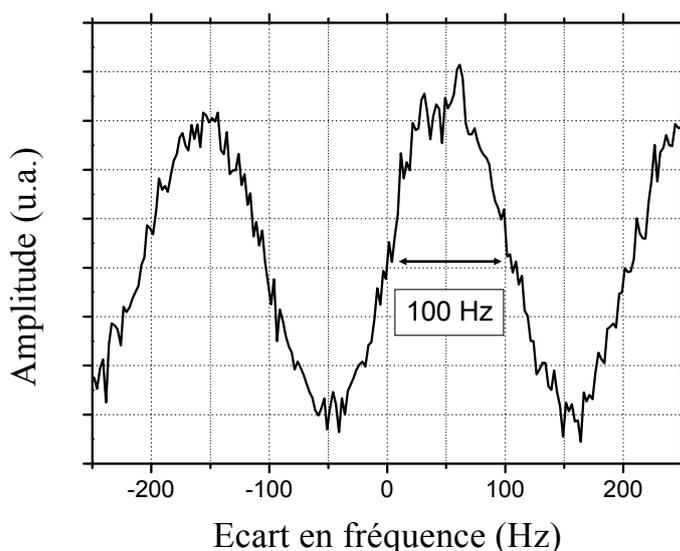


Figure 8 : signal de frange de Ramsey à 2 photon en jet supersonique de SF_6

L'idée a donc été d'adapter cette expérience de franges de Ramsey à deux photons à ce projet. Il faut en outre souligner que le contrôle de l'axe des fréquences des sources lasers a été considérablement amélioré au cours des dernières années : le laser à CO₂ utilisé comme oscillateur local est raccordé à la fontaine atomique de l'observatoire de Paris via le laser femtoseconde du LPL et une liaison par fibre optique de 43 km [30] dont nous contrôlons la longueur optique au niveau de 10⁻¹⁸. Nous disposons ainsi d'une stabilité de la fréquence laser de l'ordre de 10⁻¹⁵ (0,03 Hz) par jour (voir chapitre II) [31, 32].

Le moyen le plus efficace de lutter contre ces effets systématiques est une expérience différentielle dans laquelle les conditions pour les deux types de molécules soient les plus identiques possibles. L'idée est de construire un double jet moléculaire afin de mettre les deux espèces gauches et droites de la molécule sélectionnée en phase gaz dans un gaz porteur (He ou Ar) qui impose les caractéristiques de distribution de vitesse et de population des niveaux aux molécules actives. Ce gaz se détend dans la zone d'interaction en utilisant la même buse et le même écorceur et collimateur, ce qui définit une identité de divergence et d'orientation des deux jets produits. Les spectres de ces deux énantiomères seront enregistrés de façon alternée, les éventuels effets systématiques dans la mesure de la différence des centres de résonance devant être considérablement compensés. Par rapport à l'expérience en cellule, la largeur de raie sera divisée par 1000 et les effets collisionnels résiduels seront réduits de plus de 3 ordres de grandeur. Le refroidissement rotationnel et vibrationnel obtenu lors de la détente supersonique permet par ailleurs, par la réduction du nombre de niveaux peuplés, de simplifier le spectre et de gagner en signal d'absorption.

Deux thèses ont été soutenues en relation avec ce sujet :

- Thibaut Marrel : Le spectre à très haute résolution de la molécule chirale CHFCIBr à 9,3 μ m : test de violation de la parité et étude de la structure hyperfine (soutenue le 15/12/2000) [33].
- Michael Ziskind : Spectroscopie infrarouge à ultrahaute résolution appliquée à l'étude de symétries fondamentales dans les molécules polyatomiques : recherche d'un effet de violation de parité et test du postulat de symétrisation (soutenue le 21/12/2001) [34].

III. Vers une mesure NCP en jet moléculaire

A. Le projet NCPMOL (ANR-05-BLAN-0091)

Malgré le gap important et en raison de l'engouement autour de ce sujet, nous avons poursuivi la réflexion en associant différents partenaires, chimistes expérimentaux et théoriciens et spectroscopistes. L'objectif est de réaliser une observation de la NCP moléculaire nette et précise afin de permettre une confrontation sérieuse avec les modèles de chimie quantique et, éventuellement, avec la théorie de l'interaction faible elle-même dans le régime des basses énergies. Pour cela, un travail impliquant 7 groupes aux compétences complémentaires est amorcé depuis 2003. Les groupes impliqués sont ceux: de J. Crassous au Laboratoire Sciences chimiques de Rennes, de L. Guy au laboratoire de Chimie de l'ENS Lyon, de P. Schwerdtfeger à Auckland (Nouvelle Zélande), de T. Saue au Laboratoire de Chimie Quantique et de Modélisation Moléculaire à Strasbourg, de T. Huet au Laboratoire de Physique des Lasers Atomes et Molécules à Lille (PhLam), de P. Asselin et P. Soulard au Laboratoire Dynamique, Interactions et Réactivité à Paris (LADIR) et enfin notre équipe au Laboratoire de Physique des Lasers (LPL) à Villetaneuse. Ce projet s'effectue dans le cadre du contrat ANR-05-BLAN-0091.

Le Laboratoire de chimie quantique et de modélisation calcule l'effet de violation de parité dans la molécule et vérifie la position des fréquences vibrationnelles dans la région de 9-12 μ m du laser CO₂. Le rôle principal de ce travail est de guider la recherche des molécules candidates pour l'expérience à haute résolution. Les deux laboratoires de Chimie travaillent à la synthèse des molécules chirales sélectionnées. La résolution chirale réalisée, il faut ensuite acquérir des informations spectroscopiques précises pour sélectionner une transition moléculaire favorable au test. Un important travail spectroscopique préliminaire est réalisé au PhLam pour la spectroscopie micro-onde, l'analyse rotationnelle et hyperfine et au LADIR pour la spectroscopie infrarouge. Ces travaux seront ensuite mis à profit pour chercher à mesurer la différence de fréquences entre les résonances des énantiomères de la molécule retenue à l'aide de notre expérience de franges de Ramsey à deux photons sur jet moléculaire.

Notre objectif est de produire un double jet moléculaire à partir des deux énantiomères de la molécule test qui aura été sélectionnée, synthétisée et étudiée spectroscopiquement [35]. Le jet moléculaire viendra interagir avec deux ondes stationnaires laser dont la fréquence sera

en résonance avec une transition à deux photons sans effet Doppler. Ces deux ondes stationnaires sont générées à partir d'une seule cavité Fabry-Perot à 4 miroirs. La condition de phase est alors automatiquement satisfaite pour observer des franges de Ramsey à deux photons dont la résolution est proportionnelle à l'inverse du temps de transit entre les deux zones. Le contrôle de la fréquence du laser à CO_2 est assuré par la chaîne de fréquence (composé d'une liaison par fibre optique et d'un laser femtoseconde) raccordant notre étalon à $10\ \mu\text{m}$ à la fontaine atomique du SYRTE (voir Figure 9 et chapitre II). Nous allons voir que ce projet se heurte à de nombreux verrous expérimentaux.

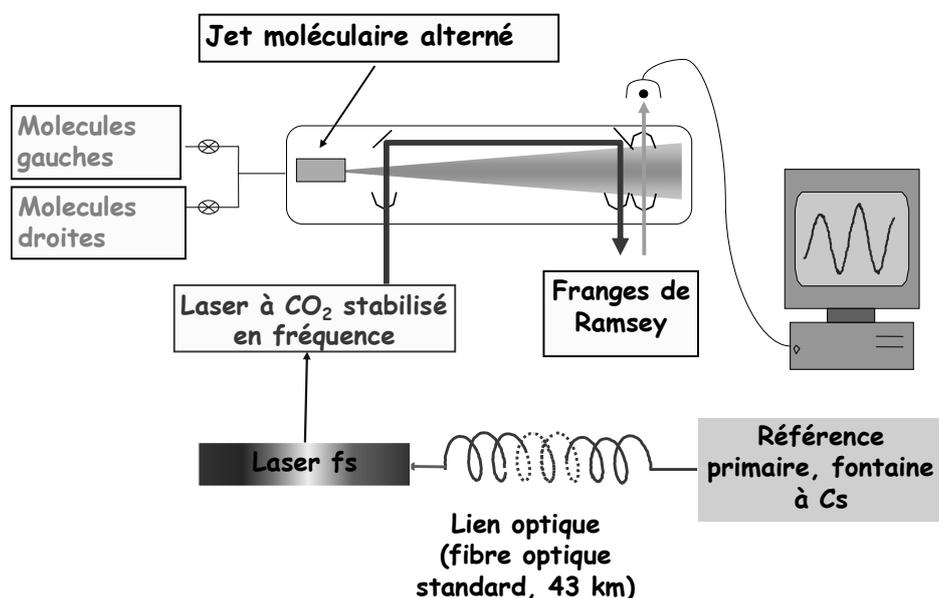


Figure 9 : dispositif expérimental composé du double jet moléculaire et du laser à CO_2 référencé à l'étalon primaire du SYRTE via une liaison par fibre optique entre les deux laboratoires

B. Résultats préliminaires

a) Spectroscopie de la molécule CHFCl_2

La première molécule envisagée pour un nouveau test NCP a été la molécule iodée CHFCl_2 proposée par P. Schwerdtfeger [27]. Cette molécule a été synthétisée au laboratoire de Chimie de l'ENS Lyon [36, 37] et étudiée par spectroscopie micro-onde, millimétrique et infrarouge au PhLam et au LADIR [38, 39].

Cependant, la molécule CHFClI est trop peu stable et ses conditions de préparation en grandes quantités et avec des puretés énantiomériques élevées quasiment impossibles à ce jour. Le travail de synthèse s'est donc réorienté vers de nouvelles classes de molécules. Après avoir proposé les molécules voisines CHFClI et CHFBrI pour lesquelles l'effet est estimé à environ 30 et 50 fois plus important que pour CHFClBr, P. Schwerdtfeger et R. Bast ont considéré des complexes de Rhénium chiraux (voir Figure 10) pour lesquels l'effet NCP dans un mode d'élongation Re-O très intense vers 30 THz a été calculée de l'ordre de 10^{-13} en valeur relative (1-3 Hz) [40, 41], soit près de 3 ordres de grandeur plus élevé que pour CHFClBr. Nous avons donc aussitôt réorienté nos travaux vers ces nouvelles molécules candidates.

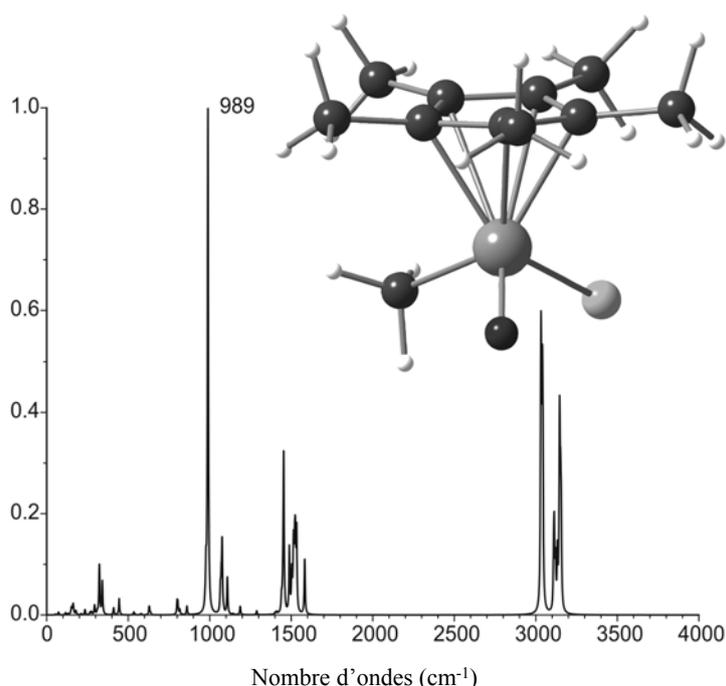


Figure 10 : complexe de Rhénium chiral proposé par P. Schwerdtfeger et R. Bast et spectre d'absorption théorique pour l'élongation Re-O autour de 10 μm

b) Spectroscopie des complexes de rhénium

Les différents complexes de Rhénium proposés, solide à température ambiante, se subliment entre 120 et 250 °C suivant l'espèce exacte considérée. Les chimistes ont pu synthétiser quelques grammes de plusieurs complexes. La production en quantité suffisante pour des expériences en jet est possible pour ces molécules. Par ailleurs la séparation chirale

peut être réalisée avec une efficacité de 100% [42], ce qui est un progrès notable par rapport à CHFClBr ou CHFCl .

Afin d'obtenir une quantité suffisante de molécules en phase vapeur mais également pour des raisons de simplicité de mise en œuvre, nous avons décidé de nous orienter vers une méthode de sublimation par chauffage et non d'ablation par laser pour la mise en phase vapeur dans le jet moléculaire.

Des tests systématiques de stabilité sur plusieurs complexes d'oxorhénium réalisés au LADIR et au PhLAM ont permis de sélectionner le composé TpRe=OEphedrine qui présente l'avantage d'une grande stabilité thermique et d'une voie d'accès fiable vers des grandes quantités énantiopures. L'inconvénient de ce complexe sur le plan spectroscopique est d'être une molécule lourde, d'une trentaine d'atomes et dotée de couplages quadrupolaires importants (voir Figure 11).

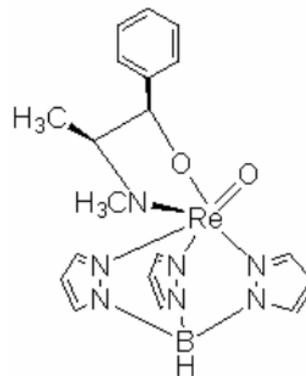


Figure 11 : molécule TpRe=OEphedrine

Des premiers tests de mise en jet supersonique ont été réalisés au LADIR par P. Asselin et P. Soulard. La sublimation débute à partir de 250°C et un flux suffisant de molécules gazeuses, entraîné avec de l'argon comme gaz porteur, est obtenu vers 280°C environ mais les molécules refroidies post-détente, ont tendance à se recondenser dans tout le volume de l'enceinte, et notamment sur le dispositif d'optique. Ainsi seules de larges absorptions correspondant au spectre infrarouge en phase solide du composé TpRe=OEphedrine ont été observées. Un test RMN sur le sublimat récupéré a prouvé qu'il n'y avait pas trace de dégradation de la molécule organométallique. Cependant, la température nécessaire pour détecter un signal infrarouge à partir d'un jetensemencé à l'argon, s'est avéré être bien supérieure à 200°C , ce qui va au-delà des limites d'utilisation de la méthode de chauffage.

Le groupe du LADIR vient très récemment de réaliser la mise en jet supersonique et la spectroscopie infrarouge d'une autre molécule, le méthyltrioxorhénium ou MTO (CH_3ReO_3) dont la thermodynamique (point d'ébullition : 65°C (10^{-3} Torr), point de fusion : 111°C) semble tout à fait favorable pour notre projet (voir Figure 12).

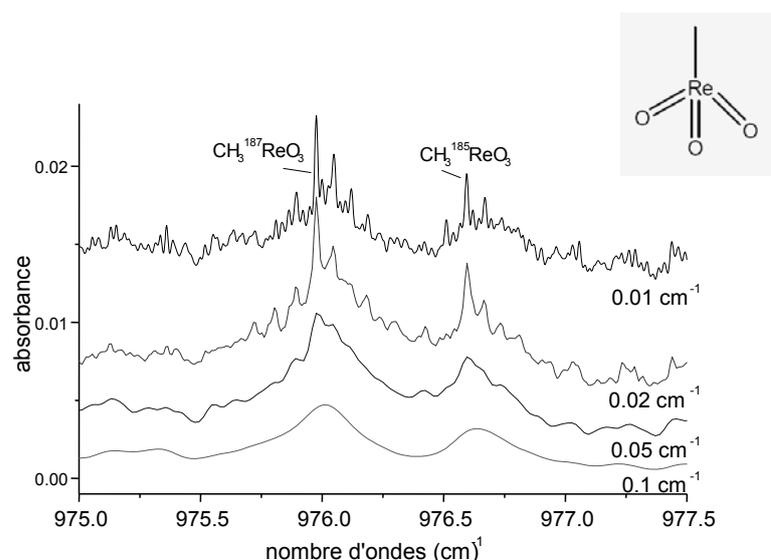


Figure 12 : spectres infrarouge en jet de la bande d'élongation Re-O de la molécule MTO diluée à 10% dans l'argon à différentes résolutions (LADIR, P. Asselin et P. Soulard)

Par la suite, nous tenterons de passer à des complexes chiraux obtenus à partir de substitutions sur le MTO, comme par exemple le composé CH_3ReOSSe . Cette nouvelle famille de molécules semble aujourd'hui la plus prometteuse.

c) Spectroscopie de l'uréthane

Afin de mieux comparer les sensibilités de détection de nos différentes techniques expérimentales (des techniques de jet moléculaire, continu au LADIR et au LPL et pulsé au PhLAM), nous avons décidé d'entreprendre l'étude simultanément sur les 3 spectromètres d'une même molécule test connue, l'uréthane ($\text{H}_2\text{NCO}_2\text{CH}_2\text{CH}_3$). Pour cette molécule, solide à 25°C, le passage en phase vapeur s'effectue entre 70 et 110 °C sans dégradation de la molécule.

Au PhLAM, la structure de rotation et la structure hyperfine des deux conformères ont été observées dans l'expansion supersonique. Au LADIR, le spectre infrarouge de ces deux mêmes conformères a été enregistré dans la région spectrale 1000-1900 cm^{-1} (voir Figure 13). Différents montages de récupération des molécules, basées sur la mise en place d'un point froid dans la chambre de détente, ont également été testés. Au LPL, un gros effort de

développement a été mené. Depuis 2007, nous nous sommes engagés dans la conception d'une nouvelle machine moléculaire.

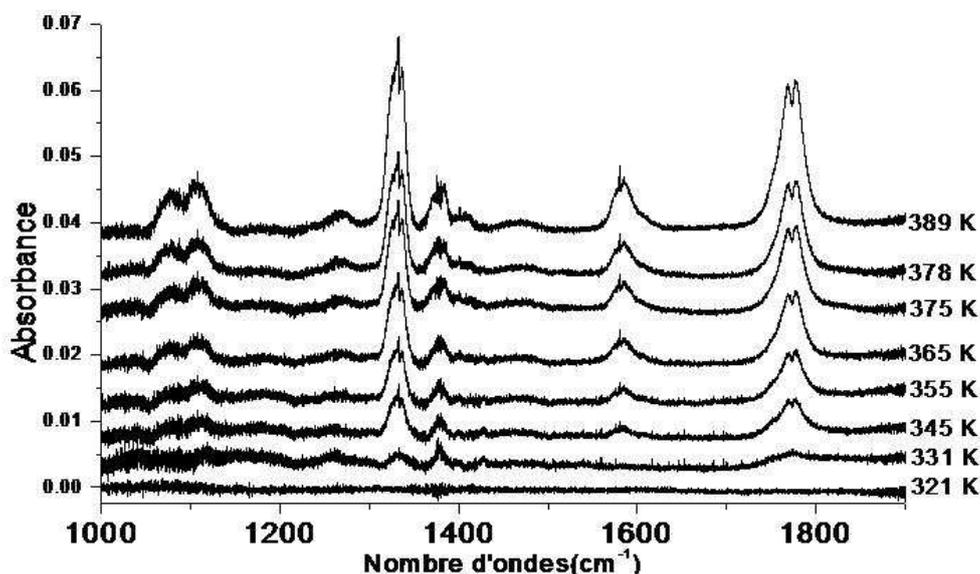


Figure 13 : spectre infrarouge en jet de l'uréthane pour différentes températures de sublimation (LADIR, P. Asselin et P. Soulard)

Les premières comparaisons, montrent que les conditions de mise en phase vapeur sont très proches au LADIR et au PhLam, mêmes si les conditions expérimentales, notamment au niveau de la pression des gaz et de leur consommation, sont très différentes [43].

Au LPL, le développement du nouveau dispositif est à présent conduit par Benoit Darquié depuis son arrivée dans l'équipe début 2008. Nous avons modifié le dispositif de mise en jet supersonique existant en simplifiant le montage. Un réservoir en acier inoxydable a été conçu et fabriqué pour permettre le stockage et le chauffage ohmique d'un échantillon de molécules test. Il est intégré à un système de valves qui permettent aisément de basculer d'un jet supersonique de SF₆ pur (ou un mélange SF₆ – gaz porteur), à un jet de gaz porteurensemencé par une vapeur de la molécule active. Une jauge permet également de mesurer la pression de vapeur de molécule active avant l'ensemencement. L'ensemble, placé en amont de la buse peut être chauffé jusqu'à 300 °C, afin d'éviter toute recondensation des molécules sur une paroi froide. Une partie du dispositif, dont la buse elle-même (simple trou de 50µm de

diamètre) est placée dans une enceinte, sous un vide secondaire, et chauffée à l'aide de fils thermocoaxiaux. L'autre partie, à l'air libre, est chauffée à l'aide de cordons chauffants. La température de l'ensemble est contrôlée à l'aide de thermocouples. Ce nouveau dispositif de chauffage a été testé dans un premier temps sur un jet de SF₆ avant les prochaines expériences sur l'uréthane. Parallèlement, nous avons mené une exploration de méthodes spectroscopiques simples de caractérisation du flux du jet supersonique. Nous avons ainsi effectué des mesures d'absorption linéaire sur une transition rovibrationnelle à un photon de SF₆. Ce type de mesure simple et rapide ne nécessite pas d'asservir le laser d'interrogation et permet de mettre en évidence des structures relativement larges en fréquence (élargies par effet Doppler). Nous avons ensuite enregistré des spectres d'absorption saturée puis d'absorption à deux photons.

Conclusion

Après une première expérience de spectroscopie laser en cellule qui a permis de réaliser un test NCP à un niveau de 4×10^{-13} , nous nous sommes engagés dans une nouvelle voie basée sur une expérience en jet supersonique.

Un certain nombre d'étapes indispensables à la réalisation du projet ont été franchies :

- un panel d'outils spectroscopiques a été expérimenté, permettant soit une analyse grossière utile à l'examen rapide des diverses molécules candidates, soit une mesure de très haute résolution, essentielle pour le test de NCP lui-même ;
- un dispositif de mise en phase vapeur puis en jet supersonique de molécules solides à température ambiante a été conçu et partiellement testé.

Dans les prochains mois, nous prévoyons d'étudier la spectroscopie en jet de la molécule uréthane. A ce stade le complexe de Rhénium à base d'éphédrine et le MTO sont les deux molécules candidates les plus prometteuses parmi celles qui ont été considérées à ce jour (synthèse, stabilité) et c'est sur elles que seront concentrés nos efforts pour réaliser un jet supersonique.

La raie à deux photons que nous étudierons sera le fruit des études amont de nos partenaires. L'idéal serait d'accéder à une raie de vibration-rotation identifiée grâce au travail de spectroscopie et d'analyse qui sera entrepris. Compte tenu de la complexité probable d'une telle étude, il est possible que dans un premier temps nous soyons conduit à nous contenter d'un repérage approximatif de la région correspondant aux raies à deux photons de faible

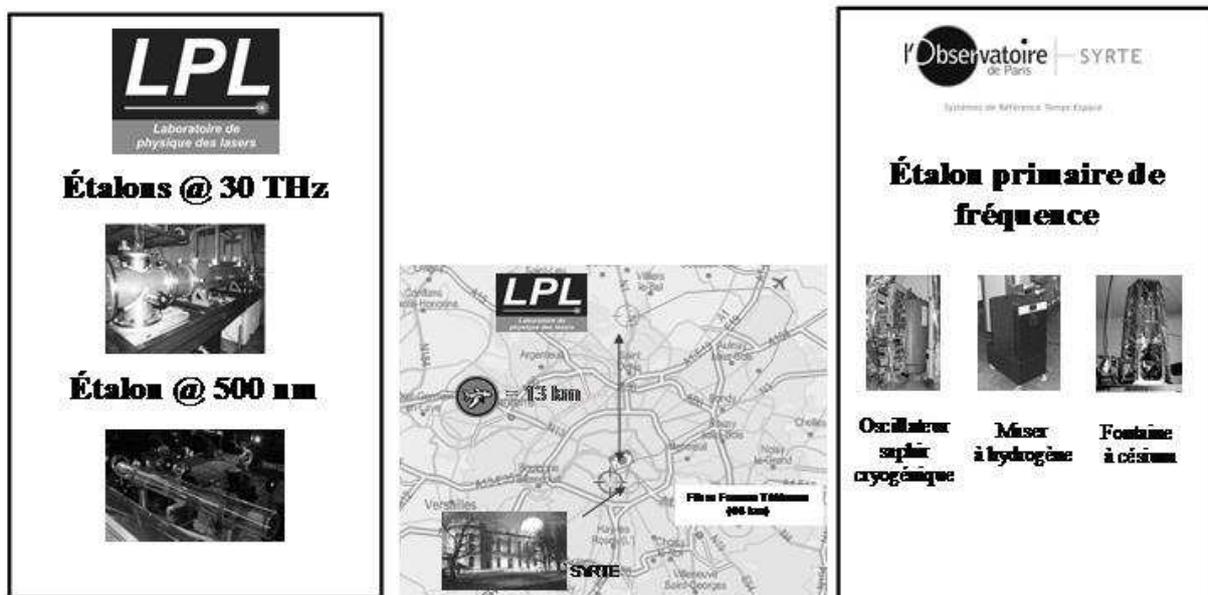
valeur de J dont la population est la plus favorable dans un jet supersonique. Ce repérage devrait permettre de réduire très sensiblement la région spectrale à explorer systématiquement par nos sources lasers pour la détection de ces transitions. La transition rovibrationnelle retenue sera affectée d'une structure hyperfine très riche et complexe compte tenu du nombre probablement élevé d'atomes ayant un spin non nul. Soulignons le fait que, contrairement à des expériences en cellule, la résolution de l'expérience ne s'en trouvera pas affectée ; nous aurons un jeu de franges de Ramsey par composante hyperfine, l'ensemble se superposant de façon plus ou moins constructive en fonction de l'écart entre composantes. Cela permet de se concentrer sur la région où le signal de franges est le plus intense. Il faut également souligner que l'effet NCP prédominant devrait être un effet d'origine vibrationnelle qui affectera en bloc l'ensemble de la structure hyperfine, la partie de la structure hyperfine étudiée n'est donc pas a priori essentielle. Une fois la transition détectée, nous enregistrerons le spectre des deux molécules énantiomères et nous comparerons le centre de résonance, un écart entre les deux spectres sera la signature de l'effet NCP recherché.

Deux chercheurs étrangers, R.J. Butcher (Cambridge, Angleterre) et A. Shelkovnikov (Institut de Physique Lebedev, Moscou, Russie) ont collaboré à ce projet en contribuant au développement de l'expérience de frange de Ramsey à deux photons sur SF_6 .

Ce thème est aujourd'hui encore un axe majeur de l'équipe. En 2007 l'équipe a recruté Benoît Darquié comme Chargé de Recherche pour conduire ce projet. Il encadre le travail de Clara Stoeffler qui a débuté une thèse sur ce sujet en septembre 2007.

Ce projet a été financé par des crédits récurrents, par la DGA, le BNM (devenu depuis LNE), un crédit spécifique du C.N.R.S. et une ANR en 2005.

CHAPITRE II. Transfert de fréquence par fibre optique et application à la métrologie des fréquences



Introduction

Un grand nombre d'horloges ont atteint des performances en terme d'exactitude de leur fréquence au niveau de 10^{-16} à 10^{-14} en valeur relative. C'est le cas des fontaines atomiques, basées sur des transitions hyperfines dans le domaine micro-onde d'atomes alcalins (Rb, Cs). Au SYRTE par exemple, ces étalons de fréquence présentent une exactitude meilleure que 10^{-15} (avec la potentialité d'atteindre la gamme des 10^{-16} sur les horloges à rubidium) et une stabilité de $2 \times 10^{-14} \tau^{-1/2}$ [44]. La nouvelle génération d'horloges utilisant des transitions optiques soit d'un unique ion piégé (Hg⁺, Yb⁺, Sr⁺, Al⁺, etc...) ou d'un grand nombre

d'atomes neutres (Hg, Sr, Mg, etc...) ont déjà permis de franchir une nouvelle étape et d'atteindre une exactitude dans la gamme des 10^{-17} [45].

Si de meilleures horloges sont essentielles à de nouvelles avancées en métrologie, il est clair que la capacité à réaliser des comparaisons de fréquence du domaine radiofréquence au visible avec le même niveau de sensibilité est également nécessaire pour tirer pleinement parti de ces performances. Jusqu'à récemment, le raccordement de tels domaines nécessitait des chaînes de raccordement de fréquences très complexes et coûteuses développées seulement dans quelques laboratoires de métrologie (au SYRTE par exemple). Depuis 1999, le groupe de T. Hänsch (Garching) puis celui de J.L. Hall (Boulder – Co) ont démontré la possibilité de comparer des fréquences très différentes, (du domaine radiofréquence jusqu'à l'UV) en exploitant les propriétés originales d'un laser à verrouillage de modes [46-49]. Ces techniques de mesures ont grandement simplifié les comparaisons locales d'horloges et cette révolution a très rapidement été reconnue comme une avancée majeure en physique, en témoigne le prix Nobel attribué en 2005 à T. Hänsch et J. Hall.

Avec des horloges ultra-stables et des techniques performantes de comparaisons locales de fréquences, se pose maintenant le problème du transfert de ces fréquences vers d'autres laboratoires pour des comparaisons d'horloges et des mesures de fréquences de très haute précision. Les méthodes les plus performantes pour ces comparaisons utilisent des liaisons satellites et l'échange d'un signal micro-onde codé par le Two Way Satellite Time and Frequency Transfer (TWSTFT) ou bien l'utilisation de la phase du signal reçu dans le transfert GPS. Ces techniques permettent des comparaisons de fréquences à l'échelle du globe avec une incertitude relative de 10^{-15} pour une journée de mesure. On mesure immédiatement que la comparaison d'horloges au niveau de 10^{-17} requièrerait avec ces outils un temps d'intégration beaucoup trop long. Une solution alternative est l'utilisation d'étalon transportable, comme la fontaine atomique transportable du Syrte. Mais ces procédures sont longues à mettre en place et ne conviennent que de façon ponctuelle.

Depuis plusieurs années, le besoin de comparaisons d'horloges tant terrestres que spatiales est devenu un enjeu majeur, en témoigne la future mission PHARAO-ACES sur la station spatiale internationale et T2L2 (Time comparison by laser pulses dating) sur JASON-2, qui devaient permettre des comparaisons à un niveau de 10^{-16} , mais uniquement pendant les quelques mois de la mission. Le seul système opérationnel au niveau mondial reste donc à ce

jour le G.P.S. (prochainement concurrencé par le système GALILEO) dont les performances sont insuffisantes pour comparer, sans dégradation, les meilleures horloges actuelles.

Un autre domaine de la physique, la radioastronomie, utilise des systèmes de distribution de fréquence RF ou micro-onde ultra stables (dans les stations d'observations par interférométrie entre autre). Les expériences de collisions à hautes énergies dans des accélérateurs géants nécessitent également des systèmes de synchronisation sur des distances comparables aux dimensions de ces instruments [50-53]. Même si le transfert des qualités métrologiques des horloges les plus performantes impose des contraintes, en terme de bruit rajouté par le système de distribution, bien au delà des systèmes développés dans les domaines de l'astronomie ou des grands accélérateurs, de tels systèmes de distribution pourraient être une solution au problème de transfert d'horloge pour la communauté des métrologues. Une fibre optique est ainsi installée depuis 1995 entre le LPTF et le LKB. Elle permet le transfert des fréquences optiques avec une précision de l'ordre du Hz, soit une précision relative meilleure que 10^{-14} [54].

C'est dans ce contexte que nous avons développé depuis 2002 une liaison par fibre optique entre le LPL (à Villetaneuse) et le SYRTE (à Paris). Au LPL, nous développons des étalons de fréquence dans les domaines visible et infrarouge. Le SYRTE dispose pour sa part du meilleur étalon primaire au monde, la fontaine à césium dans le domaine micro-onde. Nous avons donc réalisé un dispositif basé sur un laser femtoseconde pour le raccordement local (au LPL) de la fréquence de l'étalon primaire du SYRTE dans le domaine micro-onde au domaine infrarouge (CO_2/OsO_4 à $10\ \mu\text{m}$) et visible (Ar/I_2) de nos étalons. Ce volet a fait l'objet du travail de HDR de Anne Amy-Klein [55].

Ce nouvel axe de recherche présente deux enjeux majeurs pour l'équipe :

- Tout d'abord, la réalisation du transfert longue distance par liaison optique d'un étalon de fréquence entre le SYRTE et le LPL afin de disposer de la référence absolue de fréquence du SYRTE pour nos différentes expériences de métrologie des fréquences à Villetaneuse.

- Ensuite, la démonstration d'un système de transfert sans dégradation des propriétés spectrales de l'horloge et utilisable sur plusieurs centaines de km pour des comparaisons à l'échelle européenne (LPL, SYRTE, PTB, NPL...).

Dans ce chapitre, nous présentons tout d'abord le lien développé, basé sur le transfert d'une référence de fréquence à 100 MHz puis 1 GHz. Dans la seconde partie, les applications de ce transfert d'horloge à la métrologie des fréquences au LPL, impliquant notamment le raccordement par laser femtoseconde, seront présentées.

I. Transfert de fréquence par liaison optique

J'ai participé aux premières étapes de développement du lien optique, les développements actuels sont menés dans l'équipe par Olivier Lopez et Fabien Kéfélian.

Après de longues négociations avec France Télécom (débutées en 1997), nous avons pu obtenir la réalisation de deux liaisons directes par fibre optique de 43 km entre nos deux laboratoires. Cette double liaison est opérationnelle depuis le début de l'année 2002.

A. Liaison par transfert d'une référence à 100 MHz

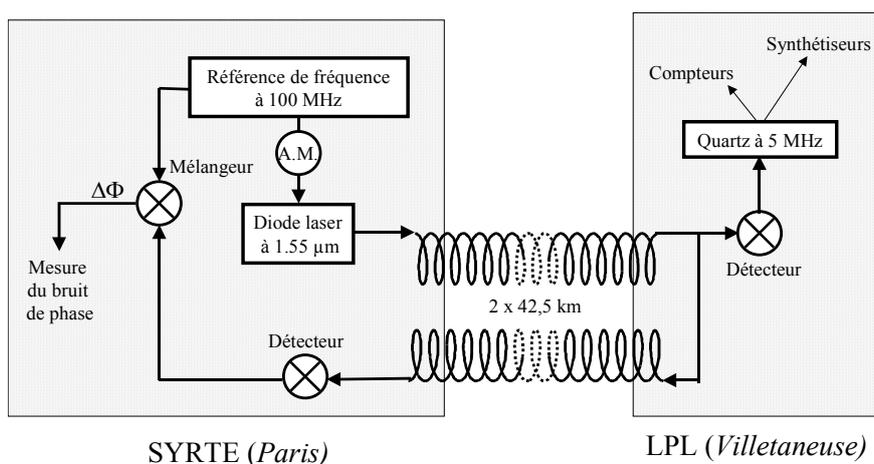


Figure 14: dispositif de transfert de fréquence entre le SYRTE et le LPL

Dans un premier temps, nous avons développé un système de transfert simple pour les premières caractérisations du lien [31]. Une diode laser DFB à 1,55 μm (de puissance 10 mW) modulée en amplitude à 100 MHz, la fréquence de transfert de l'étalon, est injectée dans la fibre optique. Le signal de référence est délivré par le maser à hydrogène du SYRTE, oscillateur d'interrogation des fontaines atomiques. La stabilité de ce signal est de quelques 10^{-13} pour un temps d'intégration d'une seconde. La fréquence du maser est quotidiennement comparée à celle de la fontaine atomique corrigée des effets systématiques. L'exactitude du signal émis est donc après correction, limité par la fontaine atomique à quelques 10^{-15} . Après transmission, la modulation d'amplitude est convertie dans le domaine électrique par une photodiode. Cette référence est alors utilisée au LPL pour asservir la fréquence à 5 MHz d'un oscillateur à quartz stabilisé en température.

Le problème essentiel que pose ce transport de fréquence est le bruit introduit le long de la fibre, soumise aux perturbations acoustiques et aux variations de température. Les bruits acoustiques affectent la qualité du signal transmis (bruit de phase ajouté) tandis que les variations de température se traduisent par de lentes variations de la longueur du lien qui dégrade la stabilité à long terme de la fréquence reçue. Le bruit de phase introduit par le lien est mesuré en comparant le signal d'horloge émis et le signal reçu après un aller retour de 2×43 km entre les deux laboratoires. La stabilité du signal est caractérisée pour différents temps d'intégration (1s ; 10s ; 100...) par sa variance d'Allan qui évalue les fluctuations relatives de la fréquence du signal introduites par la fibre. Nous avons ainsi pu démontrer un transfert de la fréquence de l'horloge entre les deux laboratoires avec une stabilité relative de 3×10^{-14} à 1 s et de quelques 10^{-15} sur quelques heures. Ces performances sont tout à fait remarquables pour une liaison Télécom standard non dédiée et permettent un transfert sans dégradation du signal du maser à hydrogène pour des temps d'intégration jusqu'à 10 000 s.

Notre objectif était de transférer avec la meilleure résolution possible une référence de fréquence et d'analyser les limites de ce transfert, en particulier dans le cas d'une extension à de plus longues distances. Cette étude intéresse fortement la communauté de la métrologie des fréquences, car elle offre la possibilité d'étendre les comparaisons d'horloges entre différents laboratoires de métrologie. Nous avons donc développé un système actif de réduction du bruit introduit par la liaison [30, 56]. Deux systèmes de compensation ont été développés, un sur chaque fibre. Le principe général de notre système de compensation

compensation ont été mesurées pour un aller retour entre les deux laboratoires (86 km) et sont reportées sur la Figure 16.

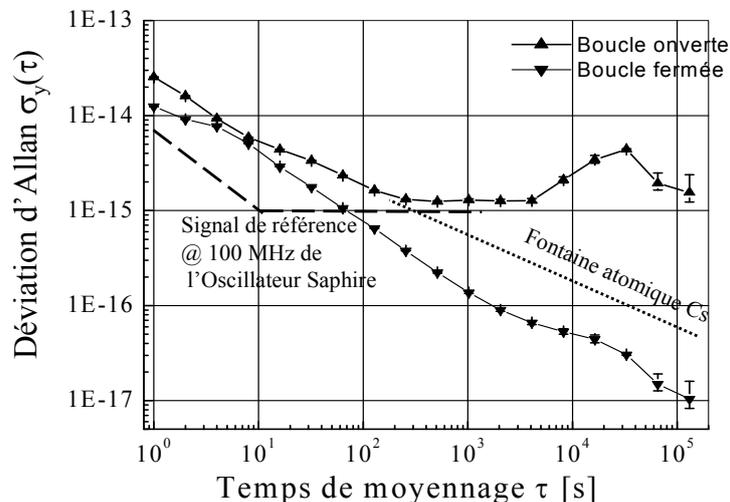


Figure 16 : déviation d'Allan du bruit introduit par la fibre, sans et avec système de compensation, déviation d'Allan du signal délivré par le SYRTE

Ce double lien contrôlé nous a permis de réaliser le transfert de l'étalon primaire de fréquence du SYRTE jusqu'au LPL, sur 43 km, avec une résolution de 10^{-14} à 1 s et 10^{-17} sur une journée, c'est-à-dire sans aucune dégradation des performances de l'étalon primaire [56]. Pour comparaison, les étalons de fréquence optique peuvent aujourd'hui être comparés par lien via un satellite mais la résolution est limitée à 7×10^{-12} à 1s pour le système GPS. Notre lien optique avec une résolution de 10^{-14} à 1 s représente donc un **progrès de 3 ordres de grandeur**.

B. Liaison par transfert d'une référence à 1 GHz

Un travail d'optimisation du système de correction du bruit de phase a permis de mettre en évidence plusieurs points clés :

- La nécessité d'utiliser deux fréquences de modulation différentes à l'aller et au retour pour limiter les effets des réflexions parasites (sur les épissures et les connecteurs, ainsi

que dues à la diffusion Brillouin stimulée). Cela permet de ne pas dégrader le rapport signal sur bruit des signaux à la détection par ces effets parasites,

- Le rapport signal sur bruit croît avec la fréquence RF transmise que l'on cherchera donc à augmenter (de 100 MHz à 1 GHz puis 10 GHz),
- Le contrôle de la polarisation dans la fibre, qui doit être identique à l'aller et au retour, mais varie à la fois du fait de la dispersion naturelle de la fibre mais également à cause de notre système de correction. En pratique, nous brouillerons la polarisation dans la fibre pour contourner ce problème de dispersion de mode de polarisation (PMD) [57].

Un nouveau dispositif de transfert de fréquence a été développé [58].

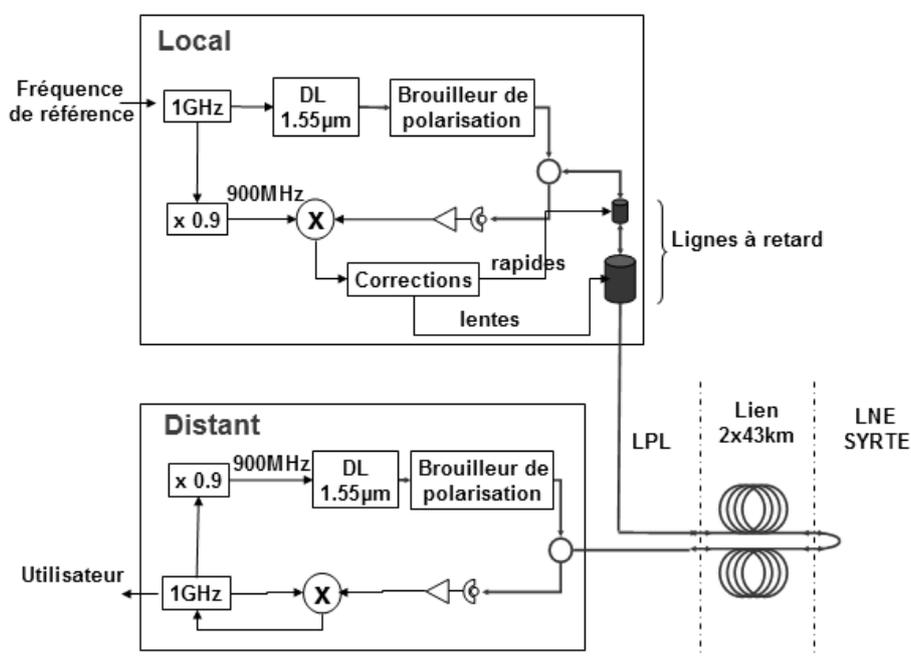


Figure 17 : dispositif de transfert de fréquence à 1 GHz sur une distance de 86 km

Le signal aller à 1GHz est transmis sur une distance de 86 km (aller retour entre les deux laboratoires). Après propagation, la modulation d'amplitude est détectée à l'extrémité de la fibre par une photodiode rapide et utilisée pour générer un signal RF à 900 MHz. Ce signal, porteur du bruit de phase introduit par la liaison, module l'amplitude d'une seconde diode laser DFB à 1,5µm pour le transfert retour (86 km dans la même fibre). Les polarisations optiques des deux diodes lasers ont été brouillées à chaque extrémité de la fibre.

Ce nouveau transfert bifréquence autour de 1 GHz et brouillage de la polarisation a permis d'atteindre une résolution de 5×10^{-15} sur 1 s et à 2×10^{-18} sur une journée [58]. La stabilité sur une journée a ainsi été améliorée d'un facteur 5 par rapport au premier système de transfert à 100 MHz.

Un transfert à 10 GHz a enfin été récemment développé et a permis d'améliorer significativement la résolution (Figure 18).

L'analyse du système de correction a ensuite permis de montrer que la limite principale à la résolution de notre lien optique est maintenant due à la dispersion chromatique de la fibre : la fréquence de la diode laser fluctue et induit une contribution parasite variable au bruit de phase détecté. L'ajout d'une portion de fibre compensatrice de dispersion pourrait améliorer ce point et est actuellement testée.

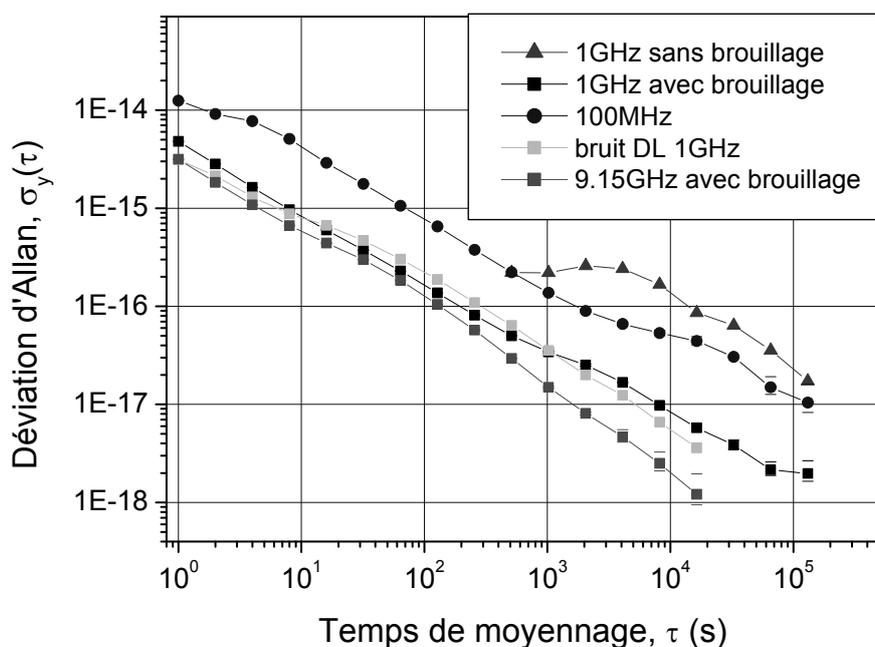


Figure 18: résolution du lien optique de 86 km à 100 MHz, 1 GHz et 10 GHz, avec ou sans brouillage de la polarisation, et bruit lié à la dispersion des lasers

Ce projet continue actuellement avec pour but principal d'accroître encore la longueur du lien pour atteindre 1000 km et rendre possible des transferts de fréquence à l'échelle des grands laboratoires européens.

II. Mesure de fréquences par laser femtoseconde

Introduction

Le dispositif de mesure de fréquence développé dans l'équipe repose sur une utilisation originale d'un laser à impulsions femtosecondes (fs), démontrée pour la première fois en 1999 en Allemagne [46, 47]. Le train d'impulsions de quelques dizaines de fs généré par un tel laser présente un spectre ayant l'allure d'un peigne de fréquences parfaitement équidistantes, dont l'écart est le taux de répétition du laser, et dont l'enveloppe est l'inverse de la durée d'une impulsion. Ce peigne peut servir de « règle » de fréquences pour comparer des fréquences très différentes allant du domaine radiofréquence jusqu'au visible. En particulier, lorsque ce peigne est étalonné par rapport à un étalon primaire de temps-fréquence (qui définit la seconde ou le Hertz), on réalise des mesures « absolues » de fréquences optiques.

Nous avons donc développé une chaîne de mesures de fréquences optiques composée [31, 59]:

- Du lien optique présenté dans la partie précédente, qui permet de transférer au LPL l'excellente référence primaire développée par le LNE-SYRTE. Cette référence, à 100 MHz ou 1 GHz, a une stabilité de l'ordre de 10^{-15} de 1 à 100 s, puis de l'ordre de quelques $10^{-14} \tau^{-1/2}$ aux temps plus longs, et est contrôlé par leur horloge à Cs.
- D'un laser fs et de deux dispositifs de mesures dédiés l'un à des fréquences visibles vers 500 nm [60] et l'autre à des fréquences infrarouges vers 9-10 μm [29, 32, 61]. Le premier dispositif nécessite un élargissement du spectre du laser fs dans une fibre à cristal photonique. Ce montage est maintenant bien connu mais reste délicat à utiliser, surtout vers les longueurs d'ondes proches du bleu. Le deuxième dispositif est plus original, car il permet de mesurer une fréquence infrarouge vers 10 μm . La somme de cette fréquence et du laser fs est générée dans un cristal non-linéaire, et la fréquence infrarouge est ainsi comparée à un harmonique élevé (≈ 30000) de la fréquence de répétition du laser fs.

Le développement de cette chaîne de mesure de fréquence, piloté dans l'équipe par Anne Amy-Klein, a permis de démontrer plusieurs résultats dans les domaines de la

métrologie des fréquences optiques, de la spectroscopie moléculaire à très haute résolution et des tests de physique fondamentale. La spécificité de notre dispositif est de s'appliquer à des systèmes moléculaires, c'est à dire de permettre la mesure de lasers stabilisés en fréquence sur des références moléculaires. A ce jour, ces applications ont porté sur :

- la mesure de la fréquence du laser à CO₂ asservi sur une transition de la molécule OsO₄ à 10 μm, qui a permis de caractériser la reproductibilité et la stabilité de notre étalon,
- la mesure de raies lasers de CO₂ à 9 μm, ainsi que la détermination des constantes moléculaires et la prédiction des positions d'autres raies [61],
- la mesure d'une raie à deux photons de SF₆, détectée dans une expérience de franges de Ramsey, qui a ensuite été exploitée pour réaliser un test de variation du rapport m_e/m_p [62],
- la mesure de raies de l'iode proches de la limite de dissociation, à 514 nm et 501 nm, très prometteuses pour améliorer la reproductibilité de cet étalon,
- la mesure de raies de l'acide formique vers 9,2 μm, en collaboration avec l'équipe de L. Hilico (LKB – Université d'Evry) [63]: ces raies serviront de référence de fréquence pour leur projet de mesure du rapport m_e/m_p.

Les expériences auxquelles j'ai participé sont détaillées dans le paragraphe suivant.

A. Mesure de l'étalon CO₂/OsO₄ à 10 μm

L'étalon de fréquence reposant sur le laser à CO₂ (à 10 μm) asservi sur une transition de la molécule OsO₄ constitue une référence privilégiée pour la spectroscopie moléculaire et les tests de physique fondamentale avec des molécules. Cet étalon secondaire possède une fréquence bien connue au niveau de quelques 10⁻¹²-10⁻¹³, valeur qui fut validée en 1986 par une intercomparaison entre le LPL et le SYRTE. Depuis, aucune comparaison directe n'a été entreprise malgré les progrès accomplis dans nos deux laboratoires (à cause du déplacement de matériels que cela impliquerait).

La première application de notre lien a donc consisté à réaliser des mesures absolues de la fréquence d'un laser CO₂ asservi sur une raie d'absorption saturée de la molécule OsO₄. Pour ces expériences nous avons utilisé un laser femtoseconde et deux oscillateurs intermédiaires (diodes laser) à 852 nm et 785 nm dont la différence de fréquence est asservie

en phase sur celle du laser à CO₂. Le peigne de fréquences du laser femtoseconde est asservi sur ces deux diodes lasers et sa fréquence de répétition autour de 1 GHz directement mesurée par un compteur référencé sur le signal provenant du SYRTE. La fréquence de répétition du laser femtoseconde reproduit à 1 GHz les fluctuations relatives de la fréquence du laser à CO₂ à 30 THz.

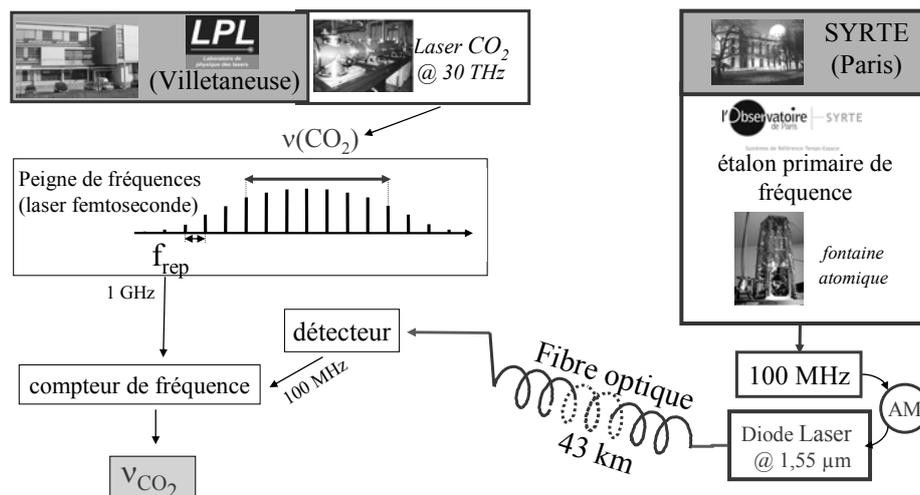


Figure 19: système de comparaison des fréquences de l'étalon primaire micro-onde du SYRTE et de l'étalon secondaire à 10 μm du LPL.

Pour ces mesures absolues de fréquences, le système simple de transfert par fibre optique, sans contrôle du bruit de phase a été suffisant. La fréquence de l'étalon CO₂/OsO₄ a été mesurée sur une période de 9 mois avec une incertitude de l'ordre de 60 Hz (2×10^{-12} en valeur relative) limitée par l'étalon lui-même [31].

La deuxième application de la liaison optique a été la caractérisation des propriétés spectrales de notre étalon à 10 μm (CO₂/OsO₄) directement par raccordement à la référence de fréquence du SYRTE. Ces mesures ont nécessité cette fois l'utilisation du système de compensation afin de réduire le bruit de phase introduit par la liaison à un niveau négligeable devant le bruit de notre étalon. La stabilité en fréquence de notre étalon à 10 μm a ainsi été complètement caractérisée de 1s à 200s, avec une stabilité relative de 3×10^{-14} à 1s.

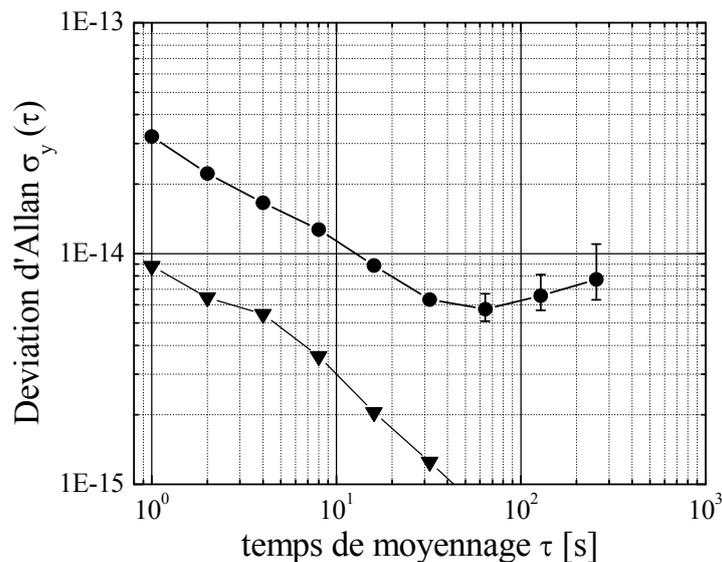


Figure 20 : stabilité relative de la fréquence du laser à CO_2/OsO_4 mesurée par la déviation d'Allan du taux de répétition du laser femtoseconde (●). Le bruit dû à la liaison par fibre optique est négligeable (▼)

Un nouveau système de mesure de fréquence par laser femtoseconde a ensuite été mis en place qui évite l'utilisation de diodes lasers comme oscillateurs intermédiaires. Le nombre d'asservissement en phase a également été réduit de 3 à 1 seul ce qui permet de limiter les sources parasites de bruit et de fiabiliser les mesures au quotidien.

Enfin, nous avons réalisé pour la première fois des mesures de fréquences du laser à CO_2 asservi sur une transition à deux photons de la molécule SF_6 [32]. Cette transition est une alternative intéressante à la résonance d' OsO_4 en absorption saturée pour le contrôle en fréquence du laser à CO_2 .

B. Mesure avec l'acide formique

En collaboration avec l'équipe de L. Hilico (LKB – Université d'Evry), nous avons mesuré plusieurs raies d'absorption saturée de l'acide formique (HCOOH) vers 9,2 μm avec une incertitude de 1 kHz [63]. Pour ces mesures, le laser de référence CO_2/HCOOH du LKB a été déménagé au LPL. Ces raies serviront de référence de fréquence pour leur projet de mesure du rapport m_e/m_p par spectroscopie de l'ion H_2^+ [64].

C. Mesure de raies de l'iode autour de 500 nm

Enfin, dans le domaine visible nous avons mesuré des fréquences absolues d'un laser à argon ionisé stabilisé sur une raie de l'iode moléculaire à 501,7 nm. Cet étalon est développé dans l'équipe par F. du Burck.

Il est connu que la durée de vie dans l'état excité de l'iode augmente lorsqu'on se rapproche de la dissociation vers 500 nm du fait des diminutions combinées de la largeur radiative des niveaux et des effets de prédissociation. On observe en cellule des raies de demi largeur à mi-hauteur d'environ 30 kHz pour la transition R(26) 62-0 à 501,7 nm. Ces résonances sont à notre connaissance les plus étroites obtenues dans l'iode en spectroscopie de saturation et présentent donc un grand intérêt métrologique. Pour comparaison, la largeur naturelle de la composante hyperfine a_3 de la transition P(13) 43-0 à 514,5 nm est de 150 kHz. Nous avons réalisé la première mesure de la fréquence absolue du laser Ar^+ à 501,7 nm verrouillée sur une composante hyperfine de la transition R(26) 62-0 détectée en cellule à basse pression [65].

Conclusion

Nous avons développé un nouveau dispositif de transfert et de raccordement de fréquence qui a été optimisé et fiabilisé au cours des dernières années. Nous avons également démontré avec ce nouveau spectromètre à 10 μm la possibilité de réaliser des mesures de fréquences, directement raccordé à l'étalon primaire du SYRTE, avec une reproductibilité et une exactitude au niveau de 0,3 Hz. Ces mesures, répétée sur plusieurs mois ont ainsi permis un test de variation des constantes fondamentales original [62]. Cette nouvelle chaîne de raccordement de fréquence sera également un élément essentiel dans notre nouvelle

expérience en jet pour la mise en évidence de la non conservation de la parité moléculaire (voir chapitre I).

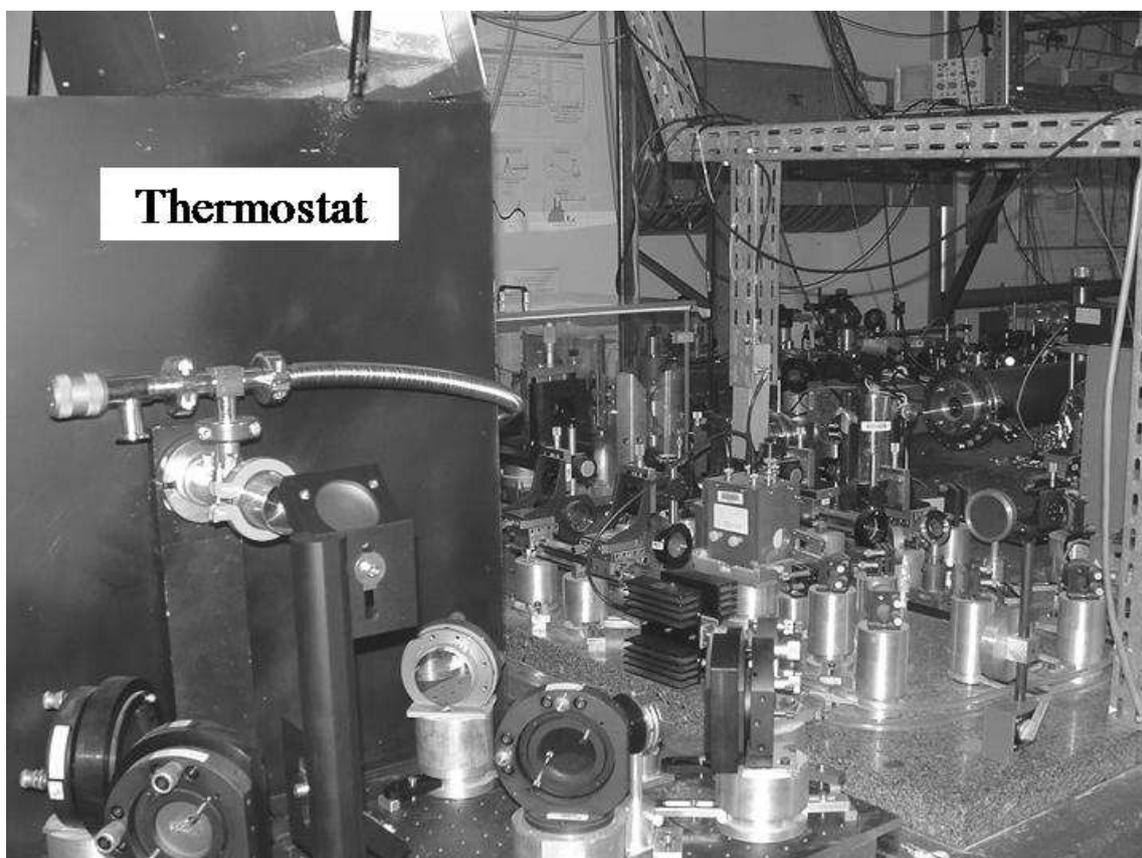
Par ailleurs, nous avons souligné l'enjeu important à généraliser notre technique de lien optique à de plus grandes distances. En effet, l'objectif est de pouvoir démontrer des comparaisons d'horloges à l'échelle européenne. Les applications concernent d'une part la métrologie, limitée justement par les techniques actuelles de comparaisons d'horloges, et la physique fondamentale, avec la généralisation des tests de variation de constantes fondamentales à une large gamme d'horloges.

Pour aller au-delà des problèmes d'atténuation et de dispersion chromatique dans la fibre, nous avons envisagé de transférer directement une référence de fréquence optique : c'est le laser à 1,55 μm qui sera ainsi la référence de fréquence.

Sur ce projet collaborent 3 chercheurs étrangers : A. Goncharov (Institut de Physique des Lasers, Novosibirsk, Russie), R.J. Butcher (Cambridge, Angleterre) et A. Shelkownikov (Institut de Physique Lebedev, Moscou, Russie).

Ce projet a été développé en collaboration avec le LNE-SYRTE et est financé depuis 2001 par un PPF impliquant 3 laboratoires (LPL,LKB,SYRTE). En 2001, ce projet a également bénéficié d'un financement FNS du ministère de la recherche. Enfin, depuis novembre 2006 une ANR coordonnée par P. Lemonde finance le développement du nouveau lien optique.

CHAPITRE III. Mesure de la constante de Boltzmann par spectroscopie laser



Introduction

Depuis 2003, je développe un nouveau projet de recherche autour de la mesure de la constante de Boltzmann par spectroscopie laser. Ce projet repose sur une idée originale de Christian Bordé [66-68] et s'inscrit comme une étape vers la redéfinition du kelvin.

La valeur actuelle de la constante de Boltzmann donnée par le CODATA (Committee on Data for Science and Technology) repose essentiellement sur une expérience unique de mesure de la vitesse du son dans un gaz datant de 1988 [69, 70]. L'incertitude admise est de $1,8 \times 10^{-6}$ (1σ). Il existe actuellement dans le monde deux projets qui reprennent cette méthode. Une autre méthode reposant sur une mesure de la constante diélectrique d'un gaz est également très prometteuse. Pour notre part, nous développons depuis 2003 une approche

nouvelle reposant sur une méthode optique qui ramène la détermination de k_B à une mesure de fréquence. Ce regain d'intérêt pour la détermination de k_B s'inscrit dans la réflexion actuelle sur la refondation du système international d'unités (SI) [71-77] et la perspective à horizon 2011 que le CGPM redéfinisse le kelvin en fixant la valeur de k_B à sa valeur admise à cette date, comme la vitesse de la lumière fut fixée en 1983, conduisant à une redéfinition de l'unité de longueur. Le kilogramme, l'ampère et la mole pourraient également être redéfinies à partir de constantes fondamentales. L'ensemble de ces redéfinitions supposent la mise en place d'un nouveau SI dans lequel, en plus de la vitesse de la lumière c , d'autres constantes fondamentales telles que la constante de Planck h , la constante d'Avogadro N_A et la constante de Boltzmann k_B soient fixées pour définir et relier entre elles les différentes unités de base [78, 79].

I. La mesure de la constante de Boltzmann

La détermination de k_B peut être obtenue par des expériences très différentes dans leur principe [80, 81]. Elle est ainsi mesurée avec des électrons par la mesure du bruit thermique dans une résistance [82-84], avec la lumière par la mesure de la luminance du corps noir [85-87], ou encore avec des atomes ou molécules par des mesures de thermométrie. Les expériences de thermométrie à gaz sont de 4 types : la thermométrie à gaz à volume constant, la thermométrie acoustique à gaz, la thermométrie à gaz par mesure de constante diélectrique et enfin la thermométrie à gaz par mesure de l'indice de réfraction.

Parmi toutes ces approches, seuls la thermométrie acoustique et la thermométrie par mesure de constante diélectrique permettent aujourd'hui d'atteindre une incertitude inférieure à 10 ppm et sont prises en compte par le CODATA.

A. La thermométrie acoustique

Les expériences de thermométrie acoustique à gaz s'appuient sur la dépendance de la vitesse de propagation du son dans un gaz avec la vitesse quadratique moyenne des molécules ou atomes, elle-même déterminée par la température du système. Si le gaz est placé dans un résonateur acoustique sphérique, les fréquences de résonance acoustique dépendent de la vitesse du son dans le gaz et du volume du résonateur. Cette relation s'exprime simplement

pour un gaz monoatomique sous la forme $k_B = \left[\frac{M}{N_A} \right] \times \left[\frac{3V^{2/3}}{5T} \right] \times \left[\frac{f_{0,n}}{r_{0,n}} \right]^2$, où M est la masse molaire du gaz, N_A la constante d'Avogadro (qui relie actuellement l'unité de masse atomique au kilogramme et donc la masse atomique m à la masse molaire M), V le volume du résonateur, T la température du gaz, $r_{0,n}$ (à une constante près) la racine $n^{\text{ième}}$ d'une équation différentielle donnant les différents modes de vibration du gaz dans un résonateur sphérique et $f_{0,n}$ la fréquence de résonance à déterminer. L'expérience consiste à mesurer la vitesse de propagation du son dans l'argon en fonction de la pression et à la température du point triple de l'eau. Le premier terme qui représente la masse atomique du gaz est déterminé avec une incertitude dominée par la présence d'impuretés résiduelles dans le gaz. Le volume du résonateur est déterminé à 0,8 ppm par une mesure de la masse de mercure qu'il peut contenir. Enfin, la valeur de $f_{0,n}$ est obtenue par une extrapolation à pression nulle des mesures de fréquences de résonance à différentes pressions de gaz ($f_{0,n} = \lim_{p \rightarrow 0} f_{p,n}$). Cette expérience donne la valeur actuelle de la constante de Boltzmann, $k = 1,380\,6505\,(24) \times 10^{-23} \text{ JK}^{-1}$ soit une incertitude relative de 1,8 ppm [69, 70, 88, 89]. Une autre mesure réalisée sur le même principe au NPL a été publiée en 1979 avec une incertitude de $8,4 \times 10^{-6}$ [90]. Plus récemment, une équipe chinoise de Xian Jiatong University a publié une mesure avec une incertitude de $3,6 \times 10^{-5}$ [91]. Ce principe est également repris depuis quelques années au LNE-INM/Cnam par L. Pitre avec un résonateur quasi-sphérique rempli d'hélium, la sensibilité atteinte est de l'ordre de 10 ppm [92, 93].

B. La mesure de la constante diélectrique

La thermométrie à gaz par mesure de constante diélectrique s'appuie sur l'équation de Clausius-Mossoti qui relie la constante diélectrique du gaz ϵ_r à sa polarisabilité molaire A_ϵ [94]:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{A_\epsilon}{V_m} = A_\epsilon \frac{p}{RT} \quad (\text{pour un gaz parfait})$$

On s'affranchit ici de la limitation associée à la mesure de quantités extensives en réalisant une mesure directe de la densité du gaz via une mesure de la constante diélectrique

relative ε_r . La mesure des isothermes à différentes pressions donne le rapport $\frac{A_\varepsilon}{R}$. A_ε est obtenu par calcul ab initio avec une incertitude meilleure que 1 ppm pour l'hélium [95]. En 2007, une expérience menée au NIST dans le groupe de M.R Moldover a atteint une incertitude sur k_B de 9 ppm par mesure de l'indice de réfraction dans ^4He [96]. Une autre expérience au PTB atteint une incertitude de 30 ppm [81, 97].

C. Principe de notre expérience

La mesure est réalisée par une expérience de spectroscopie laser où une vapeur moléculaire, contenue dans une cellule, et à l'équilibre thermodynamique est en interaction avec une onde laser progressive. On enregistre le profil d'absorption linéaire autour d'une fréquence de résonance. Dans la limite d'un élargissement purement Doppler, la forme de raie est une exponentielle de gaussienne quand le signal est intégré le long du chemin optique. Dans nos conditions expérimentales, le profil est dominé par l'élargissement Doppler et la raie reste très proche d'une exponentielle de gaussienne avec une largeur croissant linéairement avec la pression. Pour extraire la largeur Doppler de la forme de raie, les mesures sont extrapolées à très basse pression, dans un régime où la forme de raie tend vers le profil Doppler. Si on appelle ν_0 la fréquence centrale et $\Delta\nu_D$ la demi-largeur (à $1/e$) du profil Doppler, la constante de Boltzmann s'obtient, en fonction des paramètres de l'expérience par

la formule : $\frac{\Delta\nu_D}{\nu_0} = \sqrt{\frac{2k_B T}{mc^2}}$ où c est la vitesse de la lumière, T la température du gaz et m la

masse moléculaire dont l'incertitude est aujourd'hui limitée par la connaissance de la constante d'Avogadro. Pour cette constante le CODATA donnait en 1998 une incertitude de $7,9 \times 10^{-8}$, revue à la hausse en 2002 ($1,7 \times 10^{-7}$). Cette confusion provient d'un désaccord au niveau de 1,3 ppm entre les déterminations directes de N_A par une sphère de silicium et des mesures indirectes par la balance du watt [98]. Pour cette raison, l'incertitude sur la valeur admise de k_B qui fait intervenir N_A pourrait être légèrement revue à la hausse. Concernant notre projet de spectroscopie Doppler où nous visons une détermination de k_B avec une incertitude de quelques ppm, nous devons d'une part tenir compte de cette nouvelle incertitude sur la constante d'Avogadro et d'autre part atteindre une incertitude sur la mesure de la température T et sur celles des fréquences $\Delta\nu_D$ et ν_0 de quelques ppm également.

On peut cependant s'affranchir de toute grandeur macroscopique, et notamment du nombre d'Avogadro en remarquant que: $\frac{\Delta\nu_D}{\nu_0} = \sqrt{\frac{2(k_B/h)T}{(m/h)c^2}}$. La mesure de la largeur Doppler apparaît alors comme une mesure du rapport k_B/h , dont l'incertitude fait intervenir outre celle sur T , celle sur la quantité mc^2/h (homogène à une fréquence) susceptible d'une mesure par interférométrie atomique à mieux que 10^{-8} près [99, 100]. L'unité de température pourrait alors être directement reliée à l'unité de fréquence en fixant les valeurs de h et de k_B .

II. Première mesure optique de la constante de Boltzmann

Nous avons développé un premier dispositif expérimental afin de réaliser une expérience simple démontrant le potentiel de cette nouvelle approche pour la détermination de k_B [101, 102]. Le spectromètre à 10 μm développé dans l'équipe depuis de nombreuses années a été le point de départ de cette nouvelle expérience [17].

L'expérience de spectroscopie est réalisée à 10 μm sur des molécules d'ammoniac (NH_3) à l'aide d'un laser CO_2 stabilisé en fréquence. Le choix de cette molécule a reposé sur deux critères principaux : avoir une bande d'absorption intense et des raies Doppler bien isolées.

A. Présentation du spectromètre

La spectroscopie de la molécule NH_3 est réalisée à l'aide d'un laser à CO_2 ultra stable dont la fréquence d'émission est stabilisée sur une transition de la molécule OsO_4 détectée à 10 μm en absorption saturée. Le balayage en fréquence du laser est réalisé grâce à un modulateur électro-optique (MEO) qui permet de générer deux bandes latérales de fréquences respectives $\nu_L + \nu_{\text{MEO}}$ et $\nu_L - \nu_{\text{MEO}}$ de part et d'autre de la fréquence fixe du laser ν_L [103, 104]. La raie choisie pour l'expérience est la raie asQ(6,3) dans la bande ν_2 de la molécule d'ammoniac $^{14}\text{NH}_3$ à la fréquence de 28 953 694 MHz et sera sondée par la bande latérale $\nu_L - \nu_{\text{MEO}}$.

En sortie du MEO les deux bandes latérales de fréquences respectives $\nu_L + \nu_{\text{MEO}}$ et $\nu_L - \nu_{\text{MEO}}$ sont polarisées linéairement à 90° du résidu de porteuse à la fréquence ν_L . Le rapport d'intensité entre ces deux bandes latérales et la porteuse laser est d'environ 10^{-4} . Un

polariseur permet d'atténuer en sortie du MEO le résidu de porteuse d'un facteur 200. Le signal est ensuite filtré en fréquence à travers une cavité Fabry-Perot (CFP) de 15 cm de long accordée sur la bande latérale $\nu_L + \nu_{\text{MEO}}$ afin d'éliminer le résidu de porteuse à la fréquence ν_L et la bande latérale à la fréquence $\nu_L - \nu_{\text{MEO}}$. Le signal d'erreur est élaboré par une technique de modulation-démodulation basse fréquence.

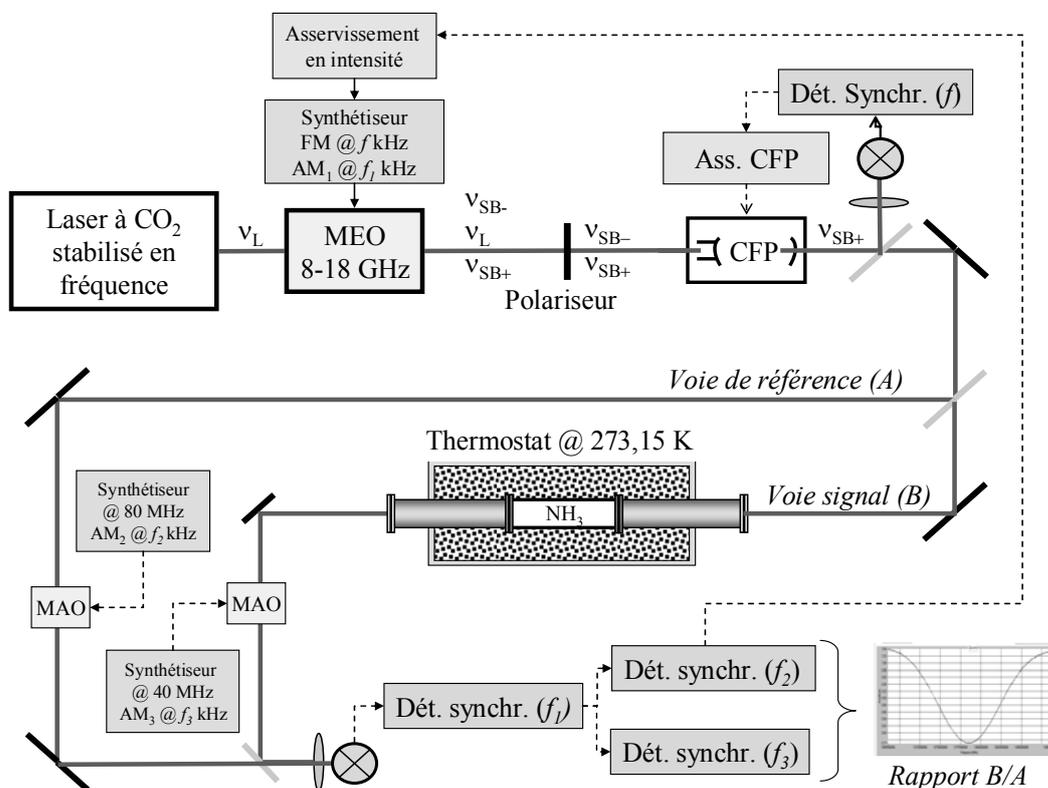


Figure 21: schéma de principe de l'expérience

(MAO : modulateur acousto-optique, MEO : modulateur électro-optique,
CFP : cavité Fabry-Perot, BL : bande latérale)

La bande latérale est modulée en fréquence via la micro-onde ν_{MEO} à une fréquence de 8 kHz avec une profondeur de 38 kHz. Le signal d'erreur est ensuite détecté grâce à un photodétecteur HgCdTe puis démodulé par une détection synchrone. Le signal de correction est enfin appliqué à une céramique piézoélectrique sur laquelle est fixé un des miroirs du résonateur. Afin d'éliminer totalement l'influence des résidus de porteuse sur le spectre d'absorption, le signal de bande latérale est modulé en amplitude via le MEO à la fréquence $f_1=17$ kHz. Les signaux seront ensuite démodulés à cette fréquence par une détection synchrone, le résidu de porteuse n'étant pas modulé, celui-ci n'est pas détecté après détection

synchrone. Le faisceau à la fréquence $\nu_L + \nu_{\text{MEO}}$ est ensuite scindé en deux grâce à une lame séparatrice 50/50 : un des deux faisceaux traverse une enceinte remplie d'ammoniac pour la spectroscopie (*voie signal (B)*) et l'autre sert de faisceau de référence (*voie de référence (A)*). Le spectre de l'ammoniac est obtenu en balayant la fréquence micro-onde ν_{MEO} pilotée par le synthétiseur. La cellule est placée dans un thermostat (eau + glace) qui permet de contrôler la température à quelques dizaines de mK près autour de 273,15 K. Les deux faisceaux optiques sont ensuite modulés en amplitude par deux modulateurs acousto-optiques (MAO) à deux fréquences différentes f_2 et f_3 , puis recombinaés et focalisés sur un même photodétecteur. Deux détections synchrones démodulent chacune le signal d'une des deux voies, qui sont donc enregistrées simultanément. Le rapport est ensuite calculé numériquement. Les deux MAO fonctionnent à deux fréquences différentes, l'un décale la fréquence optique de 40 MHz et l'autre de 80 MHz, ce qui permet d'éliminer au niveau de la détection les interférences optiques entre les voies *A* et *B*.

La qualité du spectre enregistré dépend directement de la stabilité de l'intensité I_0 du laser. Les variations lentes de I_0 affectent la ligne de base tandis que les fluctuations rapides sont à l'origine du bruit observé sur les spectres enregistrés. Afin de maintenir l'intensité laser constante à l'entrée de la cellule d'absorption au cours de l'acquisition d'un spectre, le signal de la voie *A* est comparé en permanence à une référence de tension très stable et asservi sur celle-ci. Le signal de correction contrôle la puissance de la micro-onde pilotant le MEO. Le contrôle de cette intensité laser et la capacité à mesurer son absorption de façon fidèle sur tout le profil Doppler affectent directement la sensibilité de notre mesure et représentent les défis majeurs de cette expérience.

Le contrôle de la température du gaz moléculaire est réalisé grâce à un thermostat constitué par une grande cuve (250 litres) d'acier inox contenant un mélange eau-glace présenté sur la Figure 22.

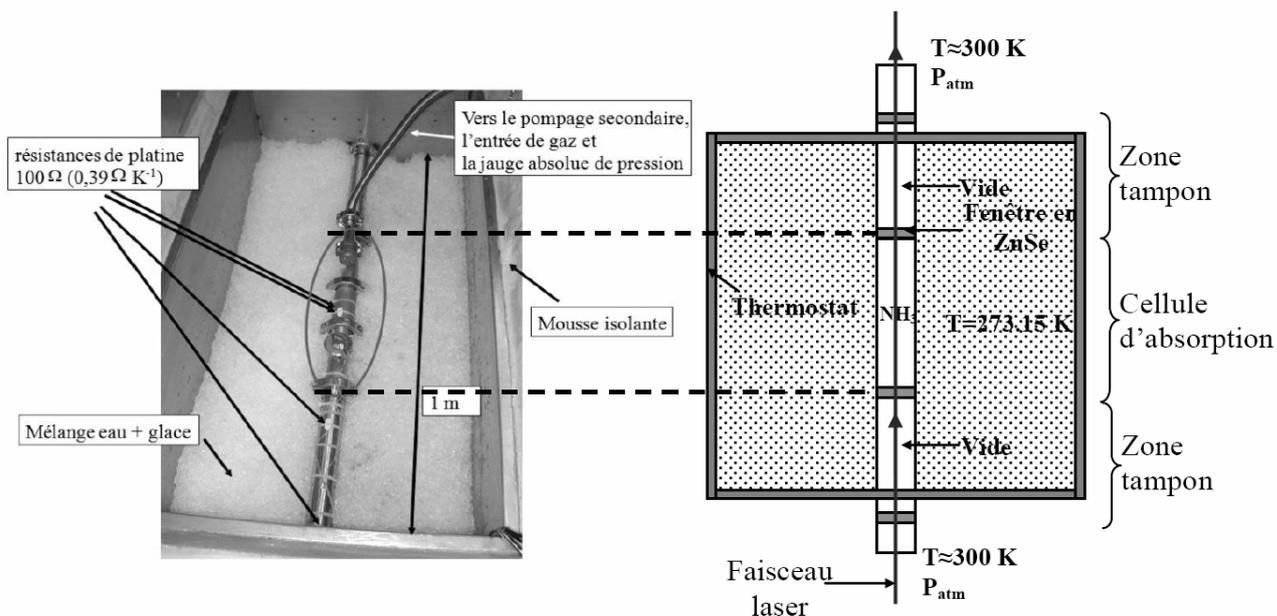


Figure 22 : thermostat et cellule d'absorption

La cellule d'absorption, de longueur 30 cm, contenant les molécules est immergée dans ce bain. La température est maintenue constante et homogène à la température de fusion de la glace (273,15 K ou 0°C) à mieux que 20 mK près, soit 7×10^{-5} en valeur relative (voir Figure 23). La température du bain ainsi que celle des parois de la cellule sont mesurées en permanence grâce à des capteurs très sensibles placés en différents points du thermostat. Ces capteurs sont régulièrement étalonnés par rapport au point fixe de l'échelle de température à 273,16 K réalisé par un point triple de l'eau.

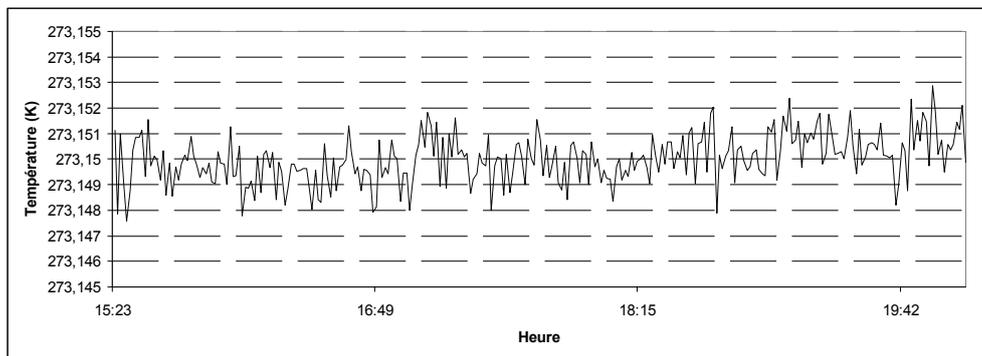


Figure 23 : évolution de la température au centre de la cellule au cours d'une après-midi de mesures

B. Premiers résultats

Des profils d'absorption linéaire ont été enregistrés à des pressions comprises entre 1 et 12 Pa (voir Figure 24). Pour chaque spectre, la demi-largeur $\Delta\nu_D$ est déterminée par l'ajustement non linéaire de la raie d'absorption par une exponentielle de gaussienne qui donne les deux paramètres: largeur de la gaussienne et l'amplitude A . La fonction modèle utilisée s'écrit sous la forme suivante :

$$P_{abs}(\nu_L) = P_0 \exp\left(A \exp\left(-\left(\frac{\nu_L - \nu_0}{\Delta\nu_D} \right)^2 \right) \right) + p(\nu_L - \nu_0)$$

Où P_0 désigne l'intensité laser incidente, et A le produit $-\alpha L$ avec α le coefficient d'absorption de la molécule pour la transition considérée. Le terme $p(\nu_L - \nu_0)$ permet de prendre en compte la pente et l'offset de la ligne de base.

La largeur Doppler est enfin obtenue par extrapolation à pression nulle (voir Figure 25) et conduit à une détermination de la constante de Boltzmann par la relation suivante : $\frac{\Delta\nu_D}{\nu_0} = \sqrt{\frac{2k_B T}{mc^2}}$. L'échelle de pression est simplement donnée par la mesure de l'amplitude d'absorption à résonance qui dépend linéairement de la pression. La valeur de la constante de Boltzmann déduite de ces mesures est de $1,38065(26) \times 10^{-23} \text{ JK}^{-1}$, soit avec une incertitude statistique égale à $1,9 \times 10^{-4}$ en valeur relative [105, 106].

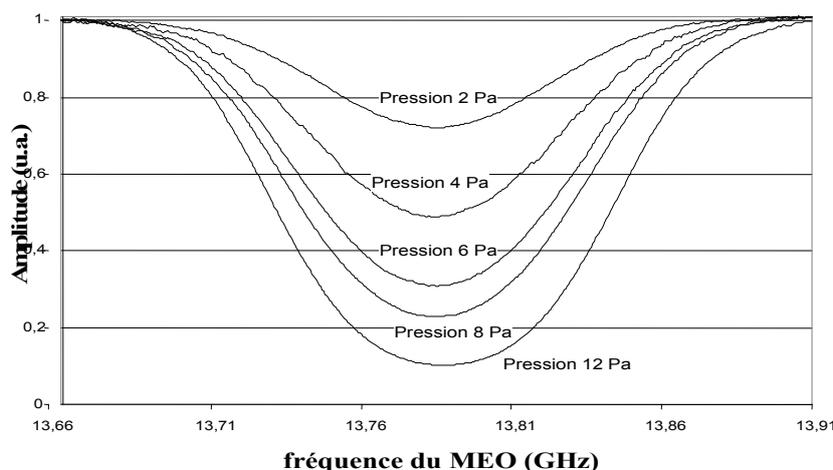


Figure 24 : spectres d'absorption pour des pressions comprises entre 2 et 12 Pa

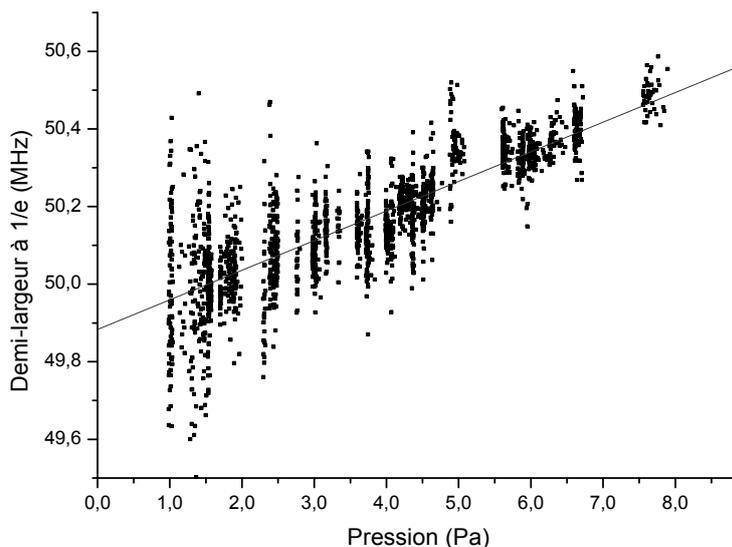


Figure 25: Dépendance en pression de la largeur de la raie supposée gaussienne (carrés noirs). Cette largeur extrapolée à pression nulle (droite rouge) donne la largeur Doppler $\Delta\nu_D$ utilisée pour la détermination de k_B

Une étude des effets systématiques a permis de montrer que leur influence sur la détermination de k_B reste inférieure en valeur relative à 10^{-4} dans nos conditions expérimentales.

Une analyse poussée de ces premiers résultats a permis d'identifier les limites du dispositif et de la technique d'analyse des données :

- Le rapport signal sur bruit limite clairement la sensibilité de la mesure et plus particulièrement aux basses pressions où le signal d'absorption est faible.
- L'ajustement du profil d'absorption par une exponentielle de gaussienne même si il est pertinent à basse pression, s'avère inadapté aux pressions plus élevées (à partir de 10 Pa). Ceci se traduit par un résidu d'autant plus important que la pression augmente.
- Nous avons pu mettre en évidence une dégradation de la sensibilité de la mesure en présence d'une pente importante sur la ligne de base ce qui indique la nécessité de réduire et contrôler au mieux cet effet.
- Enfin, le contrôle de la température, même si il n'a pas été un facteur limitant pour ces premières expériences, devra être amélioré et atteindre le ppm.

Après avoir réalisé la première mesure de la constante de Boltzmann par spectroscopie laser, l'enjeu a été pour nous de concevoir une nouvelle expérience et de mettre au point une nouvelle méthode d'ajustement numérique et d'analyse des données afin de démontrer le potentiel de cette technique spectroscopique pour une mesure au niveau du ppm.

C. *Forme de raie et analyse des données*

a) **La forme de la raie d'absorption**

Même si le principe de cette expérience est extrêmement simple, il n'en demeure pas moins que la détermination de la largeur Doppler nécessite une modélisation précise de la forme de raie [107-110]. Dans la limite d'un élargissement purement Doppler, la forme de raie est une exponentielle de gaussienne. Cette forme de raie approchée s'est révélée insuffisante pour reproduire les profils observés autour de quelques Pascal comme l'illustrent les résidus des Figure 26 et Figure 27.

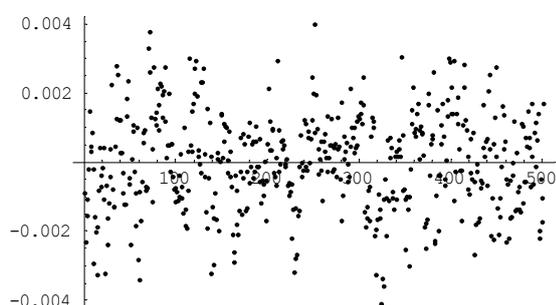


Figure 26 : résidu normalisé de l'ajustement numérique par un profil Gaussien d'un spectre enregistré à 2 Pa

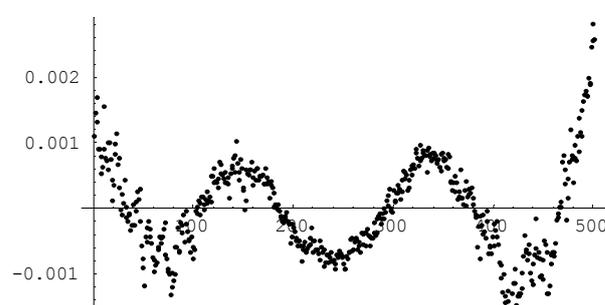


Figure 27 : résidu normalisé de l'ajustement numérique par un profil Gaussien d'une série de 30 spectres enregistrés à 10 Pa

En effet, plusieurs autres sources d'élargissement de la forme de raie doivent être considérées. Tout d'abord, la durée de vie finie des états internes de la molécule donne la largeur naturelle de la transition (négligeable dans nos expériences). Cette largeur homogène est augmentée sous l'effet des collisions molécule-molécule à l'origine d'un élargissement proportionnel à la pression. De plus, si les molécules ne se trouvent pas dans un régime de

champ faible, un élargissement supplémentaire par saturation est observé. Dans ce cas la forme de raie est décrite par une exponentielle de profil de Voigt, convolution d'une distribution gaussienne et d'une lorentzienne de largeur γ_{hom} égale à la somme des élargissements homogènes. En spectroscopie d'absorption linéaire et pour une distribution isotrope des vitesses moléculaires, les effets de transit sont complètement pris en compte par le simple profil Doppler [111]. A plus haute pression, un autre effet doit également être considéré, c'est l'effet Lamb-Dicke-Mossbauer qui se traduit par une réduction de la largeur Doppler avec la pression [112]. Cette forme de raie est cependant encore incomplète. En effet, dans nos expériences deux autres effets doivent être pris en compte : la structure hyperfine non résolue de la transition et les différentes modulations de fréquence et d'amplitude appliquées au faisceau laser pour détecter les signaux. En première approximation, ces deux effets affectent la forme de raie de la même façon : dans le premier cas, la forme de raie correspond exactement à la somme des différentes composantes hyperfines individuelles et dans le second cas, le spectre du laser modulé en fréquence se traduit par une série de signaux d'absorption qui reproduisent le spectre laser (en position et en intensité). Pour la raie $asQ(6,3)$, la structure hyperfine est composée de 12 composantes étalées sur environ 100 kHz. Le calcul précis de cette structure est en cours et elle sera prochainement mesurée par spectroscopie d'absorption saturée [113, 114]. Sa contribution à la largeur de raie est de l'ordre de 10^{-6} (car elle intervient au 2^{ème} ordre) et pourra être précisément prise en compte, réduisant ainsi l'incertitude associée à un niveau totalement négligeable.

b) Nouvelle procédure d'analyse des données

Même si la forme de raie complète est bien comprise d'un point de vue théorique, elle ne peut être directement utilisée dans nos expériences pour l'ajustement des spectres expérimentaux. L'ajustement est obtenu avec des formes plus simples au nombre de paramètres réduits. Ainsi la première analyse a été menée avec un profil Gaussien. Plusieurs simulations ont été réalisées afin de déterminer très précisément l'impact sur la mesure de la largeur Doppler de cette procédure d'ajustement simplifiée. Ces simulations ont montrées que l'ajustement d'un profil de Voigt par un profil Gaussien conduit dans nos conditions expérimentales à une erreur systématique de 2×10^{-4} sur la largeur Doppler, du même ordre de grandeur que l'erreur statistique (dans la gamme de pression 1-10 Pa).

Pour aller au-delà, nous avons ensuite mené des simulations qui nous ont permis de mettre au point une procédure d'ajustement avec un profil de Voigt, plus proche de la forme réelle de la raie.

La fonction modèle utilisée est de la forme :

$$P_{abs}(\nu) = P_0 \exp \left[-A \int_{-\infty}^{+\infty} \frac{\exp \left(-\left(\frac{\nu_L - \nu_0}{\Delta \nu_D} \right)^2 \right)}{(\nu_L - \nu_0)^2 + \left(\frac{\Delta \nu_h}{2\pi} \right)^2} d\nu \right] + P(\nu_L - \nu_0)$$

L'amplitude d'absorption A ainsi que l'élargissement homogène de la raie $\Delta \nu_h$ varient linéairement avec la pression P :

$$\begin{cases} A = A_0 P \\ \Delta \nu_h = \gamma P \end{cases}$$

γ est le coefficient d'élargissement par pression et A_0 le coefficient d'absorption linéaire qui dépend entre autre de la longueur d'interaction molécules-laser. En fixant ces deux paramètres, l'élargissement collisionnel est directement déduit de la pression du gaz qui est déterminée par l'amplitude d'absorption de la raie. Il est ainsi possible de réduire l'ajustement numérique à 5 paramètres. Le coefficient d'élargissement par pression est choisi et fixé à la valeur qui permet de rendre la largeur Doppler indépendante de la pression.

Dans l'hypothèse d'un tel profil de raie, cette nouvelle technique d'analyse permet, pour chaque spectre, d'obtenir la largeur homogène et la largeur Doppler sans aucune extrapolation à pression nulle. Ce nouveau traitement, appliqué à la première série de mesure conduit à une valeur de la constante de Boltzmann de $1,380\,880(99) \times 10^{-23} \text{JK}^{-1}$, soit une incertitude statistique réduite à **72 ppm** (voir Figure 28).

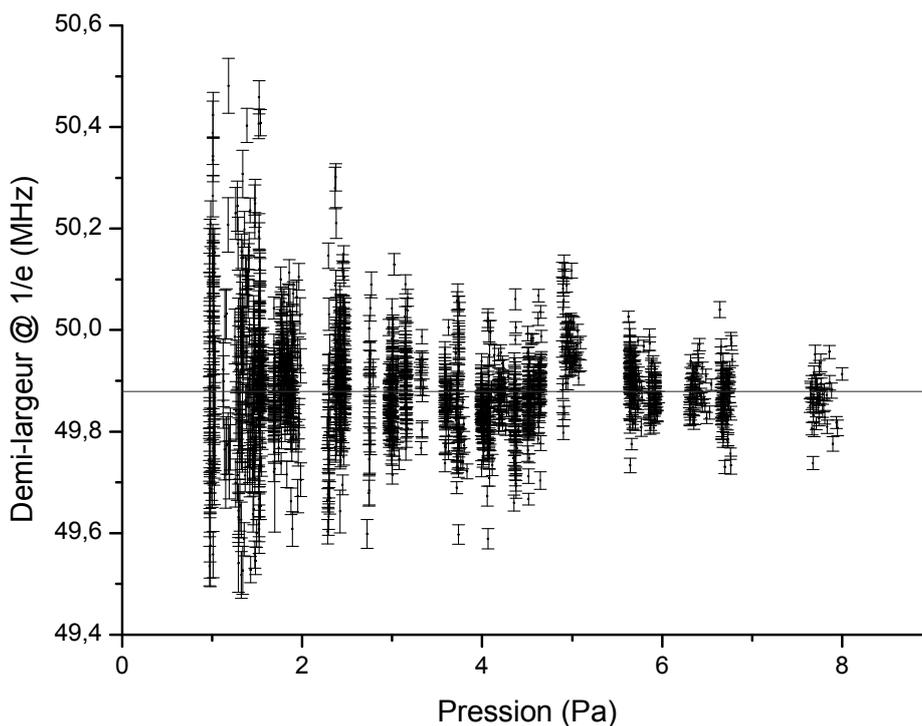


Figure 28 : demi-largeur Doppler mesurée jusqu'à 8 Pa

III. Vers une mesure au niveau du ppm

A. L'expérience de deuxième génération

Ces premiers résultats très prometteurs ont ouvert la voie à un nouveau dispositif expérimental, développé depuis 2006 avec comme objectifs principaux : l'amélioration du rapport signal sur bruit, la réduction des effets systématiques liés à la ligne de base et un contrôle au niveau du ppm de la température du gaz moléculaire [115].

Une analyse complète de la chaîne de détection et des différentes sources de bruit ainsi que plusieurs modifications des techniques de détection des signaux et d'asservissement ont permis une réduction du bruit de mesure d'un facteur 3 et du temps d'acquisition par spectre d'un facteur 3 également. Le schéma de détection a été simplifié et le nombre de modulations appliquées au faisceau laser a été réduit de 3 AM + 1 FM à 1 seule modulation AM. Les asservissements en fréquence de la CFP de filtrage et en intensité du laser ont été repensés et

simplifiés. Le nombre de boucles d'asservissement a ainsi été réduit de deux à une. Un travail sur le montage optique a permis par filtrage spatial des faisceaux et optimisation de l'isolation optique de réduire d'un facteur 30 l'amplitude des fluctuations résiduelles observées sur la ligne de base.

Le nouveau dispositif expérimental est présenté sur la figure suivante.

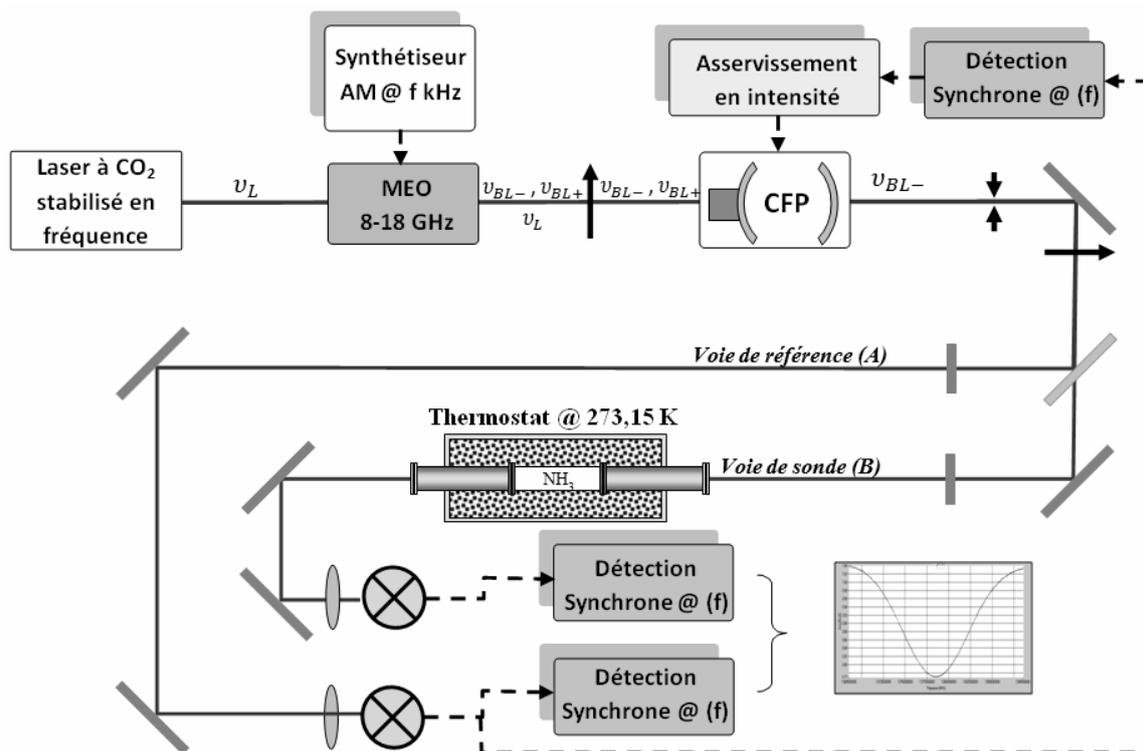


Figure 29: schéma du nouveau dispositif expérimental

Le développement d'une nouvelle cellule d'absorption multipassages a également permis, en augmentant la longueur d'absorption d'un facteur 10, d'accroître d'autant le rapport signal sur bruit à basse pression (voir Figure 30). Cette cellule peut être utilisée en configuration simple passage (longueur d'absorption = 380 mm) ou multipassages (longueur d'absorption = 3800 mm) afin d'étendre la gamme d'étude en pression.

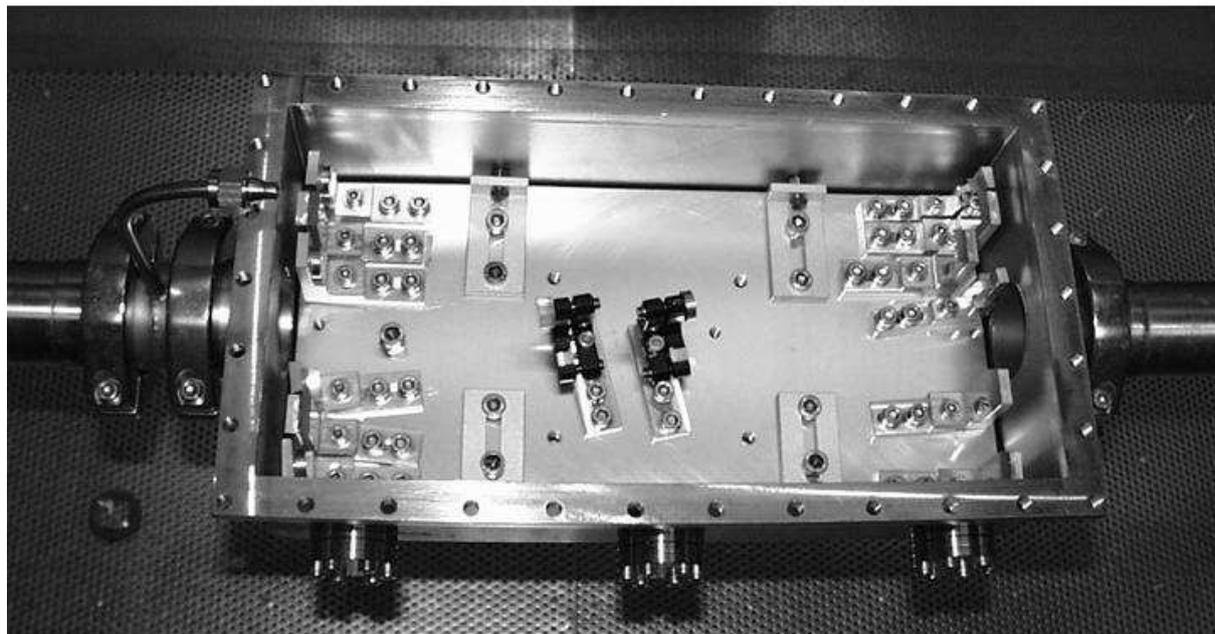


Figure 30 : cellule multipassages

Un nouveau thermostat régulé en température au niveau de 1 ppm ainsi qu'une nouvelle chaîne de mesure de la température du gaz ont été développés et sont actuellement en cours de caractérisation.

B. Derniers résultats et développements en cours

Une série de spectres d'absorption enregistrés en cellule multipassages, pour des pressions comprises entre 0,4 et 5 Pa, est présentée sur la Figure suivante.

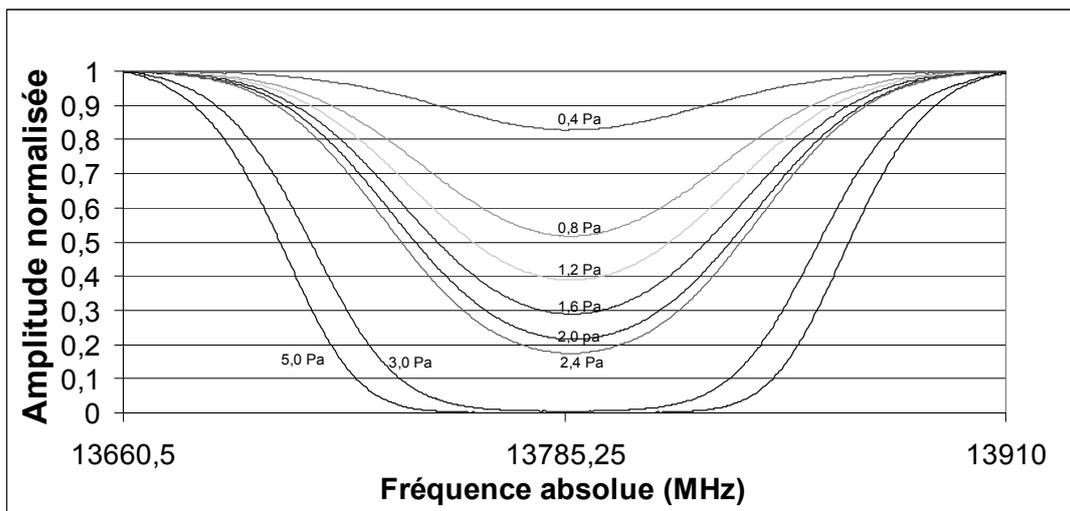


Figure 31 : spectres d'absorption de l'ammoniac à des pressions de 0,4 à 5 Pa en cellule multipassages

Le gain obtenu en terme de sensibilité de mesure est illustré sur la Figure 32 qui présente la largeur Doppler obtenue par ajustement non linéaire des spectres expérimentaux enregistré à différentes pressions. Le profil utilisé pour l'ajustement est un profil de Voigt.

Ces mesures conduisent à une nouvelle détermination de la largeur Doppler. Après seulement 11 heures d'accumulation nous avons été capables d'obtenir une nouvelle mesure de k_B avec une incertitude statistique à un niveau de **38 ppm**, soit pour des temps de mesure comparables, le gain d'un facteur 20 par rapport à la première expérience [116].

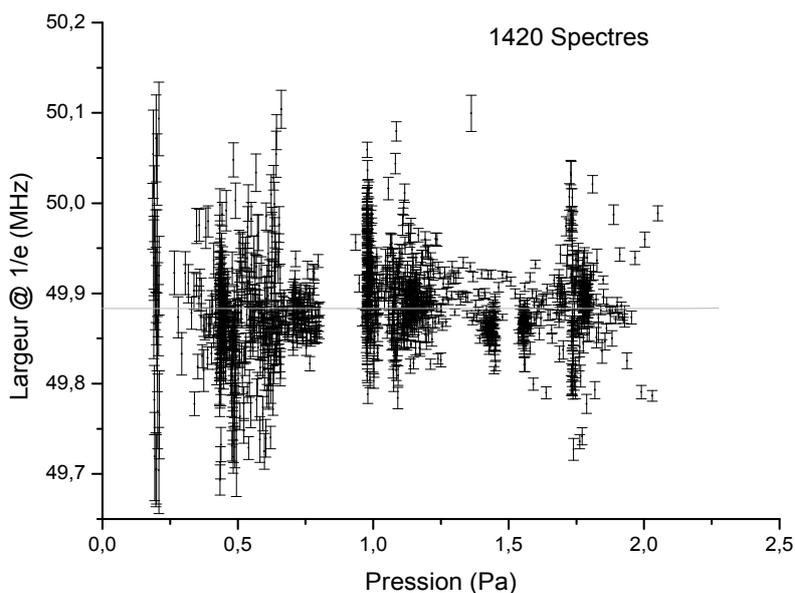


Figure 32 : Largeur Doppler en fonction de la pression obtenue par ajustement avec un profil de Voigt

A ce stade, l'étude exhaustive des effets systématiques est en cours.

La réduction du bruit a permis de montrer clairement que le profil de Voigt ne reproduit pas parfaitement la raie d'absorption aux pressions les plus élevées comme l'illustre la Figure 34.

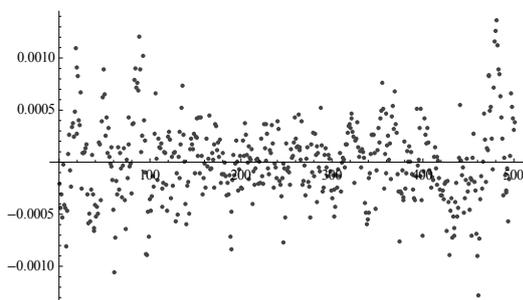


Figure 33 : résidu normalisé de l'ajustement numérique par un profil de Voigt d'un spectre enregistré à 0,8 Pa en cellule multipassages

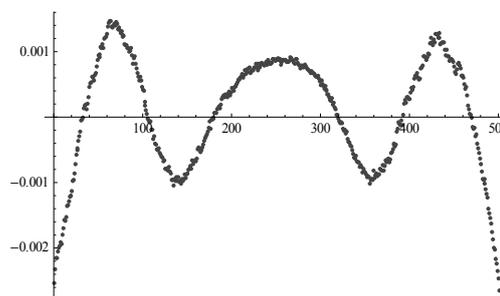


Figure 34 : résidu normalisé de l'ajustement numérique par un profil de Voigt d'une série de 40 spectres enregistrés à 20 Pa en cellule simple passage

Cet écart est dû très probablement à l'effet Lamb-Dicke-Mossbauer qui s'accompagne d'un rétrécissement de la raie. Cet effet peut être modélisé par différents profils suivant le type de collisions entre molécules: profil de Galatry [117] ou de Rautian (en fait introduit pour la première fois en spectroscopie par M. Nelkin et A. Ghatak en 1964 [118, 119]). Ces nouveaux profils font intervenir un paramètre supplémentaire lié à la diffusion du gaz. Dans le modèle de Galatry, ce paramètre est le coefficient de diffusion qui est très bien connu pour l'ammoniac [120, 121]. Des simulations en cours semblent montrer que dans nos conditions expérimentales, l'ajustement des spectres par un simple profil de Voigt est suffisant pour une détermination de la largeur Doppler dans la gamme des 10^{-5} pour des pressions de 0,1 à 1 Pa. Au-delà une prise en compte de l'effet Lamb-Dicke-Mossbauer est incontournable. La détermination de k_B au niveau du ppm passera donc nécessairement par une analyse complète de cet effet.

Conclusion

Ce projet de recherche initié en 2003 donne aujourd'hui des résultats très encourageants. La mesure de la constante de Boltzmann par spectroscopie laser, au niveau du ppm, semble accessible dans un avenir proche (voir Figure 35).

Ces résultats ont également permis de démontrer la possibilité de mesurer des profils d'absorption avec une très grande précision par spectroscopie laser. Ceci nous conduit à étudier les formes de raie d'absorption dans des régimes de basse pression très peu explorés. L'effet des collisions et en particulier le régime Lamb-Dicke restent à étudier. Ceci intéresse aussi le domaine de la spectroscopie atmosphérique et planétaire. La structure hyperfine doit être déterminée par l'expérience et le calcul, les écarts au gaz parfait estimés et pris en compte, la saturation modélisée et contrôlée, etc ...

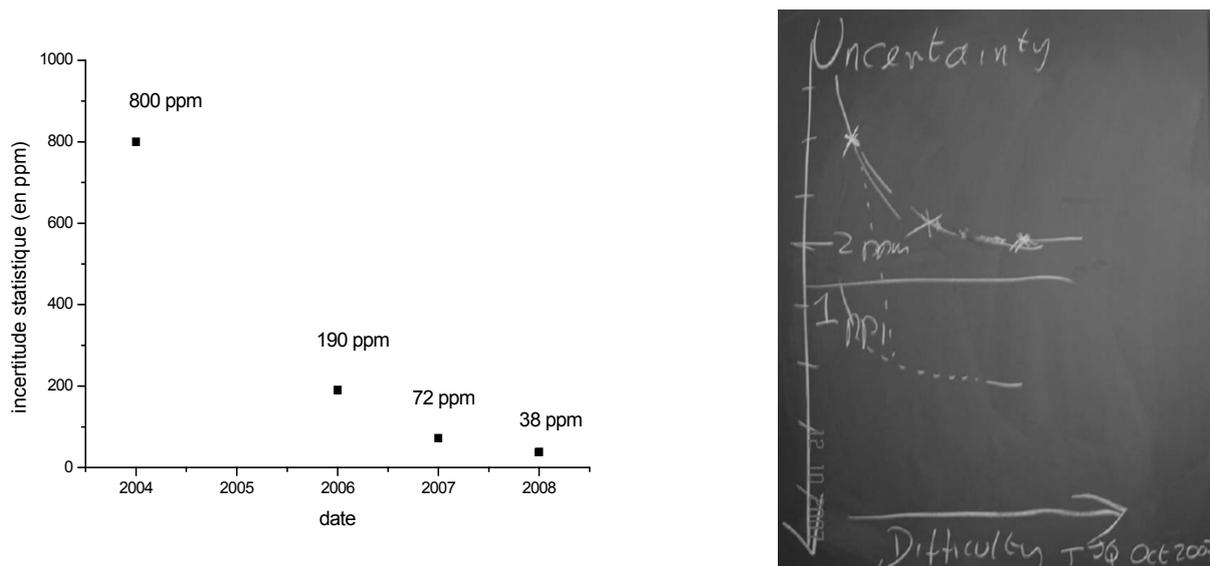


Figure 35 : évolution de l'incertitude statistique de mesure de la constante de Boltzmann par spectroscopie laser au LPL depuis les premières expériences en 2004 (à droite : Ecole de Physique des Houches 2007, T. Quinn)

Le développement du premier montage a été conduit au cours du travail de thèse de Mickaël Guinet (« première détermination de la constante de Boltzmann par une méthode optique » soutenue le 23 novembre 2006) [122]. Le deuxième dispositif a été développé par Khélifa Djerroud (doctorant depuis le 09/2005, soutenance fin 2008) et une nouvelle campagne de mesures est actuellement conduite par Cyril Lemarchand qui a débuté sa thèse en septembre 2008.

Ce travail a été mené en collaboration avec Stephan Briaudeau et Yves Hermier de l'Institut National de Métrologie pour la partie métrologie des températures.

Ce projet est soutenu financièrement par le LNE depuis 2006.

Enfin, dans le cadre de ce projet, nous participons à l'EraNet IMERA et plus particulièrement au « workpackage » *mesure optique de la constante de Boltzmann* qui regroupe 4 laboratoires Européens.

Conclusion et perspectives

Mon travail de recherche depuis environ 10 ans au Laboratoire de Physique des Lasers s'est articulé autour de 3 axes principaux dont les avancées majeures sont présentées dans ce manuscrit.

Le premier axe de recherche que j'ai conduit dans l'équipe a porté sur le développement d'une nouvelle expérience de spectroscopie laser avec pour but la recherche d'un effet NCP dans des molécules chirales. Nous avons pu réaliser un test NCP avec une sensibilité à un niveau de 10^{-13} sur les énantiomères de la molécule CHFCIBr. Nous avons atteint les limites de cette expérience et seule une expérience sur jet moléculaire où les effets collisionnels peuvent être rendus négligeables pourra donner lieu à une sensibilité supérieure. Le travail de réflexion mené en étroite collaboration avec nos collègues théoriciens, spectroscopistes et chimistes a montré que le choix de molécules plus favorables (pour lesquelles l'effet est 3 à 4 ordres de grandeur supérieur à celui calculé dans la molécule CHFCIBr) passera par des molécules composées d'atomes lourds telle que le complexe de Rhénium à base d'éphédrine, candidate la plus prometteuse à ce jour. Plusieurs difficultés restent à surmonter : la synthèse d'échantillons énantiopurs en quantité suffisante pour des expériences en jet supersonique continu, la mise en jet de ces molécules lourdes puis l'étude spectroscopique et l'identification d'une raie propice à notre expérience et enfin la réalisation du test NCP.

A notre connaissance, un seul autre groupe au monde, celui de M. Quack à Zürich, développe un projet avec pour objectif la mise en évidence de l'effet NCP dans des molécules. Il travaille actuellement sur la spectroscopie de molécules chirales par substitutions isotopiques. Ainsi la spectroscopie à haute résolution en jet des molécules $\text{CH}^{35}\text{Cl}^{37}\text{ClF}$ et $\text{PF}^{35}\text{Cl}^{37}\text{Cl}$ a été réalisée récemment [123, 124]. Pour ce type de molécules, deux problèmes majeurs se posent : la séparation des deux énantiomères et la très faible amplitude de l'effet NCP par l'absence d'atome lourd amplificateur de l'effet. Enfin la résolution de leur spectromètre est encore largement insuffisante, même pour observer un effet à un niveau de 10^{-13} !

Dans la configuration actuelle de notre expérience en jet sur SF_6 , la spectroscopie est réalisée sur une transition à 2 photons. Les premières expériences NCP seront réalisées en

absorption linéaire puis absorption saturée afin de trouver le bon compromis entre résolution et rapport signal sur bruit. La spectroscopie de telles molécules risque par ailleurs de poser problème en termes de rapport signal sur bruit à cause du grand nombre de modes de vibration basses fréquences. La détection directe à 10 μm du signal d'absorption même si elle est très performante en terme de résolution reste assez médiocre en terme de sensibilité de détection. Une réflexion devra donc être menée afin de comparer de façon quantitative les différentes techniques de détection compatibles avec notre expérience à ultra haute résolution. Un travail préliminaire a déjà été engagé par la spectroscopie de la molécule d'uréthane dans le domaine micro-onde et infrarouge au LADIR, au PhLAM et au LPL.

Si aucune molécule favorable pour un test NCP et compatible avec notre expérience en jet n'est identifiée, nous serons peut être conduit à relâcher la contrainte spectroscopique imposée par la faible plage d'accordabilité de notre spectromètre, entre 9 et 11 μm . Se poserait alors la question des sources adaptées pour réaliser la spectroscopie rovibrationnelle à ultra haute résolution dans d'autres gammes spectrales.

L'expérience en jet moléculaire sur SF_6 a démontré la possibilité d'atteindre un pouvoir de résolution de 10^{11} , limité par le temps de transit des molécules entre les deux zones d'interaction laser-molécules. L'augmentation du temps d'interaction cohérente laser-molécule pourrait peut être passer dans l'avenir par le développement d'une expérience de spectroscopie sur des molécules froides comme cela a été démontré dans plusieurs groupes [125-133]. Ces molécules chirales pourraient être ensuite refroidies en présence d'un nuage d'ions atomiques refroidis optiquement. Le temps d'interaction cohérent laser-molécule peut, dans ces conditions, atteindre des durées de l'ordre de la seconde, proches de la durée de vie des niveaux moléculaires. La résolution pourrait alors atteindre quelques Hz ce qui représenterait un gain d'environ 2 ordres de grandeur par rapport au test envisagé jusqu'ici. Une réflexion sur l'opportunité de développer un tel projet à la frontière des domaines de la métrologie, de la spectroscopie moléculaire et des atomes froids est actuellement en cours au Laboratoire.

L'observation d'un effet NCP dans une molécule, prédite et attendue depuis plus de trente ans, ne manquerait pas d'avoir un impact important dans la communauté scientifique. Ce projet devrait également avoir des retombées dans plusieurs domaines : une plus grande flexibilité des méthodes de calcul de chimie quantique, le développement de nouvelles méthodes de synthèses chirales et la capacité à réaliser des études de spectroscopie à haute

résolution dans divers domaines spectraux pour des molécules complexes, notamment d'intérêt biologique. La vérification expérimentale de cet effet, étayé par des calculs théoriques serait également une percée décisive vers la mise en relation de l'interaction faible avec l'origine de l'homochiralité biologique. Le deuxième enjeu est la confrontation avec les calculs de la chimie quantique relativiste qui n'auront jamais été testés à ce niveau de sensibilité. En particulier, en fonction de la précision expérimentale, il sera possible de valider certaines approximations présentes dans le modèle. Suivant le degré de précision du modèle théorique – estimé aujourd'hui à mieux que 10% – et des données expérimentales, il sera possible d'apporter des informations sur l'interaction faible elle-même. Outre le fait que l'approche spectroscopique est tout à fait originale, une précision de l'ordre du 1% des mesures et de l'analyse théorique serait compétitive par rapport aux expériences NCP réalisées en physique des hautes énergies et en physique atomique pour améliorer la connaissance de l'interaction faible. Il faut noter que la théorie prédit un mécanisme d'amplification plus important en systèmes moléculaires que atomiques (Z^5 contre Z^3 , Z étant la charge nucléaire).

Le deuxième projet de recherche auquel j'ai participé porte sur le développement d'une liaison par fibre optique pour le transfert longue distance d'étalons de fréquence. Nous avons mis en place deux liaisons optiques de 43 km entre le LPL et le SYRTE et réalisé un transfert de la fréquence d'une horloge entre les deux laboratoires avec une stabilité relative de 5×10^{-15} à 1 s et de quelques 2×10^{-18} sur une journée, ce qui représente un progrès de 3 ordres de grandeur par rapport au transfert par liaison GPS. Parallèlement, le développement d'une chaîne de mesure de fréquence locale basée sur l'utilisation d'un laser femtoseconde, nous a permis de démontrer plusieurs résultats dans les domaines de la métrologie des fréquences optiques, de la spectroscopie moléculaire à très haute résolution et des tests de physique fondamentale.

Pour aller au-delà des problèmes d'atténuation et de dispersion chromatique dans la fibre, nous avons envisagé de transférer directement une référence de fréquence optique : c'est un laser à 1,55 μm qui est ainsi la référence de fréquence. Ce passage à une fréquence optique s'inscrit dans l'évolution actuelle de la métrologie des fréquences : les horloges les plus prometteuses sont actuellement développées dans le domaine optique et il est donc logique d'envisager de les comparer via une référence optique, sans avoir besoin de

redescendre dans le domaine RF. De plus, la maîtrise des techniques RF concerne un nombre de laboratoires limité tandis qu'un transfert optique serait accessible à un plus grand nombre d'applications. Enfin, cette application se rapproche des solutions recherchées pour les transferts haut débit par fibre optique par multiplexage en longueur d'onde. Ce sujet est en plein développement sur le plan international et des équipes de métrologie allemandes (en collaboration avec le SYRTE et notre laboratoire) et américaine se sont lancées dans des projets comparables. Ce projet, développé depuis deux ans au Laboratoire, toujours en collaboration avec le SYRTE, a permis d'obtenir des stabilités remarquables, 10 fois meilleures qu'en RF, limitées par le système correcteur (performances limitées par le temps aller-retour).

Il faudra enfin démontrer la comparaison complète de deux horloges optiques via cette liaison à $1,55 \mu\text{m}$, et l'objectif est alors de comparer notre horloge moléculaire à SF_6 avec une des horloges atomiques du LNE-SYRTE, à Strontium ou à Mercure. Enfin, ce transfert pourra servir pour le contrôle en fréquence du laser d'interrogation de notre expérience de test de violation de parité.

Le troisième axe de recherche que j'ai développé dans l'équipe porte sur la réalisation d'une première mesure optique de la constante de Boltzmann. Ce dernier volet repose sur une connaissance et une mesure très fine des formes de raies d'absorption des molécules à basse pression. L'enjeu est une première détermination de la constante de Boltzmann à partir d'une largeur Doppler reposant donc sur une mesure de fréquence. Nous avons développé un nouveau dispositif expérimental qui a permis de démontrer une première mesure avec une incertitude au niveau de $1,9 \cdot 10^{-4}$ en valeur relative. Ce premier résultat, très prometteur, a ouvert la voie à un nouveau dispositif expérimental qui sera totalement opérationnel au cours de l'année 2009. Les premières études montrent déjà un gain de plus d'un ordre de grandeur en terme de rapport signal sur bruit. La possibilité de mesurer des profils d'absorption avec une très grande précision nous conduira à étudier les formes de raie d'absorption dans des régimes de basse pression très peu explorés. Plusieurs effets bien connus viennent se conjuguer dans ce régime de très basse pression et une métrologie fine devrait permettre dans les années qui viennent de valider tout un ensemble de théories qui lui sont applicables. L'effet des collisions et en particulier le régime Lamb-Dicke restent à étudier. La structure hyperfine doit être déterminée par l'expérience et le calcul, les écarts au gaz parfait estimés et

pris en compte, la saturation modélisée et contrôlée, etc... Il y a là une belle synthèse en perspective pour déterminer de façon réaliste les vraies limites de cette méthode.

Suite à nos premiers résultats, d'autres groupes se sont engagés dans cette nouvelle voie. En Italie, le groupe de L. Gianfrani a développé à Naples une expérience de spectroscopie sur la molécule CO_2 , dans l'infrarouge proche (autour de $2 \mu\text{m}$) [134]. La mesure de la largeur Doppler en fonction de la température, entre le point triple de l'eau et le point de fusion du Gallium, leur permet de déterminer la constante de Boltzmann avec une incertitude de 160 ppm. L'ajustement des spectres est réalisé avec un profil de Voigt (aucun rétrécissement Dicke n'est observé entre 70 et 130 Pa). L'expérience est principalement limitée par le contrôle en fréquence des diodes lasers utilisées pour la spectroscopie. Un travail pour améliorer le rapport signal sur bruit et réduire les fonds parasites est en cours. Enfin une expérience de spectroscopie sur H_2O autour de $1,4 \mu\text{m}$ est également prévue.

Très récemment, une équipe japonaise du NMIJ a publié une mesure sur la molécule d'acétylène autour de $1,5 \mu\text{m}$ [135]. Dans cette expérience, le contrôle en fréquence de la diode laser est assuré par asservissement sur un peigne de fréquence référencé à un maser à hydrogène. L'ajustement des spectres par un profil de Voigt conduit à une mesure de k_B avec une incertitude relative limitée à un niveau de 10^{-3} . La largeur spectrale de la diode laser, une centaine de kHz, ainsi que le contrôle en température de l'expérience sont les principales limites actuelles de l'expérience. Dans cette expérience, la gamme de pression explorée est comprise entre 40 et 670 Pa et contrairement aux expériences précédentes, le régime Lamb-Dicke-Mossbauer est ici très clairement observé.

Enfin une expérience est en cours de développement au Danish Institute of Fundamental Metrology. L'expérience sera réalisée à $1,5 \mu\text{m}$ sur l'acétylène puis sur l'ammoniac ce qui permettra des comparaisons avec notre expérience et celle menée au NMIJ. Le gaz sera placé dans une cellule thermostatée au point triple de l'eau ou au point de fusion du Gallium. Ce Laboratoire développe depuis plusieurs années des expériences de spectroscopie d'absorption dans des fibres photoniques creuses. La spectroscopie de l'acétylène et de l'ammoniac sera réalisée à l'intérieur d'une telle fibre. Une étude approfondie de l'impact des interactions molécules-surface sur le profil de la raie d'absorption et donc sur la mesure de la largeur Doppler sera menée.

D'un point de vue conceptuel, cette méthode est extrêmement générale et repose sur une application des premiers principes : la mesure directe de l'énergie thermique associée à un

degré de liberté du système. Ceci lui confère certains avantages originaux. En effet, le profil de raie reflète la distribution des vitesses le long de l'axe du faisceau laser pour les molécules situées dans un niveau rovibrationnel donné. La température mesurée étant, quant à elle, celle de l'échantillon dans son ensemble, déterminer une valeur commune de k_B sur différentes transitions, différentes molécules et à différentes températures est une vérification partielle du principe d'équipartition. Contrairement aux autres expériences de mesure de k_B passées ou envisagées, cette méthode permet ainsi d'étudier facilement des systèmes physiques différents dans une très large gamme de températures. Cet aspect n'est certainement pas le moins important lorsque sera venu le moment de fixer la valeur de k_B pour harmoniser le système international d'unités. En outre, la mesure de la largeur Doppler des raies dans les gaz fournit un moyen élégant et universel de mesurer la température thermodynamique de façon absolue.

Un prolongement plus appliqué de notre projet pourrait être la construction d'un thermomètre absolu opérationnel vers plusieurs centaines de degrés celsius, gamme où l'exactitude de notre expérience pourrait excéder assez aisément les méthodes actuelles reposant sur quelques points triples. Cette évolution dépendra des progrès actuels et de l'intérêt industriel d'une telle voie (le soutien du LNE serait alors indispensable).

Annexe : principales publications

-
- Ch. Chardonnet, Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen et Ch. J. Bordé, *Parity violation test in chiral molecules by laser spectroscopy*, paru dans *"Parity Violation in atomic Physics and Electron Scattering"*, World Scientific, ed. B. Frois and M.A. Bouchiat, 325-355 (1999)
 - Ch. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, Ch. J. Bordé and Ch. Chardonnet, *Limit on the Parity Nonconserving Energy Difference between the Enantiomers of a Chiral Molecule by Laser Spectroscopy*, Phys. Rev. Lett. **83**, 1554-1557 (1999)
 - M. Ziskind, T. Marrel, C. Daussy and Ch. Chardonnet, *Improved sensitivity in the search for a parity-violating energy difference in the vibrational spectrum of the enantiomers of CHFC1Br*, EPJ D **20**, 219-225 (2002)
 - J. Crassous, F. Monier, J.-P. Dutasta, M. Ziskind, C. Daussy, C. Grain, C. Chardonnet, *Search for resolution of chiral fluorohalogenomethanes and parity violation effects at the molecular level*, ChemPhysChem **4**, 541-548 (2003)
 - Amy-Klein, A. Goncharov, C. Daussy, C. Grain, O. Lopez, G. Santarelli, C. Chardonnet, *Absolute frequency measurement in the 28 THz spectral region with a femtosecond laser comb and a long-distance optical link to a primary standard*, Appl. Phys. B **78**, 25-30 (2004)
 - C. Daussy, O. Lopez, A. Amy-Klein, A. Goncharov, M. Guinet, C. Chardonnet, F. Narbonneau, M. Lours, D. Chambon, S. Bize, A. Clairon, G. Santarelli, M.E. Tobar, A.N. Luiten, *Long-distance frequency dissemination with a resolution of 10^{-17}* , Phys. Rev. Lett. **94**, 203904 (2005)
 - C. Daussy, M. Guinet, A. Amy-Klein, K. Djerroud, Y. Hermier, S. Briaudeau, Ch.J. Bordé, and C. Chardonnet, *First direct determination of the Boltzmann constant by an optical method*, Phys. Rev. Lett. **98**, 250801 (2007)
 - O. Lopez, A. Amy-Klein, C. Daussy, Ch. Chardonnet, F. Narbonneau, M. Lours, and G. Santarelli, *90-km optical link with a resolution of 2×10^{-18} for RF frequency transfer*, EPJ D **48**, 35–41 (2008)

PARITY VIOLATION TEST IN CHIRAL MOLECULES BY LASER SPECTROSCOPY

Ch. CHARDONNET, Ch. DAUSSY, T. MARREL, A. AMY-KLEIN,
C.T. NGUYEN and Ch. J. BORDE

*Laboratoire de Physique des Lasers, UMR 7538 du CNRS,
Université Paris-Nord, avenue J.-B. Clément, 93430 Villetaneuse, France*
E-mail: chardonnet@lpl.univ-paris13.fr, borde@lpl.univ-paris13.fr

A laser nonlinear spectroscopy experiment has been designed and implemented to test the conjecture that enantiomers of chiral molecules may have different spectra because of the parity violation associated with neutral currents in the weak interaction between electrons and nuclei. We review the theoretical reasons that lead to this prediction and we outline the method currently used to calculate energy and frequency differences between mirror image molecules. Preliminary experimental tests have been conducted on hyperfine components of vibration-rotation transitions of CHFCIBr in the $9.3 \mu\text{m}$ spectral range. The frequencies of saturation resonances of separated enantiomers have been compared and found identical within 13 Hz ($\Delta\nu/\nu < 4 \cdot 10^{-13}$).

1 Introduction and historical background

We address ourselves to the general problem of the role that parity-violation in weak interactions^{1,2} and especially those associated with neutral currents^{3,4,5}, has in molecular physics. Besides consequences for all molecules⁶⁻⁹ similar to those already known in atomic physics¹⁰⁻¹⁹, a very interesting new feature comes from the fact that the molecular structure may be chiral and hence not correspond to a parity eigenstate. A difference in energy may then arise between mirror configurations of the molecule²⁰⁻²⁹, depending on their handedness.

The specific question that we wish to raise in this paper, both from a theoretical and from an experimental point of view, is the following: **do enantiomers of chiral molecules have identical spectra in the absence of any external field**^a? As an example, that we will consider in more detail later, two methane molecules substituted with four different atoms (Figure 1) should have exactly the same absorption frequencies if mirror symmetry was respected.

If parity is violated, this might not be true anymore and modern ultra-high resolution spectroscopy is able to test the difference with a very high accuracy

^aThe same question in presence of a large magnetic field, for nuclear magnetic resonance spectra, has been studied in detail by Gorshkov³⁰ and by Barra and coll.³¹⁻³⁴ and we will not consider this case here.

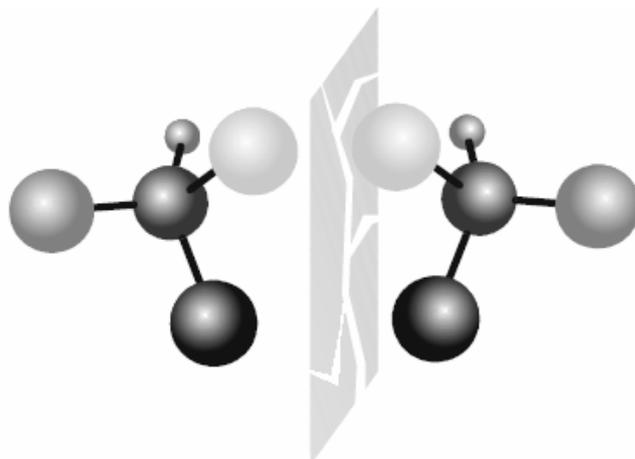


Figure 1: Because of parity violation in weak interactions enantiomeric species may not be faithful mirror images and may have different spectra.

as we shall see^{35,36}.

The fact that parity violation could manifest itself in chiral molecules as an energy shift of opposite sign for the two enantiomers was first suggested by D.W. Rein²⁰ in September 1973, a few years only after the introduction of neutral currents in weak interactions^{3,4,5}. It was later conjectured by V.S. Letokhov²⁴ that this difference in energies could manifest itself as a difference in vibrational or rotational frequencies. Many theoretical studies have been pursued to obtain quantitative estimates of the effect in various molecules and we shall outline one of these approaches, but none of them is yet able to provide even a crude estimate of the expected frequency shift. In this context, it was of great interest to perform an experiment. Another major issue is, of course, the possible role of the weak interaction in the emergence of the homochirality of L- α -aminoacids and D-sugars associated with living organisms on earth³⁷⁻⁴⁷.

2 Theoretical background

2.1 Parity and chirality

What is so special in chiral molecules that cannot be found in atoms and other molecules? **Chiral molecules may exist in states that differ only by their handedness or by their parity, all other quantum numbers being the same.** In other polyatomic molecules, we have shown, experimentally and theoretically^{48,49,35}, that, because of the Pauli principle, states which differ by their parity also differ by some other property of their wave functions, as it is the case also for atoms.

For chiral molecules, if $|\Psi^R\rangle$ is a possible state with a right-handed configuration, then, there exists also a state $|\Psi^L\rangle$ which is left-handed but otherwise identical. As we shall see, from this “handedness” basis one can construct two other states $|\Psi^\pm\rangle$ which differ only by their parity. The potential energy curve for the chiral molecules is symbolically represented in Figure 2 as a function of the internuclear coordinate along which the molecule may invert itself. If the tunneling barrier is not too high, mirror symmetry is dynamically

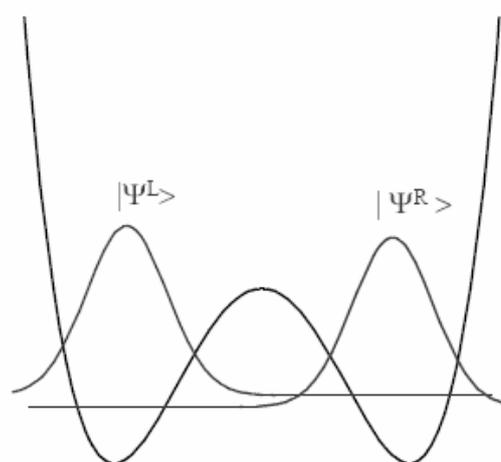


Figure 2: If the familiar double well potential curve exhibits a barrier of sufficient height, tunneling inversion between right and left-handed species may not occur and handedness is a good quantum number over long time scales. If parity is violated this figure loses its symmetry about the vertical axis.

restored by the inversion mechanism. Parity commutes with the Hamiltonian and energy eigenstates are parity-eigenstates. In the handedness-eigenstates basis the Hamiltonian matrix will have off-diagonal elements representing the tunneling coupling terms between the right and left-handed species:

$$H_H = \begin{pmatrix} E_0 & \delta \\ \delta^* & E_0 \end{pmatrix} \quad (1)$$

Going to the parity-eigenstates basis^b:

$$|\Psi^\pm\rangle = \frac{1}{\sqrt{2}}(|\Psi^R\rangle \pm e^{i\varphi}|\Psi^L\rangle) \quad (2)$$

^bThe phase φ , which appears in this combination, is the phase of the coupling matrix element δ (modulo π , because there is an ambiguity in the correspondence between parity-eigenstates and eigenvalues which can be resolved only by a more detailed knowledge of the Hamiltonian). Such a phase may manifest itself in the phase difference in a molecular interferometry experiment⁵⁰ in which, for example, Raman two-photon interactions convert enantiomers in their opposite form along each arm of the interferometer.

this coupling will remove the degeneracy of the energy eigenvalues of states of opposite parity:

$$H_P = \begin{pmatrix} E_0 + |\delta| & 0 \\ 0 & E_0 - |\delta| \end{pmatrix} \quad (3)$$

The handedness-eigenstates, which are superpositions of two parity eigenstates with different energies, are clearly time-dependent and chiral molecules tunnel back and forth between the right and left limiting forms.

On the other hand, if the potential barrier is very high, the molecule does not invert itself, the enantiomorphic left and right-handed species are stable and handedness is a good quantum number for energy eigenstates. If parity is violated, the Hamiltonian matrix which is not diagonal in the parity-eigenstates basis will remain diagonal in the handedness-eigenstates basis but the corresponding degeneracy will be removed:

$$H_P = \begin{pmatrix} E_0 & \varepsilon \\ \varepsilon^* & E_0 \end{pmatrix} \quad (4)$$

in the basis $|\Psi^\mp\rangle$ becomes:

$$H_H = \begin{pmatrix} E_0 + |\varepsilon| & 0 \\ 0 & E_0 - |\varepsilon| \end{pmatrix} \quad (5)$$

with eigenvectors:

$$|\Psi^{R,L}\rangle = \frac{1}{\sqrt{2}}(|\Psi^+\rangle \pm e^{i\chi}|\Psi^-\rangle) \quad (6)$$

An equivalent argument was followed by Rein²⁰: let U_P be the mirror reflexion (parity) operator which transforms left-handed into right-handed states:

$$U_P|\Psi^{R,L}\rangle = |\Psi^{L,R}\rangle \quad (7)$$

then the corresponding energies are related by:

$$\langle\Psi^R|H^{PV}|\Psi^R\rangle = \langle\Psi^L|U_P^{-1}H^{PV}U_P|\Psi^L\rangle = -\langle\Psi^L|H^{PV}|\Psi^L\rangle \quad (8)$$

where

$$H^{PV} = -U_P^{-1}H^{PV}U_P$$

is the parity-violating part of the Hamiltonian and their difference is:

$$\begin{aligned} 2|\Delta E^{PV}| &= |\langle\Psi^L|H^{PV}|\Psi^L\rangle - \langle\Psi^R|H^{PV}|\Psi^R\rangle| \\ &= 2|\langle\Psi^-|H^{PV}|\Psi^+\rangle| = 2|\varepsilon| \end{aligned} \quad (9)$$

We shall now briefly outline the calculation of ΔE^{PV} following the early approach of Rein, Hegstrom and Sandars^{27,51}.

2.2 The molecular Hamiltonian

2.2.1 The parity-violating Hamiltonian

The parity-violating part of the electron-nucleus interaction Hamiltonian may be written as^{10,19,31}:

$$H^{PV} = H_1^{PV} + H_2^{PV} + H_3^{PV} \quad (10)$$

where:

$$H_1^{PV} = \frac{G_F}{2\sqrt{2}m_e c} \vec{s} \cdot \left[\vec{p}, \delta^{(3)}(\vec{r}) \right]_+ \mathbf{Q}_W \quad (11)$$

is the dominant term. In this equation, G_F is the Fermi constant (1.43×10^{-62} J.m³), m_e the electron rest mass, c the speed of light, $\vec{s} = \vec{\sigma}/2$ the dimensionless electron spin operator, $\left[\vec{p}, \delta^{(3)}(\vec{r}) \right]_+$ is the anticommutator of the electron momentum operator \vec{p} and of the 3D Dirac distribution. Finally the nucleus has a weak charge given by:

$$\mathbf{Q}_W = \mathbf{Z} (1 - 4 \sin^2 \theta_W) - \mathbf{N}$$

where \mathbf{Z} and \mathbf{N} are respectively the proton and neutron numbers and where the Weinberg angle θ_W is given by $\sin^2 \theta_W \simeq 0.2236$.

The next terms in the Hamiltonian:

$$\begin{aligned} H_2^{PV} &= -\lambda_N \frac{G_F}{2\sqrt{2}m_e c} \vec{I}_N \cdot \left[\vec{p}, \delta^{(3)}(\vec{r}) \right]_+ (1 - 4 \sin^2 \theta_W) \\ H_3^{PV} &= i\lambda_N \frac{G_F}{\sqrt{2}m_e c} \left(\vec{s} \times \vec{I}_N \right) \cdot \left[\vec{p}, \delta^{(3)}(\vec{r}) \right] (1 - 4 \sin^2 \theta_W) \end{aligned} \quad (12)$$

with $\lambda_N \sim 1$ ¹², depend on the nuclear spin operator \vec{I}_N , and they are usually neglected in atomic and molecular physics^c. So, in the following, we shall consider only the first term and write the total parity-violating Hamiltonian as a sum of one-electron operators $\vec{s}_i = \vec{\sigma}_i/2$ and \vec{p}_i , where each nucleus α has a weak charge \mathbf{Q}_W^α :

^cOne should also consider the anapole term introduced by Zel'dovich^{52,53}.

$$\begin{aligned}
H^{PV} &= \frac{G_F}{4\sqrt{2}m_e c} \sum_{i,\alpha} \vec{\sigma}_i \cdot \left[\vec{p}_i, \delta^{(3)}(\vec{r}_{i\alpha}) \right]_+ \mathbf{Q}_W^\alpha \\
&= \frac{1}{4\sqrt{2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha \right) \alpha (m_e c^2 \alpha^2) \\
&\quad \left\{ a_0^4 \hbar^{-1} \sum_{i,\alpha} \vec{\sigma}_i \cdot \left[\vec{p}_i, \delta^{(3)}(\vec{r}_{i\alpha}) \right]_+ \mathbf{Q}_W^\alpha \right\} \quad (13)
\end{aligned}$$

where:

$$\left(\frac{G_F m_e^2 c}{\hbar^3} \alpha \right) = \frac{G_F}{a_0^3 (m_e c^2 \alpha^2)} \simeq 2.2 \cdot 10^{-14} \quad (14)$$

is usually taken as the dimensionless coupling constant and where we have introduced the atomic units of energy and distance:

$$m_e c^2 \alpha^2 = 2Ry = 1 \text{ Hartree and } a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{m_e e^2} = \frac{1}{\alpha} \frac{\hbar}{m_e c} \quad (15)$$

We will need the matrix element of the Hamiltonian 13, which is easily obtained from:

$$\left\langle \varphi \left| \left[\vec{p}, \delta^{(3)}(\vec{r}) \right]_+ \right| \varphi' \right\rangle = i\hbar \left[\varphi'(\vec{r}) \vec{\nabla} \varphi(\vec{r}) - \varphi(\vec{r}) \vec{\nabla} \varphi'(\vec{r}) \right]_{(\vec{r}=0)} \quad (16)$$

In atoms, owing to its contact character, the parity-violating Hamiltonian may thus connect only s and p orbitals:

$$\left\langle n' p_z \left| \left[p_z, \delta^{(3)}(\vec{r}) \right]_+ \right| n s \right\rangle = \frac{i\hbar\sqrt{3}}{4\pi} R_{n0}(0) \left[\frac{d}{dr} R_{n'1}(r) \right]_{r=0} \quad (17)$$

and

$$\begin{aligned}
\langle n s_{1/2} | H^{PV} | n' p_{1/2} \rangle &= \frac{3i}{16\pi\sqrt{2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) m_e c^2 \alpha^2 \mathbf{Q}_W \\
&\quad a_0^4 R_{n0}(0) \left[\frac{d}{dr} R_{n'1}(r) \right]_{r=0} \quad (18)
\end{aligned}$$

in the coupled $| (sl)j \rangle$ basis, where $R_{n0}(r)$ and $R_{n'1}(r)$ are respectively the radial parts of the ns and of the $n'p$ wave functions:

$$\varphi_{ns} = \frac{1}{\sqrt{4\pi}} R_{n0}(r) \quad ; \quad \varphi_{n'p} = Y_{1m}(\theta, \varphi) R_{n'1}(r).$$

These functions can be taken from the work of M.-A. Bouchiat and C. Bouchiat¹⁰ and using their formulas, one gets:

$$\left\langle n' p_z \left| \left[p_z, \delta^{(3)}(\vec{r}) \right]_+ \right| n s \right\rangle \simeq (-1)^{n_* + n'_* - 1} \left(\frac{i\hbar}{\pi\sqrt{3}a_0^4} \right) \frac{K_{rel.}}{(n_* n'_*)^{3/2}} \mathbf{Z}^2 \quad (19)$$

and

$$\langle n s_{1/2} | H^{PV} | n' p_{1/2} \rangle \simeq \left(\frac{i}{4\sqrt{2}\pi} \right) \frac{K_{rel.}}{(n_* n'_*)^{3/2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) m_e c^2 \alpha^2 \mathbf{Z}_\alpha^2 \mathbf{Q}_W \quad (20)$$

in the coupled basis, where n_* , n'_* , are effective radial quantum numbers and where $K_{rel.}$ is a relativistic correction factor increasing with \mathbf{Z} .

For molecules, in the nonrelativistic limit :

$$\langle 0^R | H^{PV} | 0^R \rangle = \langle 0^L | H^{PV} | 0^L \rangle = 0 \quad (21)$$

because the electronic wavefunction $\psi_0^{R,L} = \langle \vec{r} | 0^{R,L} \rangle$ may be chosen purely real, while \vec{p}_i is purely imaginary as expected from time reversal invariance (one should remember that the Hamiltonian H^{PV} has time reversal symmetry). As pointed out by Gajzago and Marx²³ it is therefore necessary to invoke the spin-orbit coupling to mix the ground state $|0^\pm\rangle$ with excited states $|n^\pm\rangle$:

$$|0'^\pm\rangle = |0^\pm\rangle + \sum_{n \neq 0} \frac{\langle n^\pm | H^{SO} | 0^\pm \rangle}{E_0 - E_n} |n^\pm\rangle \quad (22)$$

and to obtain a non-zero contribution at the second perturbation order:

$$\begin{aligned} \varepsilon = \langle 0'^- | H^{PV} | 0'^+ \rangle &= \sum_{n \neq 0} \frac{\langle 0^- | H^{PV} | n^+ \rangle \langle n^+ | H^{SO} | 0^+ \rangle}{E_0 - E_n} \\ &+ \frac{\langle 0^- | H^{SO} | n^- \rangle \langle n^- | H^{PV} | 0^+ \rangle}{E_0 - E_n} \end{aligned} \quad (23)$$

where, as we shall see, the second term is complex conjugate of the first and ε is thus real. We will therefore now introduce this spin-orbit coupling and recall some of its properties.

2.2.2 The spin-orbit interaction

The corresponding Hamiltonian is written:

$$H^{SO} = -\frac{e\hbar}{4m_e^2c^2} \left\{ \sum_{i,\alpha} \vec{\sigma}_i \cdot (\vec{E}_\alpha(\vec{r}_{i\alpha}) \times \vec{p}_i) - \sum_{i \neq j} \vec{\sigma}_i \cdot (\vec{E}_j(\vec{r}_{ij}) \times (\vec{p}_i - 2\vec{p}_j)) \right\} \quad (24)$$

where in the first term $\vec{E}_\alpha(\vec{r}_{i\alpha}) \times \vec{p}_i/m_e c^2$ is a motional magnetic field corresponding to an electric field created by the nucleus α and seen by the electron i (neglecting the motion of the nucleus) and where the second term is the spin-other orbit interaction in which the motional magnetic field is created by the other electrons $j \neq i$.

An important approximation made by all authors this far, is to assume that the electric field seen by each electron can be replaced by an effective spherically symmetric field around each nucleus α :

$$\vec{E}_\alpha(\vec{r}_{i\alpha}) = -\frac{\vec{r}_{i\alpha}}{r_{i\alpha}} \frac{dV_\alpha(r_{i\alpha})}{dr_{i\alpha}} = \frac{Z_\alpha e}{4\pi\epsilon_0} \frac{\vec{r}_{i\alpha}}{r_{i\alpha}} \frac{d}{dr_{i\alpha}} \left(\frac{1}{r_{i\alpha}} U(r_{i\alpha}) \right) \quad (25)$$

$$H^{SO} = \frac{\alpha^2}{4} (\alpha^2 m_e c^2) \sum_{i,\alpha} Z_\alpha \left(\frac{a_0}{r_{i\alpha}} \right)^3 \left(U - r_{i\alpha} \frac{dU}{dr_{i\alpha}} \right) \vec{\sigma}_i \cdot \vec{l}_{i\alpha} = \sum_{i,\alpha} a_\alpha(r_{i\alpha}) \vec{s}_i \cdot \vec{l}_{i\alpha} \quad (26)$$

where $\vec{l}_{i\alpha} = (\vec{r}_{i\alpha} \times \vec{p}_i)/\hbar$ is the dimensionless orbital angular momentum of electron i around the nucleus α and $a_\alpha(r_{i\alpha})$ is the spin-orbit coupling parameter of the atom α :

$$a_\alpha(r_{i\alpha}) = \alpha^2 Z_\alpha \left(\frac{a_0}{r_{i\alpha}} \right)^3 \left(U - r_{i\alpha} \frac{dU}{dr_{i\alpha}} \right) Ry \quad (27)$$

For atoms the matrix elements, that we will need later on, are given by :

$$\langle np_x | a(r) l_z | n' p_y \rangle = -i \int_0^{+\infty} a(r) R_{np}(r) R_{n'p}(r) r^2 dr \quad (28)$$

and the diagonal elements of the spin-orbit Hamiltonian in the coupled basis $| (ls)jm \rangle$ are⁵⁴:

$$\Delta E_{jlm}^{SO} = \langle n(ls)jm | H^{SO} | n(ls)jm \rangle = \zeta_{nl} [j(j+1) - l(l+1) - s(s+1)]/2 \quad (29)$$

with

$$\zeta_{nl} = \int_0^{+\infty} a(r) R_{nl}^2(r) r^2 dr \quad (30)$$

In the case of a multielectron atom:

$$\zeta_{nl} = \alpha^2 \frac{Z_\alpha^2 H_r(lZ_\alpha)}{n_*^3 l(l+1)(l+1/2)} Ry \quad (31)$$

where Z_α is an effective charge and where H_r is a relativistic correction given in ⁵⁴.

If we combine formulas 20 and 31 to estimate the order of magnitude of ΔE^{PV} in 23, we see that if $E_0 - E_n \approx 1$ Hartree then:

$$\Delta E^{PV} \sim \left(\frac{G_F m_e^2 c}{\hbar^3} \right) \alpha^4 Z^4 Q_W Ry \sim 8.5 \cdot 10^{-21} Z^5 \text{ Hartree} \quad (32)$$

Further theoretical work by Zel'dovich et al.²⁵, Harris and Stodolsky²⁸, Rein et al.²⁷, I.B. Khriplovich²⁹ introduce a multiplicative asymmetry factor η to include the effect of the molecular environment. Now, the whole problem is to calculate this asymmetry factor from basic principles, i.e. from formula 23 and from the molecular orbital theory.

2.3 Quantum chemistry calculations

The second important approximation made by Hegstrom, Rein and Sandars^{27,51} to simplify the problem is to assume that the electronic wave functions can be written as a single Slater determinant: for closed shell molecules (with an even number $2N$ of electrons), the ground state wave function is approximated by a determinant of one-electron orthonormal orbitals φ_i each associated with spin functions $\chi_i = \alpha, \beta$:

$$\psi_0 = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \varphi_2(1)\alpha(1) & \dots & \dots & \dots \\ \varphi_1(2)\alpha(2) & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \varphi_N(2N)\beta(2N) \end{vmatrix} \quad (33)$$

which can be written symbolically as $\psi_0 = \det\{\varphi_1\tilde{\varphi}_1\varphi_2\tilde{\varphi}_2\dots\varphi_N\tilde{\varphi}_N\}$ (the normalization factor is left out for simplicity in this short notation).

In addition to the N occupied orbitals $\varphi_i = \varphi_1, \dots, \varphi_N$, there are unoccupied molecular orbitals $\varphi_n = \varphi_{N+1}, \varphi_{N+2}, \dots$ which can be used to construct approximate wave functions for excited states. The only ones, that we need to

consider here, are those obtained by the excitation of a single electron from an occupied molecular orbital φ_i to an unoccupied one φ_n . For each excitation, there are four such states, resulting in one singlet and one triplet:

$$\begin{aligned} \psi_{i \rightarrow n}^{(1)} &= [\det\{\varphi_1 \tilde{\varphi}_1 \dots \varphi_i \tilde{\varphi}_n \dots\} + \det\{\varphi_1 \tilde{\varphi}_1 \dots \varphi_n \tilde{\varphi}_i \dots\}]/\sqrt{2} \\ \psi_{i \rightarrow n}^{(3)} &= \left\{ \begin{array}{l} \det\{\varphi_1 \tilde{\varphi}_1 \dots \tilde{\varphi}_i \tilde{\varphi}_n \dots\} \\ [\det\{\varphi_1 \tilde{\varphi}_1 \dots \varphi_i \tilde{\varphi}_n \dots\} - \det\{\varphi_1 \tilde{\varphi}_1 \dots \varphi_n \tilde{\varphi}_i \dots\}]/\sqrt{2} \\ \det\{\varphi_1 \tilde{\varphi}_1 \dots \varphi_i \varphi_n \dots\} \end{array} \right\} \quad (34) \end{aligned}$$

with excitation energies $E_{i \rightarrow n}^{(1)} - E_0$ and $E_{i \rightarrow n}^{(3)} - E_0$. Only the excited triplet states can be mixed with the ground state by the Hamiltonians that we consider here.

Since it involves only one-electronic operators, formula 23 can then be applied to molecular orbitals by interpreting the E_n as orbital energies and ψ_n as molecular spin orbitals:

$$\Delta E_{el}^{PV} = \sum_i^{occ} \sum_n^{unocc} \frac{\langle \varphi_i \chi_i | H^{PV} | \varphi_n \chi_n \rangle \langle \varphi_n \chi_n | H^{SO} | \varphi_i \chi_i \rangle}{\varepsilon_i - \varepsilon_n} + c.c. \quad (35)$$

where i and n run respectively on the occupied and unoccupied orbitals of the ground state with energies ε_i and ε_n . The excitation energy $E_{i \rightarrow n}^{(3)} - E_0$ has been approximated by the difference of one-electron energies $\varepsilon_n - \varepsilon_i$, therefore neglecting the Coulomb interactions between electrons (for a better approximation see⁴⁴).

Using

$$(\vec{\sigma} \cdot \vec{A})(\vec{\sigma} \cdot \vec{B}) = \vec{A} \cdot \vec{B} + i \vec{\sigma} \cdot \vec{A} \times \vec{B} \quad (36)$$

$$\begin{aligned} \Delta E_{el}^{PV} &= \frac{1}{2\sqrt{2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) (m_e c^2 \alpha^2) \\ & \alpha_0^4 \sum_{i,n,\alpha,\beta} \mathbf{Q}_{W}^{\alpha} \frac{\langle \varphi_i | \{ \vec{p}/\hbar, \delta^{(3)}(\vec{r}_{\alpha}) \}_+ | \varphi_n \rangle \cdot \langle \varphi_n | a_{\beta}(r_{\beta}) \vec{l}_{\beta} | \varphi_i \rangle}{\varepsilon_i - \varepsilon_n} \end{aligned} \quad (37)$$

where \vec{r}_{α} stands for $\vec{r} - \vec{r}_{\alpha}$.

The similarity between this expression and the corresponding one giving optical rotation has been emphasized²⁷. In many aspects, this calculation is also quite similar to the calculation of the molecular Zeeman effect or to the calculation of hyperfine coupling constants.

The LCAO approach, in which, molecular orbitals are expanded on a basis of real atomic orbitals is then generally adopted:

$$|\varphi_i\rangle = \sum_{\alpha,\gamma} c_{i\gamma}^{\alpha} |\varphi_{\gamma}^{\alpha}\rangle \quad (38)$$

which gives finally:

$$\begin{aligned} \Delta E_{el}^{PV} &= \frac{1}{2\sqrt{2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) (m_e c^2 \alpha^2) \\ & a_0^4 / \hbar \sum_{\substack{i,\epsilon \\ \alpha,\beta,\gamma,\dots}} c_{i\gamma}^{\alpha} c_{\epsilon\gamma'}^{\alpha} c_{\epsilon\gamma''}^{\beta} c_{i\gamma'''}^{\beta} \mathbf{Q}_{i\gamma}^{\alpha} \\ & \langle \varphi_{\gamma}^{\alpha} | \left\{ \vec{p}, \delta^{(3)}(\vec{r}_{\alpha}) \right\}_+ | \varphi_{\gamma'}^{\alpha} \rangle \\ & \langle \varphi_{\gamma''}^{\beta} | a_{\beta}(r_{\beta}) \vec{l}_{\beta} | \varphi_{\gamma'''}^{\beta} \rangle \\ & (\epsilon_i - \epsilon_{\epsilon})^{-1} \end{aligned} \quad (39)$$

To write this formula, a simplification has been made, which consists in restricting each matrix element to a single center, therefore neglecting the overlap: the same nucleus α or β is selected for the atomic orbitals and for the interaction.

It was shown, by Hegstrom, Rein and Sandars⁵¹ that, in this formula, the one-center terms ($\alpha = \beta$) are much smaller and vanish for a pure and single *sp* basis set. This is what they called the single center theorem: $\alpha \neq \beta$. As a consequence, the parity-violating terms will be proportional to $\mathbf{Z}_{\alpha}^3 \mathbf{Z}_{\beta}^2$ for each pair of nuclei.

Also, one can understand that if a given nucleus α has a symmetric environment, terms corresponding to partners β, β', \dots symmetrically located will cancel each other since they will change signs by mirror reflection.

The total energy shift ΔE_{el}^{PV} is then a sum of separate contributions $\Delta E_{el}^{PV}(\alpha)$ from each of the nuclei composing the molecule.

Using this theoretical approach, Hegstrom, Rein and Sandars have performed the first ab initio molecular orbital calculation of the parity violating energy shift of an enantiomer, the (R) isomer of the chiral ethylene-2⁵¹ for which they found $\eta = 3.10^{-4}$.

Following the work of Hegstrom, Rein and Sandars, this ab initio approach based on MO/LCAO was applied to a number of molecules, especially by Mason, Tranter, MacDermott and co-workers^{42,43,44,55-66}, using the GAUSSIAN program to construct Slater type orbitals from a number of Gaussian functions. They studied H_2O_2 , L-alanine for which $\Delta E_{el}^{PV} \sim 10^{-20} a.u.$ ⁵⁵; for H_2O_2 ⁵⁵,

L-alanine^{55,56} and L-peptides⁵⁶ they performed studies vs dihedral angle. For H₂S₂⁵⁷ the ratio of the effect to that in H₂O₂ is ~ 500 which is larger than the Z^5 ratio equal to 32; studies of the L- α -amino acids, specifically the L-alanine and the glycine yield $\Delta E_{el}^{PV} \sim -10^{-20} a.u.$ ⁵⁷ which means that the L-series are preferentially stabilized by the electroweak interaction; this was confirmed on the series: glycine, alanine, valine, serine, aspartic acid $\Delta E_{el}^{PV} \sim -0.84$ to $-2.29 \cdot 10^{-20} a.u.$ ⁴⁴. Similar results on the D-Sugar series gave some credit to the speculations about biochemistry.

The most recent calculations confirm a large enhancement (3 orders of magnitude) when carbon is replaced by sulfur⁶⁵. As another example, L.Ivanov and V. Letokhov⁶⁷ have considered hypothetical four-atom molecules such as NFCI₂Br, BiFCI₂Br, and NFCI₂At, for which the calculated ΔE_{el}^{PV} are respectively 10^{-16} , $8 \cdot 10^{-16}$ and 10^{-13} eV, illustrating both the atomic number dependence and the role of the location of the high-Z atom. These authors also point out the importance of relativistic effects for the electron wave function in the nuclei vicinity, which could be a major source of error in the previous approach.

2.4 Letokhov's conjecture²⁴

The difference between electronic energies of enantiomers is very difficult to detect directly since it comes on top of the rest mass energy of the molecule. The only consequence that we might expect is a slight difference in Boltzmann factors for the populations or in reaction rates leading to a preference in the chemical formation of one of the two species (one should emphasize that a number of kinetic dissymmetry amplification mechanisms have been suggested, such as the Kondepudi catastrophic bifurcation mechanism⁶⁸, or the Yamagata cumulative amplification mechanism⁶⁹). If we want to probe the difference by means of spectroscopy, it is necessary to estimate a possible difference in the spectra, that is a difference between the parity-violating energy differences in the two levels involved in the transition. As is well-known, in molecular spectroscopy, we may have electronic, vibrational or rotational degrees of freedom. There is a general relationship between the energies associated with these three degrees of freedom⁷⁰ :

$$\begin{aligned} E_{vib} &\approx \left(\frac{m_e}{M}\right)^{1/2} E_{el} \implies \Delta E_{vib} \approx \left(\frac{m_e}{M}\right)^{1/2} \Delta E_{el} \\ E_{rot} &\approx \left(\frac{m_e}{M}\right) E_{el} \implies \Delta E_{rot} \approx \left(\frac{m_e}{M}\right) \Delta E_{el} \end{aligned} \quad (40)$$

where M is of the order of an atomic mass. So that a relative change in vibrational or rotational frequencies between right and left-handed molecules is expected to scale with the relative change in electronic energy:

$$\frac{\Delta E_{el}}{E_{el}} \approx \frac{\Delta E_{vib}}{E_{vib}} \approx \frac{\Delta E_{rot}}{E_{rot}} \quad (41)$$

This argument is based on a global and rather indirect relationship and needs to be refined to be fully credible, because it is not the overall electronic energy which is directly related to the vibrational frequency, but rather its second-derivative with respect to the internuclear distances. In fact, $\Delta E_{el}^{PV}(\vec{r}_\alpha)$ acts as a PV-potential between the nuclei. It depends explicitly on the nuclear coordinates corresponding to the vibration modes of the molecule. A detailed calculation of the expansion of ΔE_{el}^{PV} in normal coordinates will be presented in a forthcoming paper. If x_i are the deviations about the parity-conserving equilibrium:

$$\Delta E_{el}^{PV}(x) = \alpha + \sum_i \beta_i x_i + \frac{1}{2} \sum_{ij} \gamma_{ij} x_i x_j \quad (42)$$

The coefficients β will be responsible for a slight difference in equilibrium geometries between the enantiomers and it has been argued that, the electromagnetic interactions being then different, this might cancel the parity-violating energy difference between the two forms. This effect has been estimated by G.E. Tranter to be of the order of 10^{-60} and hence negligible⁵⁹.

The coefficients γ in the expansion give the difference in force constants C and hence a difference $\approx \pm \nu \gamma / 2C$ of vibration frequency between the enantiomers. With a typical force constant of the order of $1 \text{ a.u.}(\text{angstrom})^{-2}$ and an order of magnitude⁴³ for the value of the parity-violating force constant in organic compounds (without heavier atom than carbon) equal to $10^{-20} \text{ a.u.}(\text{angstrom})^{-2}$, one obtains $\Delta \nu / \nu \sim 10^{-20}$. We see that the $Z_\alpha^3 Z_\beta^2$ dependence and the associated relativistic factors will be essential to bring this value to a reasonable level.

3 Experimental test using nonlinear spectroscopy

3.1 Historical background

Although the theoretical work on parity violation in chiral molecules has been quite intense and regular over the past twenty years, the experimental efforts have been more modest, mainly because such a project appeared to be a very difficult challenge involving both physics and chemistry. The first challenge

concerned our ability to compare the energies of two molecules with a very high accuracy. As stated previously, only energy differences can be measured with sufficiently high accuracy, thanks to the developments of new methods in modern nonlinear spectroscopy. These methods use combinations of several light waves either copropagating or counterpropagating, to get rid of the Doppler broadening and obtain extremely narrow resonances. With one of these techniques, called saturation spectroscopy⁷¹⁻⁷⁸, it is now possible to reach resolving powers in the 10^{11} range and linewidths less than 100 Hz in almost any part of the spectrum from microwaves to near U.V.. Furthermore, these very narrow resonances may be used as error signals to lock a laser frequency to their line center with unprecedented stabilities, reproducibilities and accuracies. The sensitivity of an experiment performed with the racemic mixture is limited by the resolution of the spectrometer. If it is possible to resolve the two enantiomers, it is possible to perform a beat experiment or to record simultaneously the spectra of the two species as we have preferred to do in the present work. The sensitivity in that case, will be limited by the precision with which the line center is determined, which is usually more precise than the limitation imposed by the resolution by several orders of magnitude.

The next challenge was to find a relevant molecule for such a test. In 1976, Letokhov and coll.⁷⁹ suggested that CHFClBr , as a chiral molecule, would be a good candidate for an observation of parity violation. They obtained a few saturation resonances of the racemic mixture of CHFClBr with a typical resolution of the order of 1 MHz but no obvious splitting could be observed. During the years 1977-1978, these experiments were repeated in our laboratory with a higher resolution (typically 50 to 100 kHz corresponding to free-running lasers) both on CHFClBr and CHFClI with the same conclusion. Experiments with resolved enantiomers of CHFClCOOH failed to exhibit any saturation resonance with the spectrometer used at that time and this effort was stopped until recently when resolved enantiomers of CHFClBr became available. We should also mention the paper of Arimondo et al.⁸⁰ where a beat experiment is reported with the enantiomers of camphor with a sensitivity of 10^{-8} , far from the requirements estimated by theory, and obvious interpretation problems given the complexity of this molecule.

Today CHFClBr is certainly one of the best molecules for such a project for different reasons : in the ground vibronic state the inversion is negligible and hence the enantiomers are stable; it contains a bromine atom with a high Z value ($Z_{Br} = 35$), located at the molecule periphery; the number of atoms is limited, which results in a moderate partition function and hence reasonable populations in each state; the vapor pressure is high at room temperature. Likely the enantiomers of CHFClI can also be resolved in the near future and

it would be an even better candidate because $Z_I=53$ but the experimental and theoretical spectroscopic data on CHFCIBr are, up to now, much more extensive. In particular, the strong ν_4 CF stretching fundamental has been fully analyzed^{81,82,83}. The knowledge of this vibration band, which matches the R branch of the 9.4 μm CO₂ laser band, is a necessary starting point for any ultra-high resolution experiment at that wavelength. Finally a number of studies of the vibrational circular dichroism have been performed^{85,86}.

Any experimental project was withheld over twenty years because the final difficulty of the resolution of CHFCIBr enantiomers was solved successfully only recently⁸⁷. The link between the conformation and the optical activity of the two isomers of CHFCIBr was established even more recently by the group of A. Collet^{88,89,90} S-(+) and R(-). This group provided us with one sample of R-CHFCIBr with an enantiomeric excess (ee) of 22 ± 2 % and one sample of S-CHFCIBr with an ee of $56,5\pm 0,5$ %. This has enabled us to try to perform a test of parity violation in molecules with a sensitivity, which is, for the first time, compatible with the expected effect.

3.2 Experimental set-up

The principle of the experiment is the following : we use a single CO₂ laser whose frequency is stabilized on a saturation peak detected in the transmission signal of a 1.5 m long Fabry-Perot resonator. The frequency stabilization scheme is described in more detail elsewhere⁹¹. It can provide a spectral purity of 6 Hz and a long-term stability of 0.1 Hz over 100 s. These performances have been achieved in the 10 μm spectral region with a strong OsO₄ saturation resonance. In the present experiment, we have operated on the R(14) CO₂ laser line of the 9.4 μm band. We have used a sample of racemic CHFCIBr and we have chosen one strong hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ rovibrational line as the reference line to stabilize the laser frequency. At that wavelength, the finesse of the cavity was degraded by a factor 2 (finesse of only 100) and the line was about 10 times broader than for OsO₄. As a consequence, we have estimated the spectral width of the laser to be about 100 Hz, which is not presently a limitation of the experiment. For the same reason, the long-term stability is also degraded but, as we shall see, a drift of the laser frequency has no impact on the sensitivity of the test, as far as the drift is much less than the width of the molecular lines involved in the left-right comparison.

In a first scheme, the laser frequency feeds an electro-optic modulator (EOM) which generates sidebands between 8 and 18 GHz on each side of the laser carrier, which is frequency-stabilized. The power in each sideband is about 10^{-4} of the power in the carrier but the crossed polarizations of the

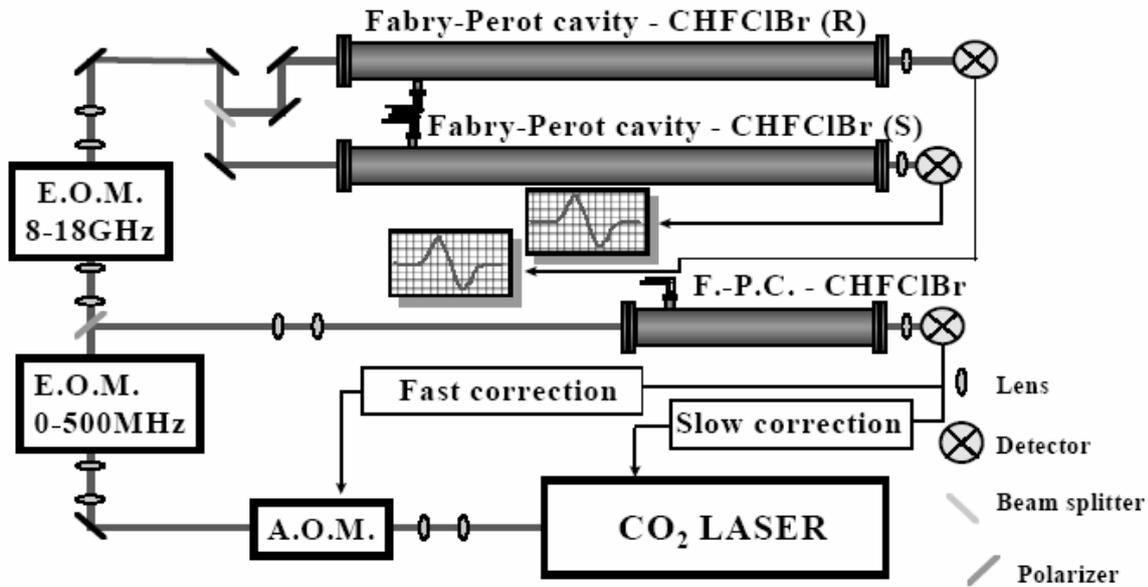


Figure 3: Schematic diagram of the experimental set-up

carrier and of the sidebands result in a quite effective rejection of the carrier. One of these sidebands feeds two twin 3 meter long Fabry-Perot resonators (cavities), whose resonance frequencies are slaved to this sideband frequency. Each of these cavities is filled by one of the enantiomers of CHFCIBr. By tuning the EOM, we tune the sideband frequency and we can record simultaneously the spectra of the two enantiomers. Through a fit of both spectra, we obtain two line centers measured relative to the frequency of the stabilized laser carrier. Thus, any drift of this carrier frequency cancels in the difference between the two line centers. This represents an elementary measurement of the parity violation effect.

After several attempts to optimize this scheme on the $(27,9,18) \leftarrow (27,10,17)$ line located at -14,4 GHz from the R(14) laser line, we have faced several difficulties : the finesse of the cavities has dropped from 200 down to 100 for the 1.5 m long resonator and from 170 to 50 for the 3 m long resonators as the spectrometer was tuned from the $10,6 \mu\text{m}$ to the $9,4 \mu\text{m}$ spectral region. We were able to resolve partially very rich hyperfine structures but the ultimate resolution was still limited by an unresolved hyperfine structure. Thus, the optimum signal was obtained at a relatively high pressure, for which the collisional broadening was dominant. In these conditions, the power available in the sideband was not sufficient to saturate efficiently the molecular transitions. Thus, we decided to adapt this scheme in the following manner: we kept the stabilization system in which the laser carrier operates at a frequency shifted

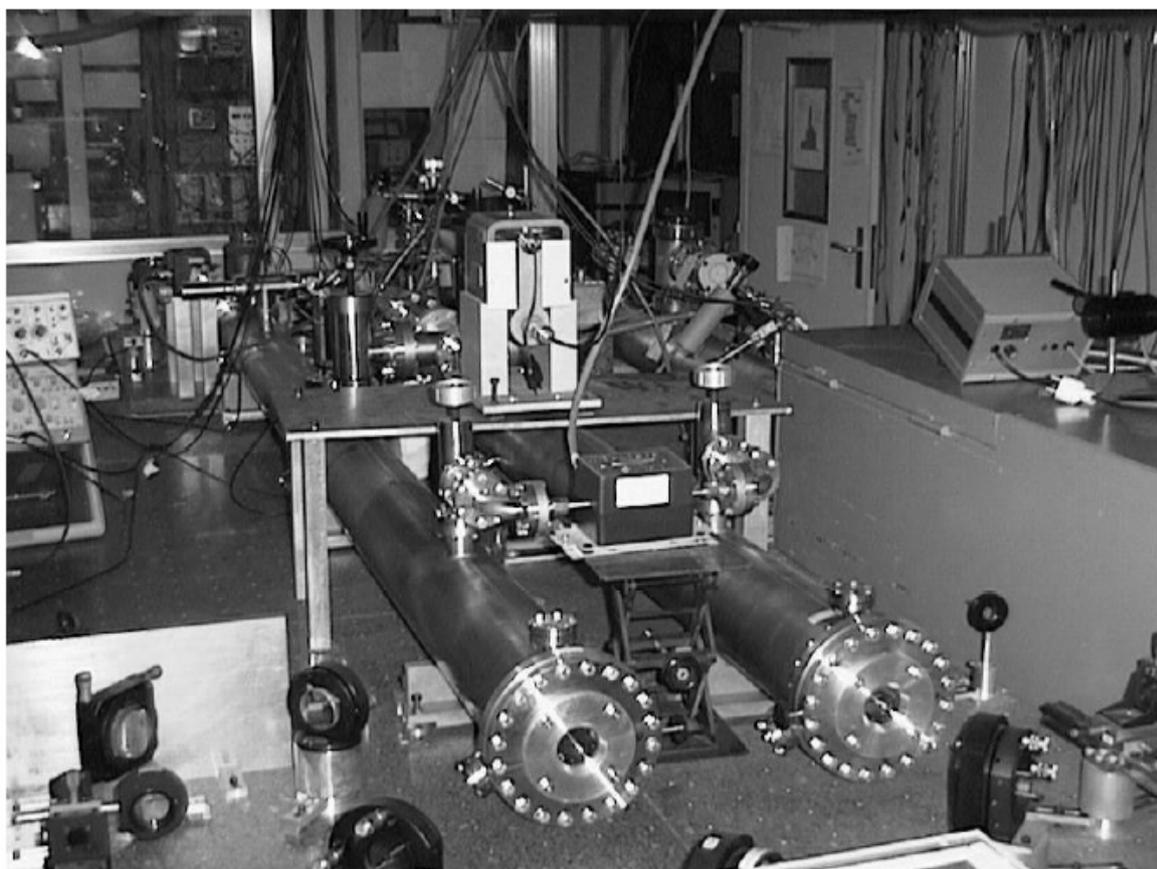


Figure 4: View of the experiment showing the two Fabry-Perot resonators

from the molecular resonance by the radiofrequency of the 0-500 MHz EOM. Then, the carrier, shifted by an acousto-optic modulator for an optical isolation purpose, fed directly the twin cavities without using the 8-18 GHz EOM, and the recording of the spectra of the two enantiomers was achieved by tuning the radiofrequency of the first EOM. With this scheme, we had enough power to saturate the transitions but we lost the broadband tunability provided by the 8-18 GHz EOM and we were limited by the coincidences between the CO_2 laser lines and the spectrum of CHFCIBr . The frequency modulations required to stabilize the resonators and to detect the molecular signals in transmission of these three cavities could not be applied to the EOMs. Thus, we applied two modulations directly inside the laser resonator via a piezoelectric transducer, one at 45 kHz was used to stabilize the optical length of the three cavities and the second one at 12 kHz was used with a third-harmonic detection to stabilize the sideband on a molecular signal and to detect the molecular resonances of the two enantiomers. The modulation parameters were optimized for the

signals in the twin cavities. This induced a slight degradation of the stability of the laser with no measurable effect on the sensitivity of the present experiment. Finally we performed the most sensitive experiments through a study of one hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ rovibrational line, while a different hyperfine component was used for the frequency stabilization. By recording the same hyperfine component in a very large cell (18 m long with an 8 cm laser beam diameter) with a resolution of 5 kHz, one can see on figure 5 that the selected line appears to be a symmetric triplet. This explains why we could not obtain a resolution better than 90 kHz in the Fabry-Perot cavity.

The difficulty of this experiment is to reduce the systematic effects in these measurements as much as possible. With this respect, the fact that the spectral properties of the laser light, which feeds the two resonators is identical is certainly very helpful. Actually, any difference in the experimental environment of the two compared enantiomers is generated from the beamsplitter which divides the laser beam in two parts directed towards the two cavities. We can try to list the parameters which could be different for the two samples:

- light polarization: we wanted to have a linear polarization in order to avoid any chirality external to the molecules. A slight discrepancy from the linear polarization of the sideband can induce some ellipticity after the beamsplitter. We estimate to control the linearity within one degree. Furthermore, the residual light chirality is strongly attenuated (by the finesse) inside the Fabry-Perot resonator since a $\sigma+$ polarization relative to the propagation axis is converted into $\sigma-$ after each reflection.

- the mode matching into the two resonators depends on the alignment of the two cavities and the adjustment of the path lengths between the beam splitter and the cavities.

- the finesse of the two cavities which depends on the reflectivity and on the losses of the mirrors.

- the laser power inside the resonators.

- the mode profile of the beam inside each resonator, which depends on the radii of curvature of the mirrors and affects the interaction time of the molecules with the light.

- the pressure in the Fabry-Perot cavities.

- the residual stray fields : the magnetic shielding in the cavities reduces the earth magnetic field by three orders of magnitude.

- the constitution of the samples : impurities can induce various collisional shifts. In particular, in each sample, two kinds of collisions can occur : "homocollisions" R-R and S-S and "heterocollisions" R-S which might give a different collisional shift. Since the enantiomeric excesses are different, we can

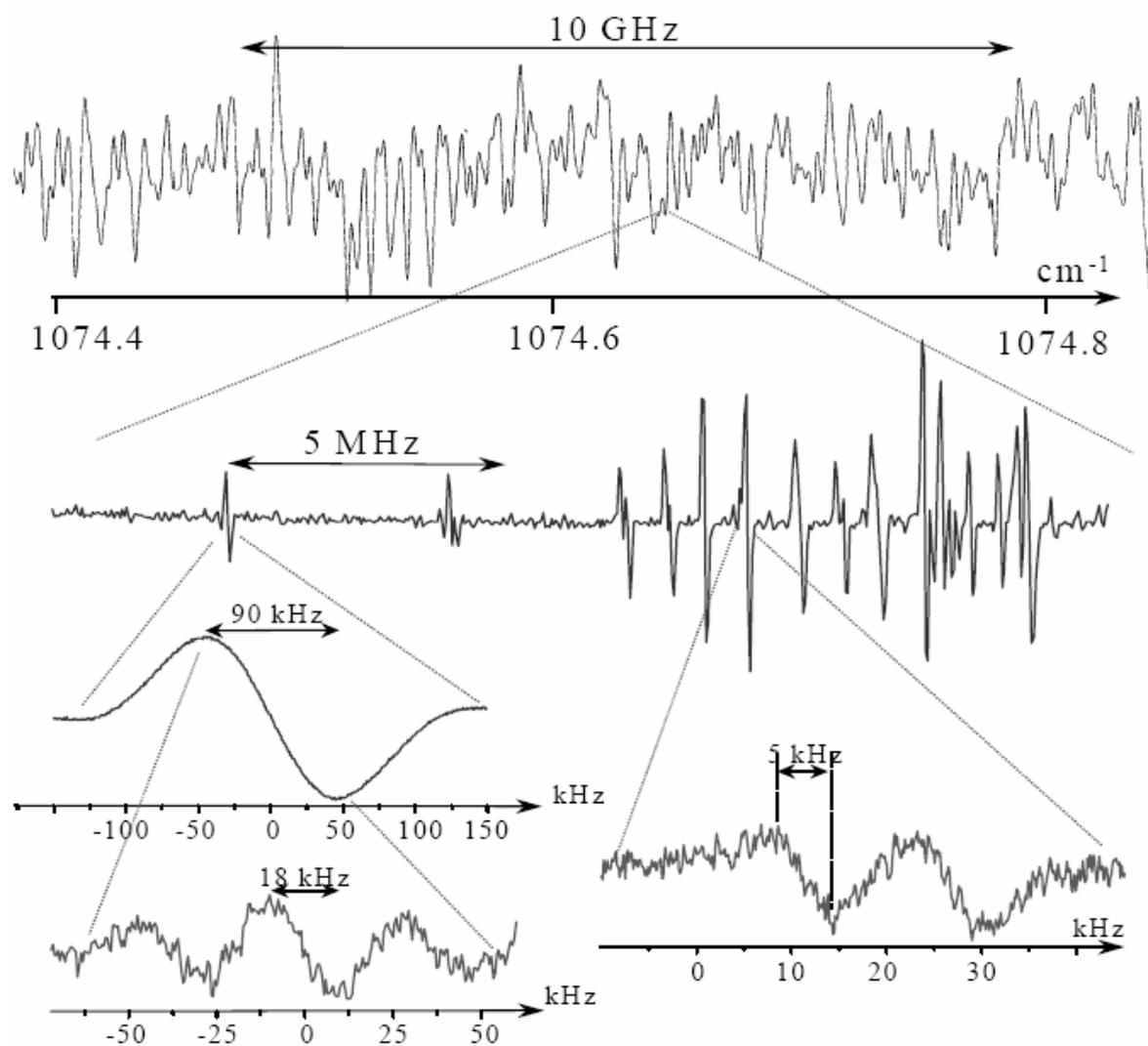


Figure 5: Spectra of CHFCIBr around 1074.6 cm^{-1} for increasing resolving powers. From top to bottom: Fourier transform spectrum, saturation spectrum with a free-running CO_2 laser exhibiting the full hyperfine structure of the line, frequency-controlled saturation spectrum of a single resonance in the twin Fabry-Perot resonators revealing its structure with the large cell.

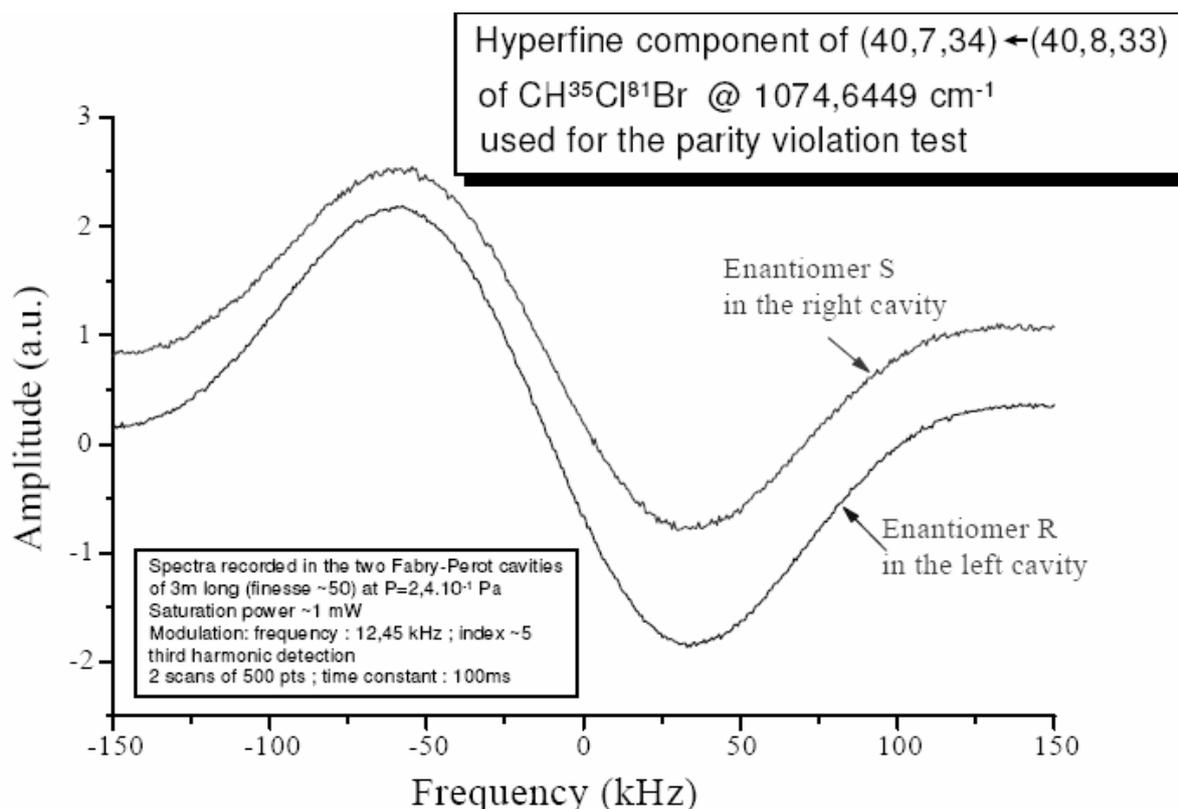


Figure 6: Saturation resonances recorded simultaneously for enantiomeric species in their respective Fabry-Perot resonator.

obtain an irreducible frequency difference whose signature would be a pressure dependence.

- the sensitivity of the photodetectors after the cavities.
- the alignment on the detectors.

Most of the differences between the two systems (in addition to the enantiomeric molecules themselves) are compensated by the exchange of the role of the two cavities performed by filling the cavities with the other enantiomer. However, this is not the case for the polarization effects and the stray fields. By changing the polarization of the laser light, it was not possible to see any influence on the line center determinations. Although we have no data about the influence of a magnetic field on the spectrum of CHFCIBr , recent measurements on OsO_4 revealed a typical dependence of about 1 Hz/G . This would be negligible at the present level of sensitivity, if the value was similar for CHFCIBr , which has still to be investigated.

The results that we present now, correspond to 10 sets of measurements performed over 10 days. For one set per day, the first half-day, each twin

cavity is filled with one kind of enantiomer and the second part of the day, the enantiomers are exchanged in the cavities. When we perform an elementary measurement as described above, we usually obtain a systematic shift of the order of 100 Hz which is reproducible. When the role of the cavities are exchanged, we observe that the sign of the difference is changed (see Figure 7(top)). This systematic effect can be associated with the difference between the two systems and, by assuming that this shift is constant over one day, we can calculate its average value and subtract it from the individual measurements. This is illustrated on Figure 7(bottom) which shows a white distribution of data close to zero.

The systematic shift, that we eliminate by the preceding procedure, has an unknown physical origin. Several mechanisms can be responsible for these shifts:

- two different saturation parameters in the twin cavities can induce different light shifts and differential saturations of the unresolved hyperfine components⁷², especially if the studied line includes crossover resonances.

- a gas lens effect in the resonators^{77,78}, an effect for which there is no good strong field theory and which is sensitive to the diaphragms at the input and output of the cavities.

This shift cannot be very easily studied experimentally, because it is of the same order of magnitude as the precision of the individual measurements. However, it is quite stable over one day as revealed by the compensation procedure. It depends certainly on the alignment conditions since the shift is not reproducible from one day to another.

Once this compensation was achieved, we could build the histogram from the 580 individual corrected measurements, which is well fitted by a Gaussian. We obtain a mean value for the frequency difference of 3,7 Hz and a standard deviation of 47,2 Hz which is very close to the typical uncertainty given by the fit of the spectra.

The global precision of this set of measurements is given by the standard deviation of this histogram divided by the square root of the number of measurements, i.e. 2 Hz. This is true if we consider only the statistical errors. However, systematic effects are present in this experiment. Although the compensation seemed to be effective, we cannot claim that it is perfect. Some residual and uncontrolled effects are persistent and must be taken into account in the uncertainty of the final result.

We estimate that these residual systematic effects are of the order of 5 Hz. Thus, the frequency difference for the resonances associated to the two samples is:

$$\Delta\nu = 3,7 \pm 2 \pm 5 \text{ Hz}$$

Systematic effects associated with the Fabry-Perot resonators

(Spectra recorded from 11 Feb 98 to 13 Mar 98)

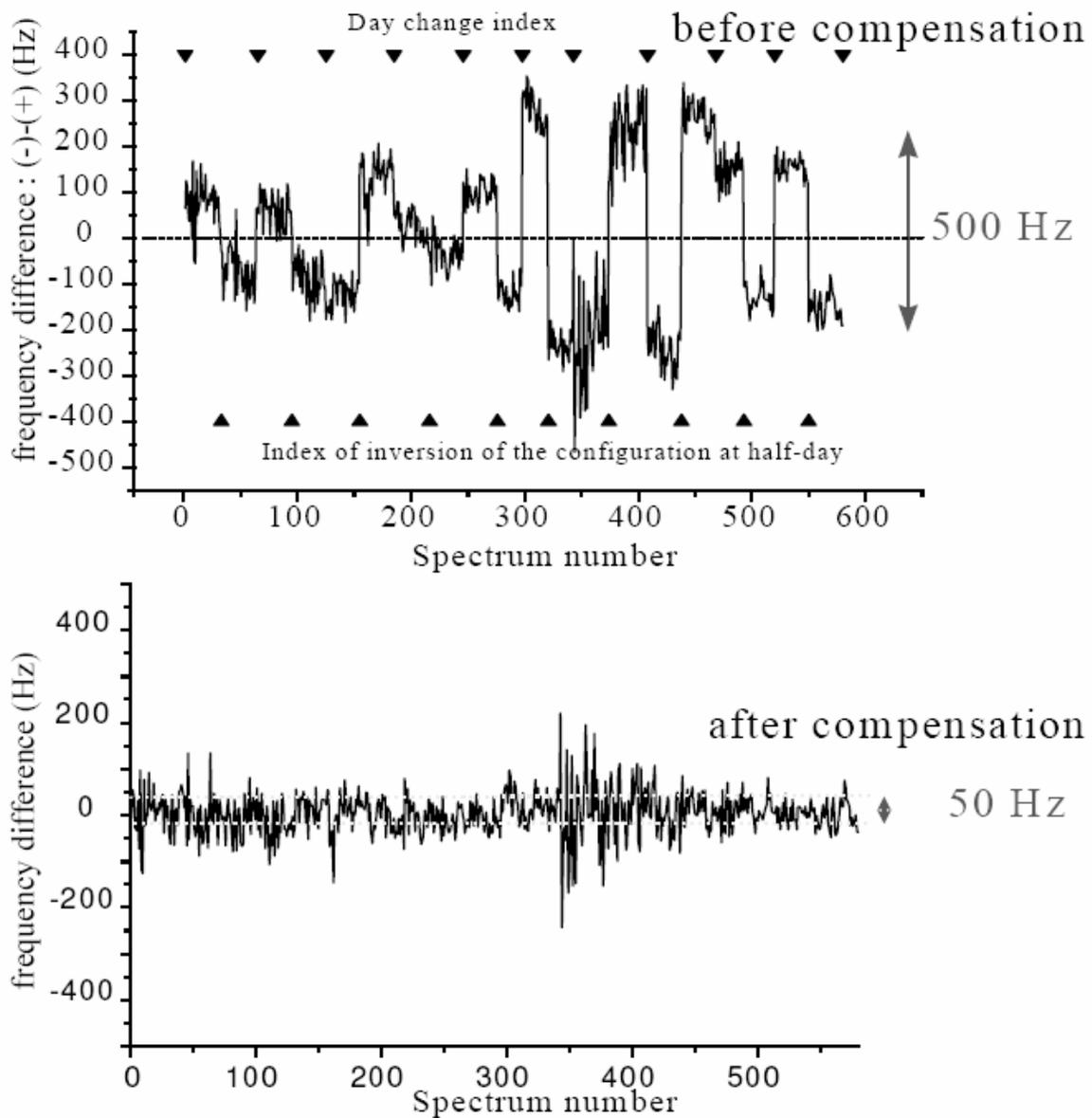


Figure 7: Compensation of the systematic errors by an exchange of the roles of the two resonators

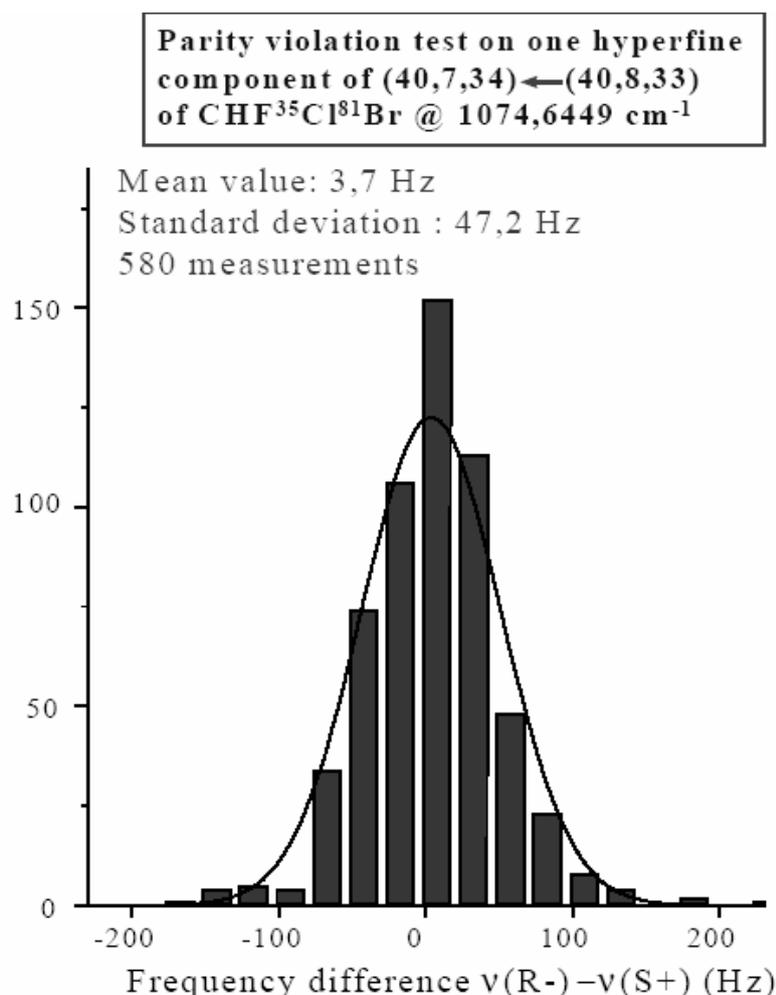


Figure 8: Histogram of the measured frequency differences for 580 measurements

In order to give the actual frequency difference for the two enantiomers, we have to take into account the enantiomeric excesses of the samples. We finally obtain the first test of parity violation on the CHFClBr molecule:

$$\nu(R-) - \nu(S+) = 9,4 \pm 5,1 \pm 12,7 \text{ Hz}$$

This result is negative. It gives an upper limit of $\Delta\nu/\nu \simeq 3,9 \cdot 10^{-13}$ for the effect.

4 Conclusion and directions of future work

The sensitivity achieved in this experiment is about five orders of magnitude higher than the previous similar test on camphor and than the upper bound inferred from the spectra of racemic CHFClBr and CHFClI. This experiment

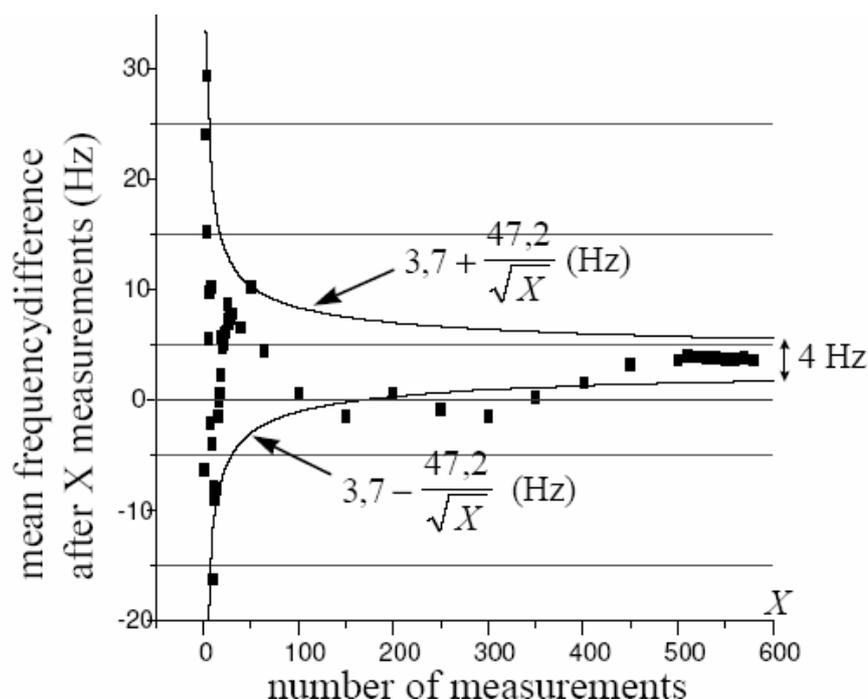


Figure 9: Convergence of the average value of the measured frequency differences $\nu(\text{R-}) - \nu(\text{S+})$ after X measurements.

is still to be considered as a preliminary test and there is clearly a lot of possibilities to improve its sensitivity. On a short term time scale, we can certainly make a better choice of line (we suspect that the resonance, which was used for these first experiments, was in fact a crossover resonance, more sensitive to light shifts than the main lines). An optimized choice will eventually require the detailed analysis of the hyperfine structure in the spectrum of CHFCIBr . We can already use higher finesse Fabry-Perot resonators, a higher enantiomeric excess (up to 80% is available now from A. Collet and J. Costante), a better control of the sample purity, of the total pressure and more generally a better understanding of systematics of our present experiment. Later we can reduce these systematic errors with a higher resolution using beams of larger diameter or possibly slow molecules⁷⁶. New experiments are already in progress with our high resolution spectrometer using a large cell. Unfortunately this cell is presently unique and experiments with enantiomers would have to be done in a sequential mode (the required frequency stability of the laser would then be provided by a Fabry-Perot device such as those described in this paper).

We may reasonably hope to improve our sensitivity by at least two orders of magnitude in the next few years. On a longer term time scale, future

experiments may use saturation spectroscopy in molecular beams to avoid any collisional shift combined with molecular interferometry⁵⁰, molecules with heavier atoms like CHFClI and more sensitive transitions: CBr or CI vibrations. Finally, it is already clear now that the theory is insufficiently developed to get a reliable estimate of the expected effect in various molecules and has to be improved substantially.

5 Acknowledgments

The authors are very grateful to A. Collet and J. Costante (Laboratoire de Stéréochimie et Interactions Moléculaires, Lyon) for the preparation of optically active CHFClBr, to H. Serne (Villetaneuse) for the preparation of racemic CHFClBr and CHFClI, to C. Wakselman and H. Molines (Thiais) for the preparation of optically active CHFClCOOH and finally to A. Valentin (Paris) for recording Fourier Transform spectra of CHFClBr (see Fig.5). We want also to thank for their efforts several other groups of chemists, who tried to resolve the enantiomers of CHFClBr for us: M. Miginiac (Poitiers) , V.I. Sokolov (Moscow), R. Pagni, D. Boyles and R. Compton (University of Tennessee). This last group succeeded a few months after the Lyon group. This work was supported in part by the Direction des Recherches Etudes et Techniques, by the Direction des Systèmes de Forces et de la Prospective and by the Bureau National de Métrologie.

6 References

1. T.D. Lee and C.N. Yang, *Question of parity conservation in weak interactions*, Phys. Rev. **104**, 254-258 (1956).
2. C.S. Wu, E. Ambler, R.W. Hayward, D.D. Hoppes and R.P. Hudson, *Experimental test of parity conservation in beta decay*, Phys. Rev. **105**, 1413-1415 (1957).
3. S. Weinberg, *A model of leptons*, Phys. Rev. Letters **19**, 1264-1266 (1967).
4. A. Salam, *Elementary Particle Theory*, Proceedings of the Eighth Nobel Symposium 367 (1968).
5. S. Weinberg, *Effects of a Neutral Intermediate Boson in Semileptonic processes*, Phys. Rev. D**5**, 1412-1417 (1972).
6. L.N. Labzowskii, *Λ -doubling and parity-nonconservation effects in spectra of diatomic molecules*, Sov. Phys. JETP **48**(5), 434-439 (1978).
7. V.V. Flambaum and I.B. Khriplovich, *P-odd nuclear forces-a source of parity violation in atoms*, Sov. Phys. JETP **52**(5), 835-839 (1980).

8. O.P. Sushkov, V.V. Flambaum and I.B. Khriplovich, *Possibility of investigating P- and T-odd nuclear forces in atomic and molecular experiments*, Sov. Phys. JETP **60**(5), 873 (1984).
9. M.G. Kozlov and L.N. Labzovskii, *Parity violation effects in diatomics*, J. Phys. B **28**, 1933-1961 (1995).
10. M.A. Bouchiat and C.C. Bouchiat, *Weak neutral currents in atomic physics*, Phys. Lett. **48B**, 111-114 (1974).
11. M.A. Bouchiat and C.C. Bouchiat, *Parity violation induced by weak neutral currents in atomic physics*, J. de Physique, **35**, 899-509 (1974); **36**, 493-509 (1975).
12. M.A. Bouchiat, in *New trends in atomic physics*, eds G. Grynberg and R. Stora, 887-950 (North Holland, Amsterdam, 1984).
13. M.A. Bouchiat, C.C. Bouchiat, *Parity violation in atoms*, Acad. Sci. Paris **322**, Série II b, 381-399 (1996).
14. M.A. Bouchiat, C.C. Bouchiat, *Parity violation in atoms*, Rep. Prog. Phys. **60**, 1351-1396 (1997).
15. S.L. Gilbert, M.C. Noecker, R.N. Watts, C.E. Wieman, *Measurements of parity nonconservation in atomic cesium*, Phys. Rev. Lett. **55**, 2680 (1985).
16. C.E. Wieman, S.L. Gilbert, M.C. Noecker, *A new measurement of parity nonconservation in atomic cesium*, Atomic physics **10**, 65 (1987).
17. M.C. Noecker, B.P. Masterson, C.E. Wieman, *Precision measurement of parity nonconservation in atomic cesium: a low-energy test of the electroweak theory*, Phys. Rev. Lett. **61**, 310 (1988).
18. C.S. Wood, S.C. Bennett, D. Cho, B.P. Masterson, J.L. Roberts, C.E. Tanner, C.E. Wieman, *Measurement of parity nonconservation and an anapole moment in cesium*, Science **275**, 1759-1763 (1997).
19. I.B. Khriplovich, *Parity nonconservation in atomic phenomena*, Gordon and Breach, 1991.
20. D.W. Rein, *Some remarks on parity violating effects of intramolecular interactions*, J. Mol. Evol. **4**, 15-22 (1974).
21. D.W. Rein, *Estimate of energy differences between optical isomers caused by parity non-conserving interactions*, Atomki Közlemények Suppl. **16/2** 185-194 (1974).
22. G. Marx, *Weak interactions outside the laboratory*, Acta Physica Austriaca, Suppl. XIII, 569-594 (Springer-Verlag, 1974).
23. E. Gajzago and G. Marx, *Energy difference of mirror molecules*, Atomki Közlemények Suppl. **16/2** 177-184 (1974).
24. V.S. Letokhov, *On difference of energy levels of left and right molecules due to weak interactions*, Phys. Lett. **53A**, 275-276 (1975).

25. B.Ya. Zel'dovich, D.B. Saakyan and I.I. Sobel'man, *Energy differences between right-hand and left-hand molecules, due to parity nonconservation in weak interactions of electrons with nuclei*, JETP Lett. **25**, 94-97 (1977).
26. R.A. Harris and L. Stodolsky, *Quantum beats in optical activity and weak interactions*, Phys. Lett. **78B**, 313-317 (1978).
27. D.W. Rein, R.A. Hegstrom and P.G.H. Sandars, *Parity non-conserving energy difference between mirror image molecules*, Physics Letters **71A**, 499-502 (1979).
28. R.A. Harris, L. Stodolsky, *The effect of the parity violating electron-nucleus interaction on the spin-spin coupling Hamiltonian of chiral molecules*, J. Chem. Phys. **73**, 3862-3863 (1980).
29. I.B. Khriplovich, *On the energy difference between optical isomers resulting from parity nonconservation*, Sov. Phys. JETP **52**, 177-180 (1980).
30. V.G. Gorshkov, M.G. Kozlov and L.N. Labzovskii, *P-odd effects in polyatomic molecules*, Sov. Phys. JETP **55**(6), 1042-1048 (1982).
31. A.L. Barra, J.B. Robert and L. Wiesenfeld, *Parity non-conservation and NMR observables. Calculation of Tl resonance frequency differences in enantiomers*, Phys. Lett. **A115**, 443-446 (1986).
32. L. Wiesenfeld, *Effect of atomic number on parity-violating energy differences between enantiomers*, Mol. Phys. **64**, 739-745 (1988).
33. A.L. Barra, J.B. Robert and L. Wiesenfeld, *Possible observation of parity nonconservation by high-resolution NMR*, Europhys. Lett. **5**(3), 217-222 (1988).
34. A.L. Barra and J.B. Robert, *Parity non-conservation and NMR parameters*, Mol. Phys. **88**, 875-886 (1996).
35. Ch. Chardonnet, A. Amy-Klein, V. Bernard, R.J. Butcher, P.E. Durand, T. George, F. Guernet, H.W. Nicolaisen, O. Pfister and Ch.J. Bordé, *Ultra-high resolution spectroscopy at 10 μm : Applications and new Trends*, in *Laser Spectroscopy*, eds M. Inguscio, M. Allegrini and A. Sasso, World Scientific 208-211(1996).
36. Ch. Daussy, T. Marrel, O. Phavorin, A. Amy-Klein, C.T. Nguyen, Ch. J. Bordé and Ch. Chardonnet, *Stabilisation en fréquence d'un laser à CO_2 au niveau de $3 \cdot 10^{-15}$ et recherche d'un effet de violation de la parité dans les molécules chirales*, Ann. Phys. Fr. **23**, C1-225-226 (1998).
37. L. Pasteur, *Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de polarisation rotatoire*, C.R. hebd. Séanc. Acad. Sci. Paris **26**, 535-538 (1848).
38. V.S. Letokhov, *Possible connection between weak interactions and the biological isomerism*, Lett. al Nuovo Cimento **20**, 107-111 (1977).

39. V.A. Kizel, *Optical activity and dissymmetry in living systems*, Sov. Phys. Usp. **23**, 277-295 (1980).
40. S.F. Mason, *Origins of biomolecular handedness*, Nature **311**, 19-23 (1984).
41. D.K. Kondepudi and G.W. Nelson, *Weak neutral currents and the origin of biomolecular chirality*, Nature **314**, 438-441 (1985).
42. S.F. Mason and G.E. Tranter, *The electroweak origin of biomolecular handedness*, Proc. R. Soc. Lond. A**397**, 45-65 (1985).
43. G.E. Tranter, *The parity-violating energy difference between enantiomeric reactions*, Chem. Phys. Lett. **115**, 286-290 (1985).
44. G.E. Tranter, *The parity violating energy differences between the enantiomers of α -amino acids*, Mol. Phys. **56**, 825-838 (1985).
45. G.E. Tranter, A.J. MacDermott, R.E. Overill and P.J. Speers, *Computational studies of the electroweak origin of biomolecular handedness in natural sugars*, Proc. R. Soc. Lond. A **436**, 603-615 (1992).
46. R. Hegstrom and D. Kondepudi, *L'Univers asymétrique*, Pour la Science **149**, 100-107 (1990).
47. V.A. Avetisov, V.I. Goldanskii and V.V. Kuz'min, *Handedness, origin of life and evolution*, Physics Today, 33-41 (July 1991).
48. R.J. Butcher, Ch. Chardonnet and Ch.J. Bordé, *Hyperfine lifting of parity degeneracy and the question of inversion in a rigid molecule*, Physical Review Letters **70**, 2698-2701 (1993)
49. O. Pfister, Ch. Chardonnet and Ch.J. Bordé, *Hyperfine-induced lifting of parity degeneracy in semi-rigid tetrahedral molecules*, Physical Review Letters **76**, 4516-4519 (27 May 1996)
50. Ch.J. Bordé, *Matter-wave interferometers: a synthetic approach*, in *Atom Interferometry*, ed. P. Berman, 257-292 (Academic Press, 1997).
51. R.A. Hegstrom, D.W. Rein and P.G.H. Sandars, *Calculation of the parity nonconserving energy difference between mirror-image molecules*, J. Chem. Phys. **73**(5), 2329-2341 (1980).
52. Zel'dovich Ya. B. Zh. Eksp. Teor. Fiz. **33**, 1531 (1957).
53. V.V. Flambaum, D.W. Murray, *The anapole moment and nucleon weak interactions*, Phys. Rev. C**56**, 1641 (1997).
54. I.I. Sobel'man, *Introduction to the theory of atomic spectra* (Pergamon Press, Oxford, 1972)
55. S.F. Mason and G.E. Tranter, *The parity-violating energy difference between enantiomeric molecules*, Chem. Phys. Lett. **94**, 34-37 (1983)
56. S.F. Mason and G.E. Tranter, *Energy inequivalence of peptide enantiomers from parity non-conservation*, J. Chem. Soc., Chem. Commun. 117-119 (1983).

57. S.F. Mason and G.E. Tranter, *The parity-violating energy difference between enantiomeric molecules*, Mol. Phys. **53**, 1091-1111 (1984).
58. G.E. Tranter, *The parity violating energy differences between the enantiomers of α -amino acids*, Chem. Phys. Lett. **120**, 93-96 (1985).
59. G.E. Tranter, *The effects of parity violation on molecular structure*, Chem. Phys. Lett. **121**, 339-342 (1985).
60. G.E. Tranter, *Preferential stabilization of the D-sugar series by the parity-violating weak interactions*, J. Chem. Soc., Chem. Commun., 60-61 (1986).
61. G.E. Tranter and A.J. MacDermott, *Parity-violating energy differences between chiral conformations of tetrahydrofuran, a model system for sugars*, Chem. Phys. Lett. **130**, 120-122 (1986).
62. G.E. Tranter, *The enantio-preferential stabilization of D-ribose from parity violation*, Chem. Phys. Lett. **135**, 279-282 (1987).
63. A.J. MacDermott, G.E. Tranter and S.B. Indoe, *Exceptionally large enantio-selective energy differences from parity violation in sugar precursors*, Chem. Phys. Lett. **135**, 159-162 (1987).
64. A.J. MacDermott and G.E. Tranter, *The search for large parity-violating energy differences between enantiomers*, Chem. Phys. Lett. **163**, 1-4 (1989)
65. A.J. MacDermott, G.E. Tranter and S.J. Trainor, *The search for large parity-violating energy differences finds fruit in thiosubstituted DNA analogues*, Chem. Phys. Lett. **194**, 152-156 (1992).
66. O. Kikuchi and H. Wang, *Parity-violating energy shift of glycine, alanine, and serine in the Zwitterionic forms : calculation using HFO-NG basis sets*, Bull. Chem. Soc. Jpn. **63**, 2751-2754 (1990).
67. L.N. Ivanov and V.S. Letokhov, *Parity violating energy difference in chiral molecules. Nuclear charge dependence in the homologous sequence of nitrogen fluorine*, submitted to Chem. Phys. Lett.
68. D.K. Kondepudi and G.W. Nelson, *Chiral symmetry breaking in non-equilibrium systems*, Phys. Rev. Lett. **50**, 1023-1026 (1983); D.K. Kondepudi, Biosystems **20**, 75 (1987).
69. Y. Yamagata, J. Theoret. Biol. **11**, 495 (1966).
70. A. Messiah, *Mécanique Quantique* 670 (Dunod, Paris, 1964).
71. Ch.J. Bordé, *Spectroscopie d'absorption saturée de diverses molécules au moyen des lasers à gaz carbonique et à protoxyde d'azote*, C.R. Acad. Sc. Paris, **271B**, 371-374 (1970).
72. Ch.J. Bordé and J.L. Hall, *Ultrahigh resolution saturated absorption spectroscopy*, in *Laser Spectroscopy*, eds. A. Mooradian and R. Brewer, 125-142 (Plenum Press, New York 1973).

73. Ch.J. Bordé, M. Ouhayoun, A. Van Lerberghe, C. Salomon, S. Avrillier, C.D. Cantrell and J. Bordé, *High resolution saturation spectroscopy with CO₂ lasers. Application to the ν_3 bands of SF₆ and OsO₄*, *Laser Spectroscopy IV*, eds. H. Walther and K.W. Rothe, Springer-Verlag (1979).
74. Ch.J. Bordé, *Développements récents en spectroscopie infrarouge à ultra-haute résolution*, in *Revue du Cethedec, Ondes et Signal NS83-1*, 1-118 (1983).
75. Ch.J. Bordé, J. Bordé, Ch. Bréant, Ch. Chardonnet, A. Van Lerberghe and Ch. Salomon, *Internal dynamics of simple molecules revealed by the superfine and hyperfine structures of their infrared spectra*, in *Laser Spectroscopy VII*, eds. T.W. Hänsch and Y.R. Shen, 108-114 (Springer Verlag, 1985).
76. Ch. Chardonnet, F. Guernet, G. Charton and Ch.J. Bordé, *Ultra-high resolution saturation spectroscopy of slow molecules in an external cell*, *Applied Physics B59*, 333-343 (1994).
77. Ch.J. Bordé, *The Physics of Optical Frequency Standards Using Saturation Methods*, in: *Frequency Standards and Metrology*, ed. A. de Marchi, 196-205 (Springer-Verlag, 1989).
78. A. Clairon, O. Acef, Ch. Chardonnet and Ch.J. Bordé, *State-of-the-Art for High Accuracy Frequency Standards in the 28 THz Range Using Saturated Absorption Resonances of OsO₄ and CO₂*, in: *Frequency Standards and Metrology*, ed. A. de Marchi, 212-220 (Springer-Verlag, 1989).
79. O.N. Kompanets, A.R. Kukudzhyanov, V.S. Letokhov and L.L. Gervits, *Narrow resonances of saturated absorption of the asymmetrical molecule CHFClBr and the possibility of weak current detection in molecular physics*, *Opt. Comm.* **19**, 414-416 (1976).
80. E. Arimondo, P. Glorieux and T. Oka, *Observation of inverted infrared Lamb dips in separated optical isomers*, *Opt. Comm.* **23**, 369-372 (1977).
81. A. Beil, D. Luckhaus, R. Marquardt, M. Quack, *Intramolecular energy transfer and vibrational redistribution in chiral molecules: experiment and theory*, *Faraday Discuss.* **99**, 49-76 (1994).
82. A. Bauder, A. Beil, D. Luckhaus, F. Müller and M. Quack, *Combined high- resolution infrared and microwave study of bromochlorofluoromethane*, *J. Chem. Phys.* **106**, 7558-7570 (1997).
83. A. Beil, D. Luckhaus and M. Quack, *Fermi resonance structure and femtosecond quantum dynamics of a chiral molecule from the analysis of vibrational overtone spectra of CHFClBr*, *Ber. Bunsenges. Phys. Chem.* **100**, 1853-1875 (1996).
84. M. Diem and D.F. Burow, *Vibrational spectra and normal coordinate analysis of bromochlorofluoromethane*, *J. Chem. Phys.* **64**, 5179-5185

- (1976).
85. C. Marcott, T.R. Faulkner, A. Moscovitz and J. Overend, *Vibrational circular dichroism in HCB₂ClF and DCB₂ClF. Calculation of the rotational strengths associated with the fundamentals and the binary overtones and combinations*, J. Am. Chem. Soc. **99**:25, 8169-8175 (1977).
 86. P.L. Prasad, D.F. Burow, *Raman optical activity. Computation of circular intensity differentials for bromochlorofluoromethane*, J. Am. Chem. Soc. **101**:4, 806-812 (1979).
 87. T.R. Doyle and O. Vogl, J. Am. Chem. Soc. **111**, 8510-8511 (1989)
 88. J. Costante, N. Ehlinger, M. Perrin and A. Collet, *The absolute configuration of bromochlorofluoroacetic acid, Enantiomer 1*, 377-386 (1996)
 89. J. Costante, L. Hecht, P.L. Polavarapu, A. Collet and L.D. Barron, *Absolute configuration of bromochlorofluoromethane from experimental and ab initio theoretical vibrational Raman optical activity*, Angewandte Chemie **36**, 885 (1997).
 90. J. Costante-Crassous, T.J. Marrone, J.M. Briggs, J.A. McCammon and A. Collet, *Absolute configuration of bromochlorofluoromethane from molecular dynamics simulation of its enantioselective complexation by cryptophane-C*, J. Am. Chem. Soc. **119**, 3818 (1997).
 91. V. Bernard, C. Daussy, G. Nogues, L. Constantin, P.E. Durand, A. Amy-Klein, A. van Lerberghe and C. Chardonnet, *CO₂ laser stabilization at the 0.1 Hz level using external electrooptic modulation*, IEEE J. of Qu. Electron. **33**, 1282-1287 (1997)

Limit on the Parity Nonconserving Energy Difference between the Enantiomers of a Chiral Molecule by Laser Spectroscopy

Ch. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, Ch. J. Bordé,* and Ch. Chardonnet†

Laboratoire de Physique des Lasers, UMR 7538 CNRS, Université Paris 13, Avenue J.-B. Clément, 93430 Villetaneuse, France
(Received 14 April 1999)

We have developed a saturation spectroscopy experiment to test the prediction that enantiomers of chiral molecules have different spectra because of the parity violation associated with neutral currents in the weak interaction between electrons and nuclei. First experimental tests have been conducted on hyperfine components of vibration-rotation transitions of CHFCIBr in the 9.3 μm spectral range. The frequencies of saturation resonances of separated enantiomers have been compared and found to be identical within 13 Hz ($\Delta\nu/\nu < 4.10^{-13}$).

PACS numbers: 33.15.Bh, 11.30.Er, 33.20.Ea

Introduction and historical background.—In 1974, it was suggested that the weak neutral currents can manifest themselves in the molecules with an original and simple signature: if we consider the two mirror image enantiomers of a chiral molecule, a parity violation induced by weak interactions will appear as a difference in the electronic energies of the two species [1]. Many theoretical studies have been pursued to obtain quantitative estimates of the effect in various molecules but none of them is yet able to provide a value of the expected relative energy shift, which is estimated to be between 10^{-13} and 10^{-20} . Therefore, there is no hope, in the short term, to improve our knowledge of the weak interaction by this way. However, this remains today one of the most exciting challenges in molecular physics because it is related to the intriguing question of the origin of the symmetry breaking between right- and left-handed biomolecules [2,3]. In this context, it was of great interest to perform an experiment. After the pioneering paper of Rein [1], Letokhov [4] proposed to observe the parity violation effect in molecules as a difference in vibrational frequencies. A beat note experiment [5] was proposed between two lasers locked on a vibrational line of the enantiomers of the chiral molecule CHFCIBr although, at that time, this molecule was only available as a racemic mixture. In this paper, we present the first test of parity violation in molecules with a sensitivity which reaches the range of the theoretical predictions. It has been performed with the enantiomers of CHFCIBr. The unique test thus far reported with separated enantiomers (on camphor with a sensitivity of 10^{-8}) [6] was far from the predictions of the theory. Other proposals using NMR on chiral molecules in an external field have been made [7].

Theoretical background.—For nonchiral polyatomic molecules we have shown, experimentally and theoretically [8–10], that one of the two states, which differ only by their parity, does not exist because of the Pauli principle applied to identical nuclei. Thus, no strict parity degeneracy can occur even if inversion and parity violation are neglected. By contrast, chiral molecules may exist in

states that differ only by their handedness or by their parity, all other quantum numbers being the same. Thanks to this unique property, a simple, in principle, spectroscopic test can reveal a parity violation without ambiguity.

For chiral molecules, we can thus consider two right- and left-image states, $|\Psi^R\rangle$ and $|\Psi^L\rangle$. If the tunneling barrier of the potential energy curve is not too high, mirror symmetry is dynamically restored by the inversion mechanism. Parity commutes with the Hamiltonian and energy eigenstates are the parity eigenstates, $|\Psi^\pm\rangle = 1/\sqrt{2}(|\Psi^R\rangle \pm |\Psi^L\rangle)$.

Conversely, when enantiomeric left- and right-handed species are stable, i.e., if the potential barrier is very high, the right and left states are also energy eigenstates. Now, if parity is violated, the enantiomers cease to be images of each other in a mirror (Fig. 1). The Hamiltonian matrix will remain diagonal in the handedness-eigenstates basis but the corresponding degeneracy will be removed:

$$H_H = \begin{pmatrix} E_0 + |\Delta E^{\text{PV}}| & 0 \\ 0 & E_0 - |\Delta E^{\text{PV}}| \end{pmatrix}. \quad (1)$$

The parity-violating molecular Hamiltonian, H^{PV} , has essentially the same origin as in atomic physics, although it involves a sum over the electrons i and the nuclei K [11]. However, for molecules, in the nonrelativistic limit, the first-order energy correction vanishes [12] and it is therefore necessary to invoke the spin-orbit coupling, H^{SO} , to obtain a nonzero contribution:

$$\Delta E^{\text{PV}} = \sum_{n \neq 0} \frac{\langle 0^- | H^{\text{PV}} | n^+ \rangle \langle n^+ | H^{\text{SO}} | 0^+ \rangle}{E_0 - E_n} + \frac{\langle 0^- | H^{\text{SO}} | n^- \rangle \langle n^- | H^{\text{PV}} | 0^+ \rangle}{E_0 - E_n}. \quad (2)$$

Taking into account the Z^3 dependence of the parity-violating term in atomic physics, the $(\alpha Z)^2$ dependence of the spin-orbit term where Z represents the atomic charge, a crude estimate of the order of magnitude of ΔE^{PV} can be obtained [13]:

$$\Delta E^{\text{PV}} \sim 8.5 \times 10^{-21} \eta Z_K^3 Z_{K'}^2, \text{ hartree.} \quad (3)$$

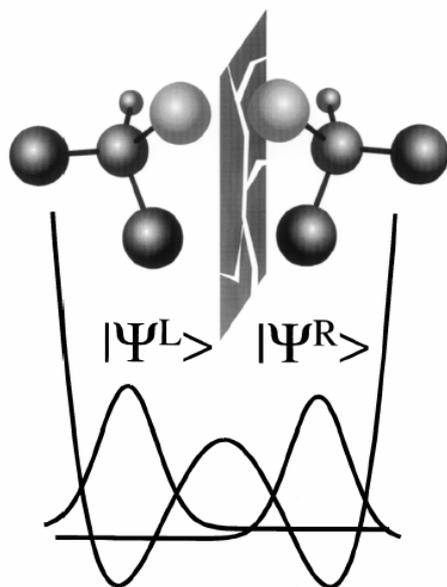


FIG. 1. Because of weak interactions, right and left enantiomers of CHFClBr are not images in a mirror.

The dominant term comes from the heaviest nuclei with the restriction that, by symmetry, the terms with $K = K'$ are negligible [14]. A multiplicative asymmetry factor η (usually $\ll 1$), which results from molecular orbital calculations, takes into account the chiral character of the molecular environment [15]. These arguments justify the choice of the molecule: we will prefer a chiral molecule with heavy nuclei located at the periphery.

Ab initio calculations have been applied to a number of molecules [16]: the *L* series of glycine, alanine, valine, serine, and aspartic acid; and the *D*-sugar series, which are actually the species existing on earth, were found to be preferentially stabilized by the electroweak interaction: $\Delta E_{\text{el}}^{\text{PV}} \sim (-0.84 \text{ to } -2.29) \times 10^{-20}$ a.u., which gave some credit to speculations in biochemistry. Recent calculations confirm a large enhancement (3 orders of magnitude) when carbon is replaced by sulfur [17]. In addition, the latest calculations based on more precise techniques (Coupled Hartree-Fock methods) lead to the same conclusions but with numerical results about 1 order of magnitude larger [18,19]. As another example [20], hypothetical four-atom molecules have been considered such as NFCIBr, BiFCIBr, and NFCIAt, for which the calculated $\Delta E_{\text{el}}^{\text{PV}}$ are respectively 10^{-16} , 8×10^{-16} , and 10^{-13} eV, illustrating both the atomic number dependence and the role of the location of the high- Z atom.

In molecular spectroscopy, we have electronic, vibrational, or rotational degrees of freedom. Letokhov [4] suggested that, because the associated energies are proportional [21], a relative change in vibrational or rotational frequencies between right- and left-handed molecules is expected to scale with the relative change in electronic

energy:

$$\frac{\Delta E_{\text{el}}^{\text{PV}}}{E_{\text{el}}} \approx \frac{\Delta E_{\text{vib}}^{\text{PV}}}{E_{\text{vib}}} \approx \frac{\Delta E_{\text{rot}}^{\text{PV}}}{E_{\text{rot}}}. \quad (4)$$

This argument is in favor of performing vibrational spectroscopy which usually provides the highest relative resolution and sensitivity.

Experiment.—Today CHFClBr is one of the best test molecules since it is one of the simplest stable chiral molecules and a bromine atom with a high- Z value ($Z_{\text{Br}} = 35$) is located at the molecular periphery. Another practical key point is the high-quality experimental and theoretical spectroscopic data available on CHFClBr. In particular, the strong ν_4 CF stretching fundamental band has been fully analyzed [22], which is a necessary starting point for any ultrahigh resolution experiment.

Experimental projects were held in abeyance over twenty years because the final difficulty of the resolution of CHFClBr enantiomers was solved successfully only recently [23]. The link between the conformation and the optical activity of the two isomers of CHFClBr was established even more recently by the group of Collet [24]: *S*-(+) and *R*-(-). This group has prepared for us a sample of *R*-CHFClBr with an enantiomeric excess (ee) of $(22 \pm 2)\%$ and a sample of *S*-CHFClBr with an ee of $(56, 5 \pm 0, 5)\%$. This has enabled us to perform the first sensitive test of parity violation in molecules.

The principle of the experiment is the following (Fig. 2): we use a CO₂ laser whose frequency is shifted by 40 MHz with an acousto-optic modulator (AOM) for optical isolation purposes. Then, a sideband generated by a 0–500 MHz tunable electro-optic modulator (EOM) is stabilized on a saturation peak detected on the transmission signal of a 1.5-m-long Fabry-Perot cavity. The frequency stabilization scheme is described elsewhere [25]. It can provide a spectral purity of 6 Hz and a long-term stability of 0.1 Hz over 100 s with an OsO₄ saturation resonance in the 10 μm spectral region. This performance is degraded by a factor of 10 with the use of one hyperfine component of the $(55, 11, 44) \leftarrow (55, 12, 43)$ rovibrational line of CHFClBr in the vicinity of the *R*(14) CO₂ laser line of the 9.4 μm band because of the broader linewidth of the

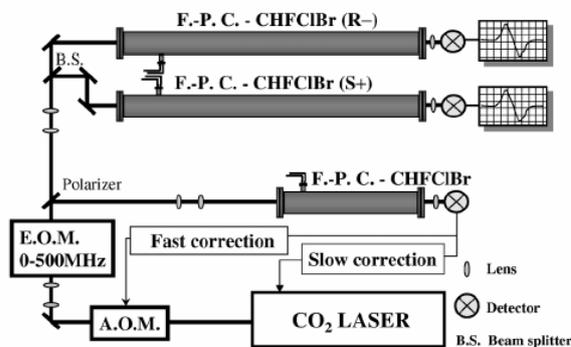


FIG. 2. Schematic diagram of the experimental setup.

reference and the reduction of the finesse of our cavity at that wavelength. However, the residual drift of the laser frequency has no impact on the sensitivity of the test.

Then, the laser carrier, shifted by the AOM, feeds twin 3-m-long Fabry-Perot cavities (7 mm waist) and the simultaneous recording of the spectra of the two enantiomers is achieved by tuning the radio frequency of the EOM. The frequency modulations required to stabilize the three resonators and to detect the molecular signals in transmission of these cavities are applied inside the laser resonator via a piezoelectric transducer, one at 41 kHz for stabilizing the optical length of the three cavities and the second at 4 kHz with a third-harmonic detection to stabilize the sideband on a molecular signal and to detect the molecular resonances of the two enantiomers. The gas pressure is 0.2 Pa and the laser power is 9 mW. The modulation parameters were optimized for the test signals and not for the stabilization. We have performed the most sensitive experiments through a study of a hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ line. The typical width of 90 kHz is due to a symmetric triplet that we can resolve in a very large cell (18 m long with an 8 cm laser beam diameter) with a linewidth of 5 kHz (Fig. 3). Actually, any difference between the two systems occurs after the beam splitter which divides the laser beam into two parts directed towards the two resonators. Most of them are compensated by the exchange of the role of the two cavities performed by filling each of them

with the other enantiomer. However, this is not the case for the polarization effects and the stray fields. In fact, the lack of mirror symmetry due to some residual ellipticity (<1%) of the polarization is attenuated by the finesse of the cavity. We have checked that even a circular polarization does not affect the line centers with the present sensitivity while, with a shielding of 1:1000, the effect of the earth's magnetic field is expected to be negligible.

Results.—We have performed ten sets of measurements over ten days. For one set per day, the first half-day, each twin cavity is filled with one kind of enantiomer and, the second half-day, the enantiomers are exchanged in the cavities. When we perform an elementary measurement as described above, we obtain a systematic shift of the order of 100 Hz which is reproducible. When the role of the cavities is exchanged, we observe that the sign of the difference is changed (see Fig. 4a). This systematic effect is associated with the difference between the two systems whatever its origin. Assuming that this shift is constant over one day, we can subtract it from the individual measurements (Fig. 4b). Once this compensation has been achieved, we have built the histogram from the 580 individual corrected measurements. We obtain a mean value for the frequency difference of 3,7 Hz and a standard deviation of 47,2 Hz, close to the uncertainties of the fits of the individual spectra (Fig. 4c).

The statistical uncertainty of this set of measurements is given by the standard deviation of this histogram divided by the square root of the number of measurements, i.e., 2 Hz. However, the systematic effects cannot be perfectly compensated and their residuals must be taken into account although we could not detect them.

We estimate that these residual systematic effects are of the order of 5 Hz, i.e., 1 order of magnitude less than the width of the histogram for two reasons: this histogram presents a nice Gaussian shape and we have checked that the data points of Fig. 4b exhibit a white distribution. Thus, the frequency difference for the resonances associated to the two samples is

$$\Delta\nu = 3,7 \pm 2 \pm 5 \text{ Hz.}$$

In addition, we have to take into account the enantiomeric excesses of the samples. We finally obtain the first measurement for the frequency difference between resonances of the two enantiomers of CHFClBr:

$$\nu(R-) - \nu(S+) = 9,4 \pm 5,1 \pm 12,7 \text{ Hz.}$$

The result of the test is, thus, negative. It gives an upper bound of $\Delta\nu/\nu = 3,9 \times 10^{-13}$ for the parity violation effect.

Conclusion.—The sensitivity of this experiment is about 5 orders of magnitude higher than the previous test on camphor. This experiment is still to be considered as a preliminary test. In the short term, higher finesse resonators might be employed and samples with higher enantiomeric excess (50% and 72%) will soon be available from Collet. A better choice of the test line should

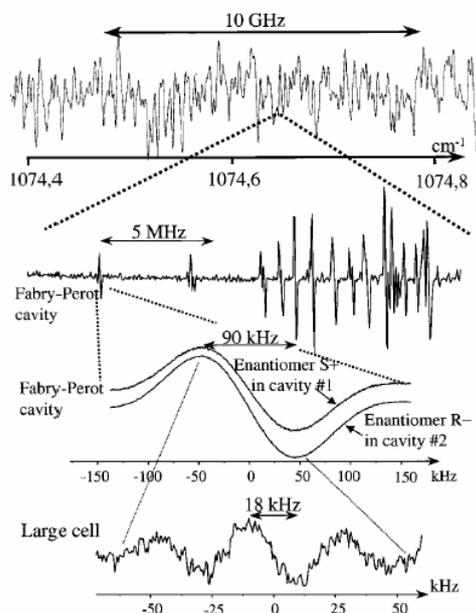


FIG. 3. ν_4 band spectra of CHFClBr at various resolutions. From top to bottom: Fourier transform spectrum (courtesy of A. Valentin—Paris VI); overview of the hyperfine structure of the $(40, 7, 34) \leftarrow (40, 8, 33)$ line; two typical spectra of the test hyperfine component recorded simultaneously; triplet substructure revealed at the highest resolution.

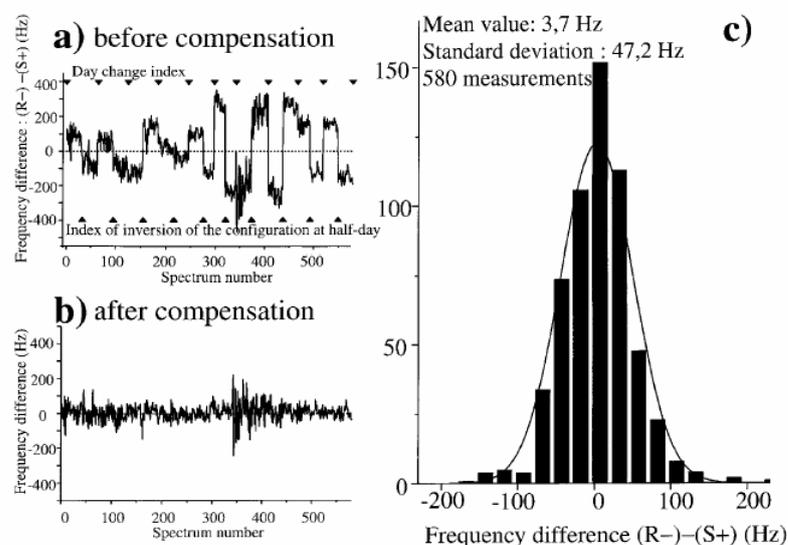


FIG. 4. (a) The measurements reveal systematic shifts induced by the differences between the cavities. (b) Compensation of systematic errors by exchange of the roles of the two cavities. (c) Histogram of the measured frequency differences for 580 measurements.

be made as we have discovered that the chosen line was a crossover resonance, sensitive to light shifts. Subsequently, higher resolution using beams of larger diameter, slow molecule detection [26], or saturation spectroscopy in molecular beams to avoid collisional shifts must be considered. Molecules with heavier atoms, such as CHFCl in which we have already observed saturation resonances, and transitions more sensitive to weak interactions, e.g., CBr or CI vibrations, must be explored. Finally, it is clear that the theory is insufficiently developed to obtain reliable estimates of the expected effects in various molecules and has to be improved substantially in order to guide further experimental developments.

The authors are very grateful to A. Collet and J. Costante for the preparation of optically active CHFClBr. This work was supported in part by the Direction des Recherches Etudes et Techniques (DGA-DRET) and by the Bureau National de Métrologie.

*Email address: borde@lpl.univ-paris13.fr

†Email address: chardonnet@lpl.univ-paris13.fr

- [1] D. W. Rein, *J. Mol. Evol.* **4**, 15 (1974).
- [2] L. Pasteur, *C. R. Acad. Sci. (Paris)* **26**, 535 (1848).
- [3] D. K. Kondepudi and G. W. Nelson, *Nature (London)* **314**, 438 (1985).
- [4] V. S. Letokhov, *Phys. Lett.* **53A**, 275 (1975).
- [5] O. N. Kompanets, A. R. Kukudzhanov, V. S. Letokhov, and L. L. Gervits, *Opt. Commun.* **19**, 414 (1976).
- [6] E. Arimondo, P. Glorieux, and T. Oka, *Opt. Commun.* **23**, 369 (1977).
- [7] A. L. Barra, J. B. Robert, and L. Wiesenfeld, *Phys. Lett. A* **115**, 443 (1986).
- [8] Ch. J. Bordé *et al.*, *Laser Spectroscopy VII* (Springer-Verlag, Berlin, 1985), Vol. 108, p. 95.
- [9] R. J. Butcher, Ch. Chardonnet, and Ch. J. Bordé, *Phys. Rev. Lett.* **70**, 2698 (1993).
- [10] O. Pfister, Ch. Chardonnet, and Ch. J. Bordé, *Phys. Rev. Lett.* **76**, 4516 (1996).
- [11] M. A. Bouchiat and C. C. Bouchiat, *Rep. Prog. Phys.* **60**, 1351 (1997), and references therein.
- [12] E. Gajzago and G. Marx, *Atomki Közlemények Suppl.* **16/2**, 177 (1974).
- [13] Ch. Chardonnet *et al.*, *Parity Violation in Atomic Physics and Electron Scattering*, edited by B. Frois and M. A. Bouchiat (World Scientific, Singapore, 1999), pp. 325–355.
- [14] R. A. Hegstrom, D. W. Rein, and P. G. H. Sandars, *J. Chem. Phys.* **73**, 2329 (1980).
- [15] B. Ya. Zel'dovich, D. B. Saakyan, and I. I. Sobel'man, *JETP Lett.* **25**, 94 (1977).
- [16] S. F. Mason and G. E. Tranter, *Mol. Phys.* **53**, 1091 (1984).
- [17] A. J. MacDermott, G. E. Tranter, and S. J. Trainor, *Chem. Phys. Lett.* **194**, 152 (1992).
- [18] A. Bakasov, T.-K. Ha, and M. Quack, *J. Chem. Phys.* **109**, 7263 (1998).
- [19] P. Lazzeretti and R. Zanasi, *Chem. Phys. Lett.* **279**, 349 (1997); R. Zanasi, P. Lazzeretti, A. Ligabue, and A. Soncini, *Phys. Rev. E* **59**, 3382 (1999).
- [20] L. N. Ivanov and V. S. Letokhov, *Dokl. Phys.* **43**, 523 (1998).
- [21] A. Messiah, *Mécanique Quantique* (Dunod, Paris, 1964), p. 670.
- [22] A. Bauder *et al.*, *J. Chem. Phys.* **106**, 7558 (1997).
- [23] T. R. Doyle and O. Vogl, *J. Am. Chem. Soc.* **111**, 8510 (1989).
- [24] J. Costante, N. Ehlinger, M. Perrin, and A. Collet, *Enantiomer* **1**, 377 (1996).
- [25] V. Bernard *et al.*, *IEEE J. Quantum. Electron.* **33**, 1282 (1997).
- [26] Ch. Chardonnet, F. Guernet, G. Charton, and Ch. J. Bordé, *Appl. Phys. B* **59**, 333 (1994).

Improved sensitivity in the search for a parity-violating energy difference in the vibrational spectrum of the enantiomers of CHFCIBr

M. Ziskind, C. Daussy, T. Marrel, and Ch. Chardonnet^aLaboratoire de Physique des Lasers^b, Université Paris 13, 99 avenue J.-B. Clément, 93430 Villetaneuse, France

Received 22 January 2002

Published online 19 July 2002 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2002

Abstract. The theoretical prediction that enantiomers of chiral molecules have different spectra because of parity violation associated with neutral currents in the weak interaction has been experimentally looked for. Last searches of a frequency difference in the vibrational spectrum of the enantiomers of CHFCIBr obtained with our infrared saturation spectrometer is presented. The frequencies of a saturation resonance of separated enantiomers of CHFCIBr have been compared at a 5×10^{-14} level. A residual pressure shift probably induced by uncontrolled impurities of the samples has been observed and found to limit our experimental sensitivity. Finally no parity violating frequency difference is observed within the present sensitivity of 2.5×10^{-13} . A new experimental scheme is proposed which should let the parity violation effect observable.

PACS. 33.15.Bh General molecular conformation and symmetry; stereochemistry – 11.30.Er Charge conjugation, parity, time reversal, and other discrete symmetries – 33.20.Ea Infrared spectra

1 Introduction

The weak interaction is the only fundamental interaction which does not respect left-right symmetry. This has been observed in 1957 in the famous experiment of β^- disintegration of the Co nucleus [1]. Thanks to the Z^0 boson which is the neutral vector of the weak interaction, it has been suggested that parity violation could show up with stable atoms [2]. Although this interaction is of extreme short range, after the first observation, several precise atomic experiments were achieved and confirmed the standard model to a high accuracy [3,4]. In 1974, it was suggested that parity violation can manifest itself in the molecules with an original and simple signature: if we consider the two “mirror image” enantiomers of a chiral molecule (Fig. 1), left-right symmetry breaking will appear as an electronic energy difference between the two species [5]. Considering the weakness of the effects, it is broadly admitted that the weak interaction may be neglected in molecular physics and even more clearly in chemistry and biology. However, it is remarkable that nature, on earth, has performed marked choices between right and left. The most well-known example is the right-handed double helix of the DNA molecule. The origin of homochirality emergence in biomolecules, and the possible role of weak interaction, is the subject of several contro-

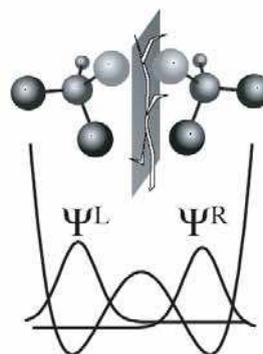
^a e-mail: chardonnet@galilee.univ-paris13.fr^b UMR 7538 du CNRS

Fig. 1. Enantiomers of a chiral molecule are image each other in a mirror except if there is parity violation.

versial conjectures [6,7]. This is meaningful only if the production in excess of the more stable molecule is larger than the unavoidable random fluctuations. This is why models of molecular dynamics establish a relation between the energy difference, the size of the sample and the time required for a complete selection of one species over the other [8]. This is one motivation of looking for a parity violation effect in molecules, which has never been observed so far.

In 1998 we performed a first attempt to observe a parity violation effect on separated enantiomers of a chiral molecule. We looked for a difference in the vibrational spectrum of the two enantiomers of CHFClBr which is one of the simplest chiral molecules. No effect has been observed and we could give an upper bound of $\Delta\nu/\nu = 3.9 \times 10^{-13}$ for the parity violation effect [9]. After a brief outline of the general theoretical and experimental background we will present our last attempt to observe a parity violation effect with our infrared saturation spectrometer on new molecular samples.

1.1 Theoretical basis

For a chiral molecule, we can consider two right- and left-handed states $|\psi^R\rangle$ and $|\psi^L\rangle$. If a molecule can change its configuration by tunnel effect, mirror symmetry is dynamically restored and energy eigenstates are the parity eigenstates, $|\psi^\pm\rangle = (|\psi^L\rangle \pm |\psi^R\rangle)/\sqrt{2}$. If now the potential barrier is very high (negligible tunnel effect), enantiomeric left- and right-handed species are stable and handedness as parity is a good quantum number for energy eigenstates.

Due to the parity violating weak interaction, the Hamiltonian matrix will remain diagonal only in the handedness-eigenstate basis and energy degeneracy lifting:

$$2|E^{PV}| = |\langle\psi^L|H^{PV}|\psi^L\rangle - \langle\psi^R|H^{PV}|\psi^R\rangle| \\ = 2|\langle\psi^-|H^{PV}|\psi^+\rangle|$$

appears between left and right enantiomers.

1.1.1 Physical origin of the lifting of degeneracy

The main term of the parity-violation Hamiltonian in atoms is [2] (for more details see also [10]):

$$H^{PV} \approx \frac{G_F}{2\sqrt{2}m_e c} s \left[\mathbf{p} \delta^{(3)}(\mathbf{r}) \right]_+ Q_W \quad (1)$$

where G_F is the Fermi constant ($1.43 \times 10^{-62} \text{ J m}^3$), m_e the electron mass, $s = \sigma/2$ the dimensionless electron spin operator, \mathbf{p} the electron momentum operator. Q_W is the weak charge of the nucleus equal to $Z(1 - 4 \sin^2 \theta_W) - N$, Z and N are the proton and neutron numbers and where the Weinberg angle θ_W enters via $\sin^2 \theta_W \approx 0.2236$.

From this elementary Hamiltonian the matrix element calculated between atomic orbitals $|ns_{1/2}\rangle$ and $|n'p_{1/2}\rangle$ increases like $Z^2 Q_W \approx Z^3$.

In the molecular case at the non-relativistic limit $\langle\varphi_0^R|H^{PV}|\varphi_0^R\rangle = \langle\varphi_0^L|H^{PV}|\varphi_0^L\rangle = 0$. Therefore, one has to consider a higher order term to obtain a non vanishing parity violating contribution. The largest second-order cross term implies the spin-orbit coupling [5,11]:

$$E_{\text{el}}^{PV} = \langle\varphi_0|H^{PV}|\varphi_0\rangle \\ = 2\text{Re} \left\{ \sum_{n \neq 0} \frac{\langle^1\varphi_0|H^{SO}|^3\varphi_n\rangle \langle^3\varphi_n|H^{PV}|^1\varphi_0\rangle}{E_0 - E_n} \right\} \quad (2)$$

where H^{PV} and H^{SO} couple a singlet state $|^1\varphi_0\rangle$ only to the triplet manifold $|^3\varphi_n\rangle$. An estimation of the spin-orbit contribution obtained from the multi-electron case shows a quadratic dependence with Z . E_{el}^{PV} is the sum of different contributions which involve the pairs of nuclei of the molecule (the terms involving identical nuclei have a negligible contribution) [12]. Finally, the evaluation of E_{el}^{PV} (Eq. (2)) leads to:

$$E_{\text{el}}^{PV} \approx 10^{-20} \eta Z_\alpha^2 Z_\beta^3 \text{ Hartree with } \alpha \neq \beta \quad (3)$$

where $10^{-4} < \eta < 10^{-2}$ is an asymmetry factor, which takes into account the chiral molecular environment around the nucleus of charge Z_β which is considered [13].

1.1.2 Quantum chemistry calculations

Since the 80's, many *ab initio* calculations have been performed on biological molecules [14]. Thus, the natural species of α -amino acids (as L-glycine, alanine, valine, serine) were found to be more stable with a lower electroweak energy ($E_{\text{el}}^{PV} \approx (-0.84 \text{ to } -2.29) \times 10^{-20}$ u.a.). These results gave credit to the speculations in biochemistry. Electroweak quantum-chemical studies (coupled Hartree-Fock method) confirmed the sign of the previous results but gave an amplitude of the effect larger by more than one order of magnitude [15–19]. However, recent calculated parity-violating energy shifts for 13 stable conformers of gaseous alanine indicate that the stabilization of a certain enantiomer is strongly dependent on its conformation (L-alanine is preferred for only 7 structures) [20]. Recent considerations suggested also that a possible answer of biomolecular homochirality could be obtained by considering rather kinetic effects at work during chemical synthesis of chiral molecules (related to the relative stability of certain possible prebiotic precursors) than the different thermodynamical stability of the mirror-image reaction products [21].

In all these calculations, only the perturbation of the electronic energy is taken into account. However, an argument of Letokhov [22] suggested that the relative difference of vibrational and rotational frequencies between left- and right-handed molecules is comparable to the electronic energy case:

$$\frac{E_{\text{el}}^{PV}}{E_{\text{el}}} \approx \frac{E_{\text{vib}}^{PV}}{E_{\text{vib}}} \approx \frac{E_{\text{rot}}^{PV}}{E_{\text{rot}}} \quad (4)$$

This qualitative argument is in favor of the vibrational spectroscopy which generally permits higher relative sensitivities. One must also mention other spectroscopic proposals [23–25] to observe a parity violation effect in molecules.

However, before our work, no calculation on vibrational shifts in any molecules was available. After the publication of our first results, three groups published independently vibrational frequency shifts corresponding to the C-F stretching mode of CHFClBr (our experimental situation) but also of other asymmetric carbons [26–29].

Table 1. Calculated energy and frequency differences in CHFClBr according different authors.

Parity shift	[28]	[26,29]	[30]
$\Delta_{\text{PV}}\nu_{\text{vib}}/\nu_{\text{vib}}$			
harmonic potential approx. \rightarrow	5×10^{-17}	6×10^{-17}	5.6×10^{-17}
anharmonic potential \rightarrow		-8×10^{-17}	-5.2×10^{-17}
$\nu_R - \nu_S$ (mHz)			
harmonic potential approx. \rightarrow	1.77	2	1.8
anharmonic potential \rightarrow		-2.6	-1.7
$\Delta_{\text{PV}}E/h$ (mHz)	74 [21]	58	69
$\Delta_{\text{PV}}\nu_{\text{rot}}/\nu_{\text{rot}}$		$1-3 \times 10^{-17}$	

More precise calculations have been recently performed for the C-F vibrational mode of a set of asymmetric carbons [30].

Explicit calculation of the second-order cross term due to the spin-orbit coupling (Eq. (2)) is necessary only within a non relativistic approach. In a fully relativistic treatment, as reported in [27], the parity violating energy shift is calculated as the matrix element:

$$E_{\text{el}}^{\text{PV}} = \langle \text{rel. } \varphi_0 | H^{\text{PV,rel.}} | \text{rel. } \varphi_0 \rangle \quad (5)$$

$E_{\text{el}}^{\text{PV}}$ (Eq. (2) or (5)), assumed to be diagonal (no coupling between different vibrational modes), is calculated as a function of the nuclear geometry and fitted to a polynomial expansion: $E_{\text{el}}^{\text{PV}}(Q_i) = \sum_{k=0}^n p_k(i)Q_i^k$; where Q_i denotes the set of normal coordinates.

$E_{\text{el}}^{\text{PV}}$ represents a small perturbation of the zero-order Hamiltonian H_0 . A first-order perturbation treatment leads to the energy shift $E_{\text{vib}}^{\text{PV}(1)} \approx \langle \phi_n | E_{\text{el}}^{\text{PV}}(Q_i) | \phi_n \rangle$, where $|\phi_n\rangle$ denotes the eigenfunction of H_0 and where the first correction to the vibrational frequency is proportional to the second derivative of the potential $E_{\text{el}}^{\text{PV}}(Q_i)$ versus molecular deformation. In [26,29] the first contribution to the anharmonicity of the electronic potential is also taken into account. The main conclusions of the three evaluations of:

$$\Delta_{\text{PV}}h\nu_{\text{vib}} = [\text{R} E_{\text{vib}}^{\text{PV}}(\nu=1) - \text{R} E_{\text{vib}}^{\text{PV}}(\nu=0)] - [\text{S} E_{\text{vib}}^{\text{PV}}(\nu=1) - \text{S} E_{\text{vib}}^{\text{PV}}(\nu=0)] \quad (6)$$

for the C-F stretching are summarized in Table 1. For this particular case, the contribution due to the anharmonicity is more important because of an accidental quasi-cancellation of the first term.

1.2 Experimental background

In 1976 it was suggested that the observation of a frequency difference of two lasers stabilized onto the saturation resonances of the enantiomers of a chiral molecule would give a signature of a parity violation effect [31]. The CHFClBr molecule [31] was proposed as a good candidate because it is a heavy molecule with a strong absorption band in the tuning range of the CO₂ laser. However,

for the highest sensitivity, the method requires a physical separation of the enantiomers which was not achieved at that time in spite of efforts of chemists since the end of last century [32] and this blocked such an experiment with this molecule. A first attempt using this method was made in 1977 by Arimondo *et al.* [33]. They compared the rovibrational transitions in the separated isomers of camphor by measuring the inverted Lamb dips. The difference frequency was found to be zero within 300 kHz ($\Delta\nu/\nu = 10^{-8}$). The first efficient resolution of CHFClBr was finally achieved in 1989 [34] and confirmed by the group of Collet who established the link between the absolute configuration and the rotatory power of the molecule: $S-(+)$ and $R-(-)$ [35,36]. They provided us a first series of samples (a few grams) with the following enantiomeric excesses (ee): $S-(+)$, $(22 \pm 2)\%$ and $R-(-)$, $(56.5 \pm 0.5)\%$ which permitted us to perform the first high sensitivity test of parity violation in molecules [9,10].

Let us recall the principle of our experiment. A slightly different method than that proposed in 1976 has been applied [9,10]: a single CO₂ laser feeds an electro-optic modulator (EOM) which generates sidebands (tunable between 0 and 500 MHz). One of these sidebands is frequency stabilized onto a saturation peak detected on the transmission signal of a 1.5 m long Fabry-Perot cavity (reference cavity). The frequency stabilization scheme is described in more detail elsewhere [37]. The stabilized laser carrier directly feeds two twin 3 m long Fabry-Perot cavities which are filled with the two enantiomers of CHFClBr. The spectra of the studied line can be recorded simultaneously since the carrier is tunable by tuning the frequency of the EOM. The principle of the test is to compare the frequencies of the line centers. It might be noted that the stability of the reference laser plays a negligible role in this experiment.

One hyperfine component of the ν_4 C-F stretching fundamental band of CHF³⁷Cl⁸¹Br (fully analyzed in [38]) was used for locking the laser side band. The test was performed on an unidentified hyperfine component with a peak-to-peak line width of 90 kHz and a signal-to-noise ratio of 300 over 30 ms. 580 measurements were performed over 10 days. A mean difference of 3.7 Hz with a standard deviation of 47 Hz and a final statistical uncertainty of 2 Hz is obtained. We had to include residual systematic effects in the final uncertainty although we could not detect them, we estimated them to 5 Hz. Finally, the difference

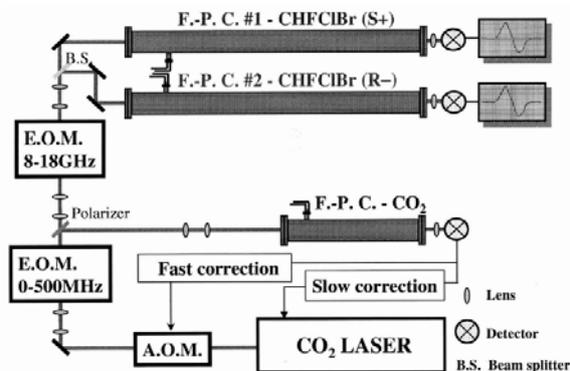


Fig. 2. Experimental set up used for the test.

between the eigenfrequencies of the two enantiomers are obtained when the enantiomeric excesses of the samples are taken into account (with statistical and systematic uncertainties): $\nu(R-) - \nu(S+) = 9.4 \pm 5.1 \pm 12.7$ Hz. So, no parity violation effect is observed at a relative sensitivity of $\Delta\nu/\nu = 3.9 \times 10^{-13}$, which is 5 orders of magnitude better than for the experiment on camphor [33].

2 New parity violation experiment

Then, we performed a new series of experiments in the spectrum of the enantiomers of CHFClBr which improved the first one in several aspects. We obtained new samples with higher ee with which an even more sensitive test could be performed with a new experimental set up. Here we present our last efforts for observing a parity violating frequency shift. The experimental scheme was the following (Fig. 2): the CO₂ laser was optically isolated with a 40 MHz acousto-optic modulator (AOM) and is stabilized as described for the first series of experiments. However the reference molecular line chosen for this stabilization was the CO₂ laser line itself which gave directly a good knowledge of the absolute frequency of the studied CHFClBr line. We implemented a second EOM, operating with a microwave between 8 and 18 GHz, on the path of the stabilized laser carrier just before two twin cavities. This provided a much broader tunability and permitted to access virtually to any rovibrational line of the various isotopic species of CHFClBr. In addition, it was now possible to apply all modulations on the two EOM's and optimize the parameters of the reference line and the CHFClBr line independently. The price is the small saturation power available due to the weak efficiency of the EOM (about 10^{-4} @20 W of microwave power) partly compensated by a higher laser power of 3 W (multiplied by 3 by changing the laser output coupler) and a higher finesse of 200 of the cavities (multiplied by 4). The characteristics of the cavities are now the following: a symmetric configuration with mirror radii of 50 m for the reference cavity and 100 m for the 3 m long twin cavities.

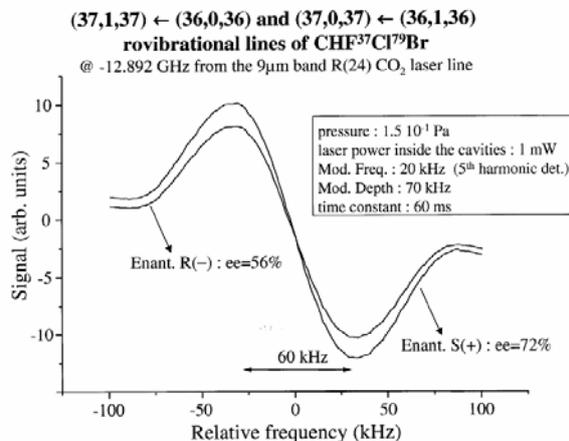


Fig. 3. Spectra of the test line. We checked that the intensity difference is mainly due to the difference of the sensitivity of the two detectors.

A new series of experiments whose principle is not different from the first one were then performed with samples of higher ee: $S - (+)$, 56% and $R - (-)$, 72%. We could perform an extensive analysis of the hyperfine structure of various isotopic species of CHFClBr [39] and were able to find a much more favorable candidate. In fact, we found that the $(37, 1, 37) \leftarrow (36, 0, 36)$ and $(37, 0, 37) \leftarrow (36, 1, 36)$ rovibrational lines of CHF³⁷Cl⁷⁹Br which are highly degenerate and present an extremely compact hyperfine structure, show up in the Fabry-Perot cavities as a unique and highly symmetric line with a peak-to-peak width of 60 kHz¹. The optimized parameters were a pressure of 1.5×10^{-1} Pa with an equal pressure in both cavities controlled with a differential gauge at a 10^{-3} Pa level and a laser power of 1 mW inside the cavities. Despite the reduced power in the cavities (divided by 9), the signal-to-noise ratio about 1000 over 30 ms was significantly improved (Fig. 3). The CHFClBr line was found at $-12\,891\,865.7$ (10) kHz from the R(24) CO₂ laser line which was used as the reference line which lead to a precise absolute calibration [40] of the CHFClBr line: $32\,397\,293\,834.1(30)$ kHz.

3 Results

The difficulty of the experiment is to reduce as much as possible any systematic effect susceptible to simulate a parity violation effect. The experiment is a differential one which ensures an automatic compensation of a large fraction of these effects due to experimental imperfections such as modulation distortions, drift of the local oscillator, etc. In fact, the experiment is identical for the two kinds

¹ However, at the highest resolution for which the signal-to-noise ratio is strongly degraded, this line appears as a symmetric doublet with a splitting of 28 kHz.

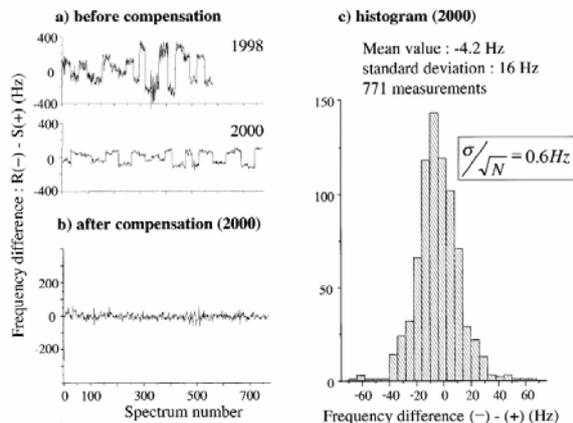


Fig. 4. (a) Crude frequency differences including measurements of 1998, (b) frequency differences after compensation of the daily systematic effects, (c) histogram of these compensated frequency differences.

of molecules until the 50/50 beamsplitter which separates the beam in two parts, directed towards the twin cavities. After that point, differences can occur but they can be partly compensated by an exchange of the role of the cavities. Most of the differences between the two cavities (in addition to the enantiomeric molecules themselves) which can induce an instrumental frequency difference, noticed f_{cavity} , are compensated by this exchange. However, it is important to avoid any chiral element in the experiment except the molecules themselves. In particular, the light polarization must be linear. This is ensured up to a few percent while no shift could be detected when a circular polarization was applied. An other source of uncompensated systematic effects could be a mirror image symmetry breaking due to different residual impurities in the two samples.

Practically, the cavities #1 and #2 are filled respectively with the enantiomers $S - (+)$ and $R - (-)$ in the morning and $R - (-)$ and $S - (+)$ in the afternoon. 771 measurements were performed over 15 days. The results of the measurements are presented in Figure 4a which represents the series of crude differences.

To illustrate the improvement of the present test, we also reported frequency measurements corresponding to our first search of parity violation performed in 1998. We retrieve the clear jump in the measurements at half-day that we attribute to systematic effects induced by uncontrolled differences in the two optical set up. These effects called f_{cavity} , are supposed to be constant over one day since we do not change any parameter. Thus, in the morning we measure $\Delta\nu + f_{\text{cavity}}$ and in the afternoon, $\Delta\nu - f_{\text{cavity}}$. The systematic error f_{cavity} can be calculated as half the difference of the mean values of the half-day measurements. Corrected values are obtained by subtracting this systematic part. We checked that these corrected values (Fig. 4b) present a white noise spectrum. The corresponding histogram (Fig. 4c) presents a clear Gaussian

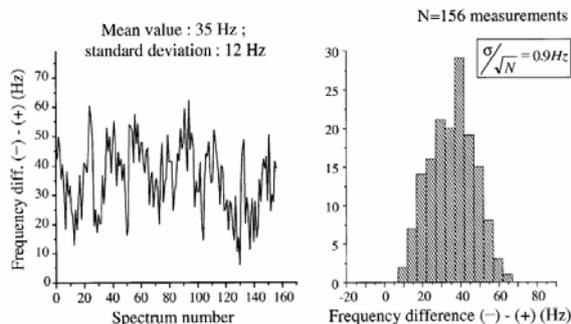


Fig. 5. Frequency difference obtained on the second test line with the samples $S - (+)(ee) = 56\%$ and $R - (-)(ee) = 56\%$.

shape. This is a strong indication that residual “cavity” systematic effects are a small fraction of the statistical error of an individual spectrum, *i.e.* 16 Hz.

Compared to the first series of experiments, the compensated systematic effects and the statistical noise are reduced by a factor at least 3. Finally, we obtained a histogram with a standard deviation of $\sigma = 16$ Hz (very close to the typical uncertainty given by the fit of an individual line) giving rise to a statistical uncertainty of $\sigma/\sqrt{N} = 0.6$ Hz while the mean frequency difference is found to be -4.2 Hz. The residual systematic effect of instrumental origin partially compensated by the inversion procedure described before have been estimated at 1.6 Hz. It is taken as one order of magnitude less than the uncertainty on one individual measurement. The resonance frequency difference associated to the two samples with statistical and systematic uncertainties is:

$$\Delta\nu = -4.2 \pm 0.6 \pm 1.6 \text{ Hz.} \quad (7)$$

This corresponds to a relative sensitivity for the frequency difference measurement of $\Delta\nu/\nu = 5 \times 10^{-14}$ (1/40 000 of the width of the signal *i.e.* 60 kHz).

The final frequency difference is high compared to the statistical and systematic uncertainties. Thus, we looked for an evidence of uncompensated systematic effects due to possible residual impurities in samples which can induce various collisional shifts. Since the impurities could be different, we can obtain an irreducible constant frequency difference, f_{sample} , whose signature would be a pressure dependence. Unfortunately because of the lack of product we could not use the new $R - (-)$ sample to check this hypothesis. For that reason, we performed the same test with the first sample of $R - (-)(ee) = 56.5\%$ and the second sample of $S - (+)(ee) = 56\%$ that we obtained. They were not prepared simultaneously. The frequency differences measured under the same conditions as previously (after compensation of the “cavity” systematic effects) are displayed in Figure 5. They reveal a clear and significant difference: $\nu(R-) - \nu(S+) = 35 \pm 0.9 \pm 1.3$ Hz. Same measurements have been performed during the first test, with a sample of racemic mixture and $R - (-)(ee) = 56.5\%$.

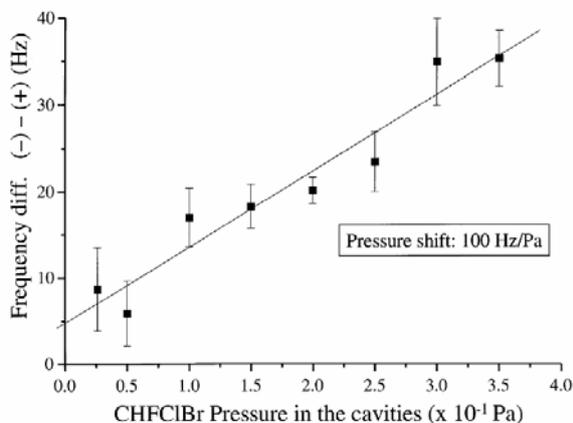


Fig. 6. Evidence for a differential pressure shift on the second test line obtained with the samples delivered in 1998.

We obtained $\nu(R-) - \nu(\text{Rac.}) = 41.2 \pm 4.3 \pm 5$ Hz. We suspected some residual impurities in the samples although they represent certainly less than 5% of CHFCIBr for $R - (-)$ and $S - (+)$ samples because the signals of the different samples were equal with this precision. However, between $R - (-)/S - (+)$ and the racemic sample, we observed a signal amplitude difference up to 30% attributed to large impurities in the racemic mixture. These could have been introduced during the preparation of the samples or their manipulation during the connection to the experiment.

In order to check this, we studied the pressure dependence of the shift. Because of the small fraction of new samples we used our old one and obtained a quite linear dependence of this shift with the pressure (Fig. 6) which cannot be a parity violation effect essentially independent on any external parameter. The extrapolated value at null pressure is +5 Hz with an uncertainty of 5 Hz. In fact, the shift of -4.2 Hz obtained at 0.15 Pa with the samples of 2000 is rather small which indicates that the fraction of impurities are probably smaller or much more identical in the new samples. The lack of molecules forbid the same extrapolation of the differential pressure shift to zero for the samples of 2000 which reduced the ultimate precision of our experiment by a factor 2 to 4.

It must be noticed that the samples from 1998 and 2000 gave similar signal amplitude within the experimental uncertainty of 5%. This gives a reasonable upper limit of the impurities in these samples. Considering 5 Hz as an upper limit of the residual uncertainty due to impurities (extrapolated value obtained with the samples of 1998 (Fig. 6) and shift obtained with the samples of 2000 (Fig. 4)), we can give a new upper limit for the frequency difference between the two enantiomers taken into account the enantiomeric excess of 56% and 72%:

$$|\nu_R - \nu_S| < 8 \text{ Hz} \Leftrightarrow |\Delta\nu/\nu| < 2.5 \times 10^{-13} \quad (8)$$

while the statistical uncertainty stays below 1 Hz.

4 Conclusion and perspectives

Our last set of experiments led to a significant improvement of the frequency difference sensitivity of 5×10^{-14} (compared to 1.6×10^{-13} in [9]). This allowed us to show evidence of a small but significant differential pressure shift of 100 Hz/Pa that we attributed to residual impurities of the samples. This last point gives probably an ultimate limit of the sensitivity for this experimental scheme. Let us suppose that we can improve by a factor 10 the purity of the samples in our cavities (fraction of impurity below 0.5%) which is probably the best that we can achieve with reasonable efforts. By extrapolation, we can expect an uncontrolled differential pressure shift of about 0.5 Hz ($\Delta\nu/\nu = 1.6 \times 10^{-14}$). This is already 10 times larger than the largest parity violation shift predicted on an asymmetric carbon by the most recent theoretical work [30]. Unless another molecule can lead to a much stronger effect, these limitations will prevent the observation of any parity violation effect with the present set up. It is thus necessary to reconsider the experimental project in order to avoid these collisional effects. For this reason, it seems that a molecular beam experiment would be much more suitable since the collisions come mainly from the background gas in the vacuum chamber which can be maintained at a very low pressure. Thus, we estimate that the most promising scheme is to develop a two-photon Ramsey fringes experiment with a double beam of chiral molecules for which the same optical set-up could be used alternatively for the two beams of enantiomers. This would be an evolution of a set up using a supersonic beam of SF₆ [41] with which we obtained already a very high resolution (200 Hz peak-to-peak) and a high signal-to-noise ratio leading to a statistical uncertainty of $0.5 \text{ Hz}/\sqrt{\text{Hz}}$ for the line center. Such a set up is obviously much more favorable for canceling any spurious systematic effects. If we can obtain the same performance with chiral molecules, the parity violation effect should be observable on molecules as CHFClI or CHFBrI for which the effects have been calculated as 23.7 mHz and 50.8 mHz, respectively [30]. This project is however still a challenge because it pre-requires the resolution of a significant amount of enantiomers of these molecules, which has never been achieved up to now, and then, a heavy spectroscopic work for identifying well-suited two-photon transitions in the infrared.

This work has been sponsored by CNRS, DGA and BNM. We are very grateful to A. Collet and J. Crassous for having provided us several samples of resolved enantiomers of CHFCIBr.

References

1. C.S. Wu, E. Ambler, R.W. Hayward, D.D. Hoppes, R.P. Hudson, Phys. Rev. **105**, 1413 (1957)
2. M.A. Bouchiat, C.C. Bouchiat, Phys. Lett. B **48**, 111 (1974)
3. M.A. Bouchiat, C.C. Bouchiat, Rep. Prog. Phys. **60**, 1351 (1997)

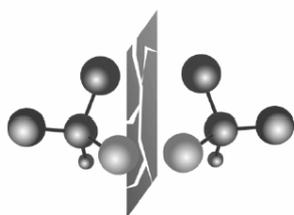
4. C.S. Wood *et al.*, *Science* **275**, 1759 (1997)
5. D.W. Rein, *J. Mol. Evol.* **4**, 15 (1974)
6. V.A. Kizel, *Sov. Phys. Usp.* **23**, 277 (1980)
7. S.F. Mason, *Nature* **311**, 19 (1984)
8. D.K. Kondepudi, G.W. Nelson, *Nature* **314**, 438 (1985)
9. C. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, C.J. Bordé, C. Chardonnet, *Phys. Rev. Lett.* **83**, 1554 (1999)
10. C. Chardonnet, C. Daussy, T. Marrel, A. Amy-Klein, C.T. Nguyen, C.J. Bordé, in *Parity violation in atomic physics and electron scattering*, edited by B. Frois, M.A. Bouchiat (World Scientific, New-York, 1999), p. 325
11. E. Gajzago, G. Marx, *Atomki Kozlemenkev* **16**, 177 (1974)
12. R.A. Hegstrom, D.W. Rein, P.G.H. Sandars, *J. Chem. Phys.* **73**, 2329 (1980)
13. B.Y. Zel'dovich, D.B. Saakyan, I.I. Sobel'man, *JETP Lett.* **25**, 94 (1977)
14. S.F. Mason, G.E. Tranter, *Mol. Phys.* **53**, 1091 (1984)
15. P. Lazzeretti, R. Zanasi, *Chem. Phys. Lett.* **279**, 349 (1997)
16. A. Bakasov, T.-K. Ha, M. Quack, *J. Chem. Phys.* **109**, 7263 (1998)
17. R. Zanasi, P. Lazzeretti, A. Ligabue, A. Soncini, *Phys. Rev. E* **59**, 3382 (1999)
18. A.J. MacDermott, G.E. Tranter, S.J. Trainor, *Chem. Phys. Lett.* **194**, 152 (1992)
19. R. Berger, M. Quack, *J. Chem. Phys.* **112**, 3148 (2000)
20. J.K. Laerdahl, R. Wesendrup, P. Schwerdtfeger, *Chem. Phys. Chem.* **1**, 60 (2000)
21. A. Soncini, A. Ligabue, P. Lazzeretti, *Phys. Rev. E* **62**, 8395 (2000)
22. V.S. Letokhov, *Phys. Lett. A* **53**, 275 (1975)
23. M. Quack, *Phys. Lett.* **132**, 147 (1986)
24. A.L. Barra, J.B. Robert, L. Wiesenfeld, *Phys. Lett. A* **115**, 443 (1986)
25. A.L. Barra, J.B. Robert, *Mol. Phys.* **88**, 875 (1996)
26. M. Quack, J. Stohner, *Phys. Rev. Lett.* **84**, 3807 (2000)
27. J.K. Laerdahl, P. Schwerdtfeger, H.M. Quiney, *Phys. Rev. Lett.* **84**, 3811 (2000)
28. R.G. Viglione, R. Zanasi, P. Lazzeretti, A. Ligabue, *Phys. Rev. A* **62**, 052516/1 (2000)
29. M. Quack, J. Stohner, *Zeit. Phys. Chem.* **214**, 675 (2000)
30. P. Schwerdtfeger, J.K. Laerdahl, C. Chardonnet, *Phys. Rev. A* (to appear, 2002)
31. O.N. Kompanets, A.R. Kukudzhanov, V.S. Letokhov, L.L. Gervits, *Opt. Commun.* **19**, 414 (1976)
32. F. Swarts, *Bull. Acad. R. Belg.* **26**, 102 (1893)
33. E. Arimondo, P. Glorieux, T. Oka, *Opt. Commun.* **23**, 369 (1977)
34. T.R. Doyle, O. Vogl, *J. Am. Chem. Soc.* **111**, 8510 (1989)
35. J. Costante, L. Hecht, P.L. Polavarapu, A. Collet, L.D. Barron, *Ang. Chem.* **36**, 885 (1997)
36. J. Costante-Crassous, T.J. Marrone, J.M. Briggs, J.A. McCammon, A. Collet, *J. Am. Chem. Soc.* **119**, 3818 (1997)
37. V. Bernard *et al.*, *IEEE J. Quant. Electron.* **QE-33**, 1282 (1997)
38. A. Bauder, A. Beil, D. Luckhaus, F. Müller, M. Quack, *J. Chem. Phys.* **106**, 7558 (1997)
39. T. Marrel, M. Ziskind, C. Daussy, C. Chardonnet, *J. Mol. Struct.* **599**, 195 (2001)
40. A.G. Maki, C.-C. Chou, K. Evenson, L.R. Zink, J.T. Shy, *J. Mol. Spectrosc.* **167**, 211 (1994)
41. A. Shelkovich, C. Grain, C.T. Nguyen, R.J. Butcher, A. Amy-Klein, C. Chardonnet, *Appl. Phys. B* **73**, 93 (2001)

A EUROPEAN JOURNAL

CHEMPHYSICHEM

OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

REPRINT



Left and right are different. The physical and chemical properties of left-handed and right-handed enantiomers are often considered to be strictly identical. In fact, the weak interaction, which is extremely weak at the molecular level, is the only force that induces a difference between left and right (see picture). It is responsible for relative frequency differences of the order of 10^{-14} – 10^{-19} between the molecular spectra. Despite the very small size of the effect, the authors show that the perspective of its observation is not an inaccessible dream anymore. In this context, the resolution of the enantiomers of the simplest chiral molecules such as fluorohalogenomethanes is of great importance.

J. Crassous, F. Monier,
J.-P. Dutasta, M. Ziskind,
C. Daussy, C. Grain,
C. Chardonnet**

541 – 548

**Search for Resolution of Chiral
Fluorohalogenomethanes and
Parity-Violation Effects at the
Molecular Level**

Search for Resolution of Chiral Fluorohalogenomethanes and Parity-Violation Effects at the Molecular Level

Jeanne Crassous,^{*[a]} Franck Monier,^[a] Jean-Pierre Dutasta,^[a] Michaël Ziskind,^[b] Christophe Daussy,^[b] Christophe Grain,^[b] and Christian Chardonnet^{*[b]}

In memory of André Collet

The first observation of a parity-violation effect in molecules induced by weak interactions is still a dream that requires the synthesis and, eventually, the resolution of the enantiomers of well-chosen simple chiral molecules together with an appropriate experimental set-up for high-resolution spectroscopy. Performing IR spectroscopy on highly enantiomerically enriched samples of bromochlorofluoromethane succeeded in giving an upper limit of 10^{-13} for the relative vibrational energy difference between the two enantiomers. These results led us to conceive a new experimental set-up based on a supersonic molecular beam and to work on other chiral molecules, such as chlorofluoroiodomethane. A synthesis of (\pm)-CHClFI from racemic chlorofluoroiodoacetic acid should, in the near future permit the preparation of optically active samples of

this haloform. The development of molecular beam spectroscopy using a two-photon Ramsey-fringes experiment should allow us to reach the precision needed to observe parity violation. These experimental challenges, which stimulate a close collaboration between chemists and physicists, are presented. The success of these projects would open the route to new information on the molecular Hamiltonian, a better knowledge of the electroweak interaction, and a better control of the various chirality-related properties of simple molecules.

KEYWORDS:

chirality · fluorohalogenomethane · IR spectroscopy · laser spectroscopy · parity violation

Introduction

Fluorohalogenomethanes are certainly the simplest chiral molecules containing heavy atoms, and for this reason they represent ideal models for the study of fundamental chirality.^[1, 2] Although bromochlorofluoromethane (**1**), discovered in 1893 by Swarts,^[3] is the most familiar example, the resolution of its enantiomers was a dream for almost one century until the success of Doyle and Vogl in 1989^[4] and the identification of the absolute configuration of the enantiomers by Collet and co-workers in 1997.^[5] Such a simple molecule is highly appreciated by quantum chemists since calculations can be more tractable and also by physicists because many properties become much more favorable experimentally when the number of atoms is low, for example, the partition function. From that point of view, the fascinating problem of the observation of a parity violation (PV) effect in molecules illustrates exactly this purpose. In 1976, V. Letokhov and co-workers suggested that CHBrClF could be an ideal molecule for the observation of a tiny PV effect induced by the weak interaction by looking for a frequency difference in the spectrum of the left- and right-handed species.^[6] Although the effect is expected to be very small, it was suggested that this energy difference between right- and left-handed enantiomers could be at the origin of the symmetry breaking which occurs in living systems. The DNA molecule, with its right-handed double

helix, and L-amino acids, in most naturally-occurring peptides, are the most famous examples of such symmetry breaking.^[7] The PV experiment on CHBrClF proposed by Letokhov required the resolution of the enantiomers since the expected effect is, by far, much smaller than the resolution of any spectrometer and, in fact, smaller than the natural linewidth of the transitions. Thus, this resolution was made possible only very recently. Quantum chemists were then able to evaluate the expected effect on that molecule and found it to be extremely small (a relative frequency difference of a few 10^{-17}); far from the experimental sensitivity but suggesting that heavier fluorohalogenomethanes such as

[a] Dr. J. Crassous, F. Monier, J.-P. Dutasta
Laboratoire de Chimie
UMR CNRS 5532 – École Normale Supérieure de Lyon
46, allée d'Italie, 69364 Lyon cedex 07 (France)
Fax: + (33) 04-72-72-84-83
E-mail: jeanne.crassous@ens-lyon.fr

[b] Professor C. Chardonnet, M. Ziskind, C. Daussy, C. Grain
Laboratoire de Physique des Lasers
UMR 7538 CNRS – Université Paris 13,
99, avenue J.-B. Clément, 93430 Villetaneuse, (France)
Fax: (33) 01-49-40-32-00
E-mail: chardonnet@lpl.univ-paris13.fr

CHEMPHYSICHEM

chlorofluoroiodomethane (2) and bromofluoroiodomethane (3) are more favorable candidates. We have then to reconsider the delicate problem of their synthesis and their resolution. In return, beyond the observation of a PV effect in the spectrum of molecules, which would be a première, this would be also an efficient test of the theoretical models^[8–12] used to calculate PV effects in molecules. Ultimately, this could be an alternative approach to the high-energy and atomic-physics experiments for evaluating and testing the electroweak theory. We wish to report here the progress that has been made in this fields during the last five years, as a result of a fruitful collaboration between organic chemists and physicists (both experimentalists and theoreticians), that is, how chiral halogenomethanes have enabled the dramatic decrease in the upper limit of a measurable PV frequency shift, and why they are still the best substrates in which to observe parity violation.

Parity Violation in Molecules: A Brief History

In 1956, Lee and Yang^[13] predicted that parity should not be conserved in experiments that involved the weak interaction (one of the four fundamental physical forces). One year after, this was experimentally proven by Wu et al.^[14] in their famous ⁶⁰Co β -decay experiment. PV effects were also predicted^[15] and observed in heavy atoms, for instance by measuring a small optical rotation in bismuth,^[16] or in cesium vapors,^[17, 18] and the most precise measurements led to information on the electro-weak model that is very complementary to the high-energy physics experiments. Yamagata^[19] and then Rein^[20] and Gajzago and Marx^[21] were the first to suggest that weak interaction is responsible for an energy difference in the spectrum of right- and left-handed chiral molecules. Due to this interaction, right- and left-handed molecules cease to be exact mirror images of each other. The link with the emergence of homochirality of biomolecules like L- α -aminoacids or D-sugars was also suggested and this idea has stimulated a lot of theoretical works up to today in order to propose mechanisms to explain this enantioselectivity.^[22, 23] In fact, this hypothesis is very controversial and contested. For a review on the subject, see, for example, the recent papers of Bonner and Quack.^[2, 24] The calculation of the PV energy differences is a very difficult problem. Since the first calculations in series of molecules,^[25–28] more realistic theoretical approaches^[29–33] as well as the development of computers permitted the evaluation of this effect more accurately, although the estimation of accuracy is still in debate.^[2] Letokhov first suggested that the PV energy difference between enantiomers of chiral molecules would also manifest itself in the rotational or vibrational spectrum:^[34] for example, due to the weak interaction which does not respect parity, the electronic potentials of right- and left-handed molecules are distorted. As the electronic energies of both species are different, the vibrational frequencies in these slightly nonsymmetric potentials will be also different; an effect which can, in principle, be detected by direct vibrational spectroscopy.

Compound 1 was first proposed by Letokhov and co-workers in 1976^[6] as an ideal candidate on which to measure PV effects, by trying to observe frequency differences in the rovibrational

spectra of the two enantiomers. The main advantages of the molecule for this purpose are: i) the presence of high-Z atoms (the PV effect is expected to vary roughly as Z^5); ii) the small number of atoms, which leads to a more favorable partition function; iii) a strong C–F stretching vibrational band in resonance with CO₂ laser sources, which can be highly frequency stabilized and controlled. However, the optical resolution of CHBrClF was not known at that time and was only achieved in 1989 by Doyle and Vogl.^[4] Before the work that we initiated in 1995 that followed a similar route to that proposed by Letokhov, only one unsuccessful experiment was achieved on camphor^[35] with a relative sensitivity of 10^{-8} , far from the expected size (10^{-18}) of the PV effect.^[36] NMR spectroscopy^[37, 38] was also proposed as a method of observing parity-violating effects and recently, a parity-violation effect may have been observed by using Mössbauer spectroscopy on a chiral iron complex,^[39] although the result seems in contradiction with the theoretical evaluations. We also mention the original proposal of directly measuring the parity-violation energy difference of a chiral molecule in its ground state.^[40] This method, which does not require the resolution of the enantiomers, does need a chiral molecule with an achiral electronic excited state; a severe constraint that has prevented any experiment of this type to date.

A Short History of CHBrClF

Before CHBrClF was suggested as an ideal candidate for a PV experiment, this molecule, one of the simplest chiral molecules, was the subject of a lot of attention.^[1, 2] More than one century ago, Swarts synthesized racemic bromochlorofluoromethane (1) for the first time, by action of a fluorinating agent ($\text{Br}_2 + \text{SbF}_3$) on chlorodibromomethane.^[3, 41, 42] In 1952, Haszeldine used the Hunsdiecker reaction to prepare a series of halogenomethanes, which included (\pm)-CHBrClF, but also (\pm)-CHClFI and (\pm)-CHBrFI.^[43] In 1985, Collet and co-workers reported the preparation of (\pm)-CHBrClF by reaction of dibromochloromethane with HgF_2 .^[44]

The optical resolution of CHBrClF has always been a difficult problem and 100% enantioenriched samples still cannot be obtained in high quantities. In 1971, Hargreaves and Modarai synthesized for the first time (+) and (–)-1 by using the haloform reaction on (+) and (–)-bromochlorofluoroacetone.^[45, 46] The respective optical rotations of (+) and (–)-1 were +0.20 and –0.13 (in cyclohexane). At that time, no method was available to measure the enantiomeric purity of these samples, but, as seen below, they actually corresponded to values of 11% and 7% *ee* (enantiomeric excess) respectively. In 1985, Wilen et al. reported the formation of an inclusion compound with brucine to prepare a sample of (+)-1, which had a specific rotation of 0.128 (neat),^[47] and an *ee* value of 4.3%. The *ee* value could be measured by Collet and co-workers by observing the ¹H NMR of the enantioselective recognition of CHBrClF by cryptophane-C, following a host–guest complexation process.^[44, 48] A value of 1.6 was then obtained for the maximum optical rotation (neat, *d* = 1.91). Finally, in 1989, Doyle and Vogl found an efficient way to prepare enantiomerically enriched CHFClBr with high *ee* values.^[4] The method is based on the highly enantioselective

decarboxylation reaction of resolved samples of the bromochlorofluoroacetate strychninium salt (Figure 1). Indeed, (+) and (-)-bromochlorofluoroacetic acid (BrClFCO₂H) were obtained by crystallization of their diastereomeric strychninium salts.^[49] Then these resolved strychninium salts were decarboxylated in ethyleneglycol at 120 °C and gave (+)-**1** with an *ee* value of 60% and (-)-**1** with an *ee* value of 31%.

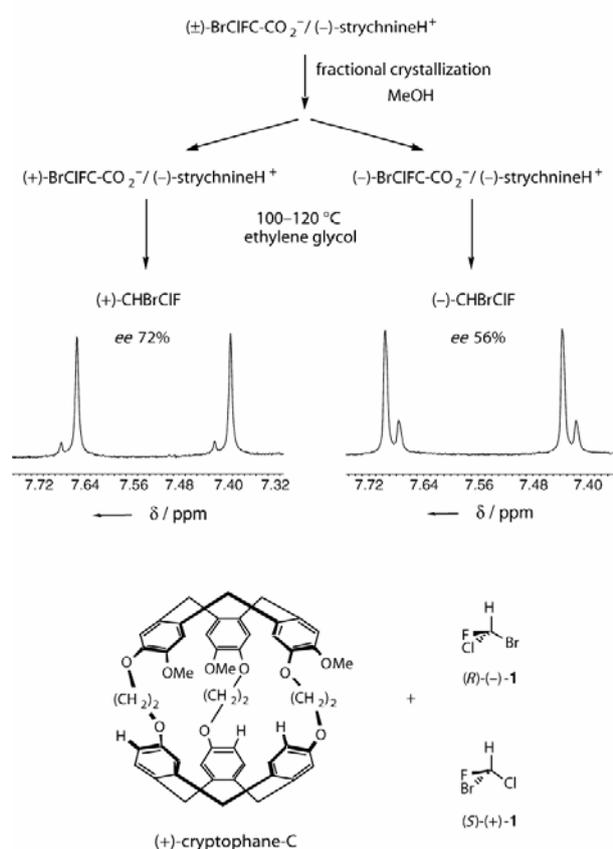


Figure 1. Synthesis of optically active samples of CHBrClF and their *ee* values by 200 MHz ¹H NMR in CDCl₃, using (+)-cryptophane-C as a chiral shift reagent.

The question of the absolute configuration of **1** was investigated by Collet and co-workers in 1997. It was determined in two independent ways. In a first method, the experimental and theoretically calculated (*ab initio*) Raman optical activity (ROA) spectra of CHBrClF were compared, which suggested that the - enantiomer had the *R* configuration.^[50] In a second method, the enantioselective host-guest recognition process between CHBrClF and cryptophane-C was reproduced by computational methods and it was found that the most stable complex was [(*R*)-CHBrClF, (-)-cryptophane-C].^[51] Besides, it was found by ¹H NMR that the most stable complex was [(*-*)-CHBrClF, (-)-cryptophane-C]. Thus, once again, (*R*)-**1** was

identified to be (-)-**1**. For these studies, (*S*)-(+)- and (*R*)-(-)-CHBrClF were prepared by decarboxylation of the strychninium salts of (*S*)-(+)- and (*R*)-(-)-BrClFCO₂H, respectively, according to the procedure of Doyle and Vogl (Figure 1). The maximum optical rotation ($[\alpha]_{D, \max}$) of **1** was found to be 1.78 in cyclohexane. Thanks to the optimization of the resolution of BrClFCO₂H with strychnine, *ee* values of up to 72% and 56% can now be obtained for (+) and (-)-**1**, respectively, after decarboxylation. The *S*,(+) and *R*,(-) absolute configuration of CHBrClF has been confirmed very recently by Polaravapu, who calculated more accurately the optical rotation and the ROA spectrum by using the DFT method.^[51] Bromochlorofluoromethane has also been the object of theoretical calculations that account for the energy difference between the *SS* and *SR* dimers.^[52] The *S*,(+) and *R*,(-) absolute configuration of BrClFCO₂H was determined by X-ray crystallography on the less soluble strychninium salt [(+)-BrClFCO₂H, (-)-strychnine],^[53] establishing the conservation of the stereochemistry during the decarboxylation reaction, as suggested earlier by Schurig et al.^[54] It must also be pointed out that the analytical resolution of CHBrClF by using chiral gas chromatography has also been performed.^[55-57] After initial spectroscopic studies performed in the 1970s,^[58] a more detailed investigation of rotational and rovibrational spectra of CHBrClF using a supersonic pulsed beam and Fourier Transform methods led, 21 years later,^[59] to a complete determination of the rotational and the rovibrational constants of the molecule as well as the quadrupolar constants of the vibrational ground state. The work permitted the identification of a few rovibrational lines in quasi-coincidence with the CO₂ laser lines, which was of great help for the PV experiment presented hereafter. Later on,^[60] we analyzed the quadrupolar hyperfine structure in the ν_4 band of CH⁸¹Br³⁵ClF and CH⁸¹Br³⁷ClF.

First PV Experiments on CHBrClF

The route for a PV experiment on the enantiomers of CHBrClF was thus open, although when we started this program in 1994, the expected amplitude of the PV effect was unknown. A first high sensitivity test of PV could then be performed on (*S*)-(+)- and (*R*)-(-)-CHBrClF, which have, respectively, 56.5 and 22% *ee* values.^[61-63] The purpose of the experiment was to measure a small difference in a selected absorption frequency of the IR spectrum. In the experiment, two twin three-meter-long Fabry-Perot cavities (Figure 2) were used, each filled with one of the two enantiomers of CHBrClF and fed with a frequency-stabilized CO₂ laser. One hyperfine component of the ν_4 C-F stretching fundamental band of CH⁸¹Br³⁷ClF was used to perform the test. Over 580 measurements (see Figure 3a), a mean difference of 3.7 Hz with a standard deviation of 47 Hz, and a final statistical uncertainty of 2 Hz was obtained. Residual systematic effects estimated to be 5 Hz had to be included in the final uncertainty. Finally, the difference between the eigenfrequencies of the two enantiomers were obtained by taking into account the *ee* values of the samples used [Eq. (1)]:

$$\nu_{\text{exp}}(R,(-)) - \nu_{\text{exp}}(S,(+)) = 9.4 \pm 5.1 \pm 12.7 \text{ Hz} \quad (1)$$

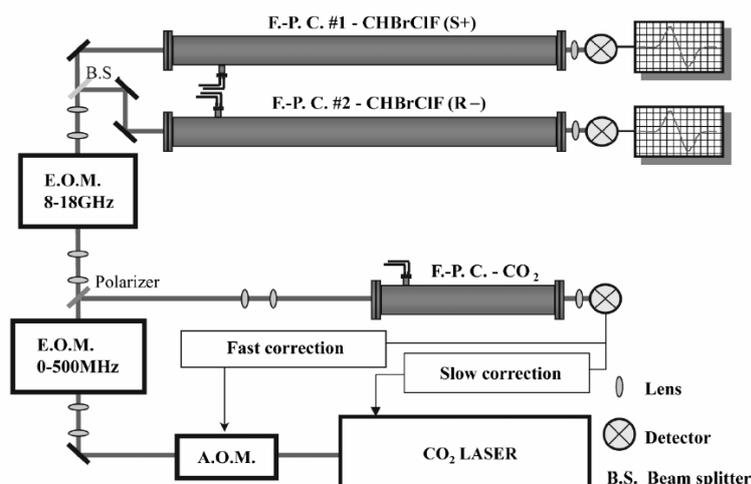


Figure 2. Experimental set-up used for the PV tests on CHFClBr. Spectra of a test molecular line of the enantiomers of CHFClBr are recorded simultaneously by using twin cavities. Residual systematic effects are strongly compensated when we exchange the role of the cavities.

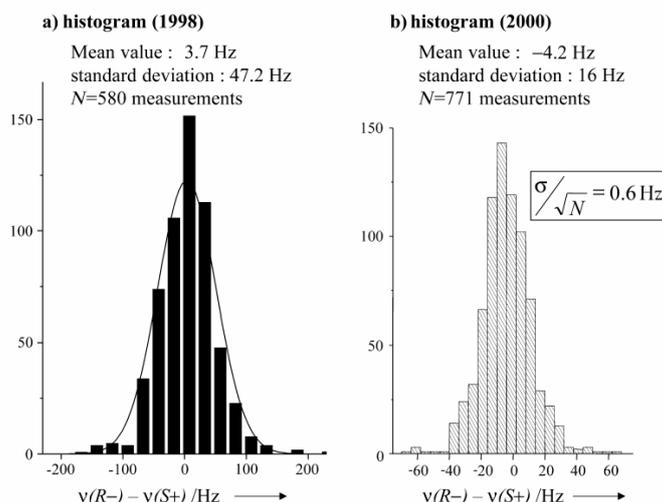


Figure 3. Crude frequency differences $\nu(R(-)) - \nu(S(+))$ obtained for **1** after test, 1998 (a) and test, 2000 (b).

The conclusion was that no PV effect could be observed at a relative sensitivity of $\Delta\nu/\nu = 3.9 \times 10^{-13}$, but an improvement of five orders of magnitude was obtained compared to the previous experiment done on camphor.^[35]

By improving the experimental set-up, selecting a stronger and narrower CHBrClF test line, and using samples of the highest ee values available for (+)- and (-)-**1** (72% and 56%, respectively, evidenced by complexation with chiral cryptophane-C; see Figure 1), a second PV experiment was performed in 2000^[64] over 771 measurements (see Figure 3 b). The final result obtained for the average frequency difference between the lines of the two samples of enantiomers was [Eq. (2)]:

$$\nu_{\text{exp}}(R(-)) - \nu_{\text{exp}}(S(+)) = -4.2 \pm 0.6 \pm 1.6 \text{ Hz} \quad (2)$$

(including statistical and systematic uncertainties due to the instrumentation), which corresponds to a relative sensitivity of $\Delta\nu/\nu = 4 \times 10^{-14}$ for the frequency difference.^[64] ν_{exp} means the observed position of the line. The final frequency difference, high compared to the uncertainties, reveals the influence of collisions under the experimental conditions ($p = 0.1$ Pa) and does not indicate a PV effect. Additional measurements confirmed that less than 5% impurities (for example, residual gases) were likely to be present in the samples and were responsible for uncompensated systematic effects due to collisional shifts. This was clearly shown by a linear pressure dependence of the frequency difference between the two enantiomers, and, thus, a PV effect below 10^{-13} cannot be unambiguously observed by that method.

In parallel to our experimental efforts, several groups published initial quantum-chemistry calculations on the expected vibrational frequency shift in the case of CHFClBr,^[8, 9, 11] which reached convergent conclusions that the PV effect is three orders of magnitude smaller than the present sensitivity.

New Experimental Program

PV Experiments

Consequently, the limit of this experimental set-up using such a chiral molecule has been reached, and a new experiment has to be considered in order to reduce collisional effects drastically. In this context, molecular-beam spectroscopy using a two-photon Ramsey-fringes experiment,^[65, 66] recently developed in Villeta-neuse, seems to be very promising and should allow us to reach a precision of

0.01 Hz on the frequency difference between the two enantiomers. The principle of this experiment is to generate a supersonic beam of chiral molecules which expands in a high-vacuum chamber. Under these conditions, the collisions inside the beam are negligible while the residual pressure in the vacuum chamber is three to four orders of magnitude less than in the twin cavities used in the previous scheme and could be pushed down, if necessary. The main limiting factor will thus be strongly reduced. In this chamber sits or hangs a four-mirror U-shaped Fabry–Perot cavity, fed by a resonant laser beam. The molecular beam interacts with the two standing waves formed by the two arms of the “U”. The laser frequency is in resonance with a Doppler-free two-photon molecular transition (Figure 4). We thus detect the Ramsey fringes by using a probe laser beam

after the second interaction zone. This signal is a sine wave within a Gaussian envelope, exactly centered at resonance and with a periodicity inversely proportional to the time of flight between the two standing waves. With an SF_6 beam (80% SF_6 , 20% He), we obtained a set of fringes with a periodicity of 280 Hz, for a distance between zones of 1 m; an unprecedented resolution at that wavelength of 10 μm . Figure 5 shows a typical Ramsey signal and a CHBrClF signal used for the last PV experiment. The ultrahigh resolution and the good S/N obtained with the beam experiment allows us to hope for a significant breakthrough in the sensitivity of the next PV experiment. For this experiment, we will have to adapt the molecular beam machine in order to be able to produce alternately the right and left molecular beams and to record the corresponding spectra quasimultaneously. This new scheme has several main advantages: first, the optical set up is strictly identical for both kinds of molecules, which should permit a very efficient compensation of most of the systematic effects; second, the resolution is more than two orders of magnitude higher than in the present PV experiment, a fact that is known to be related to much smaller or better-controlled systematic effects.

However, it will be also necessary to change the test molecule since it turns out that the PV effect in the C–F stretching band of CHBrClF is accidentally small and is dominated by the anharmonic part of the vibrational motion;^[9] indeed, accurate relativistic ab initio calculations^[67] were performed on the fluorohalogenomethanes CHBrClF, CBrClFI, CHClFI, and CHBrFI,^[9, 12] and a set of left–right parity-violating differences in frequencies ($\nu(R) - \nu(S)$) were obtained for the C–F stretching fundamental transition and are shown in Table 1.

We will certainly prefer to try a new experiment on CHClFI or CHBrFI. In fact, these results illustrate the single-center theorem pointed out by Hegstrom et al.^[68] that two different nuclei with high electric charges are preferable for a high PV effect. Note that PV effects as large as 10 and 20 Hz were recently calculated for

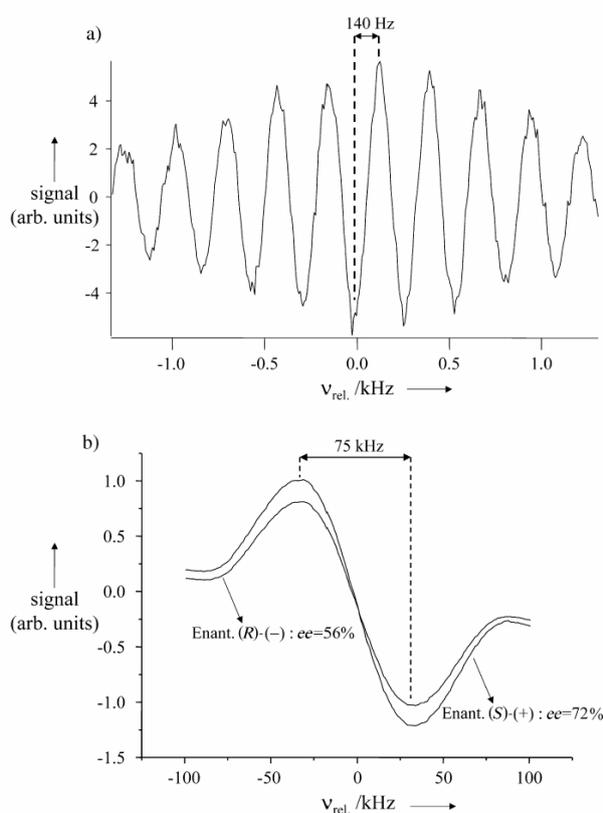


Figure 5. a) Typical Ramsey signal obtained with an interzone of 1 m (two-photon transition of the $P(4)$ E^0 line in the $2\nu_3$ band of SF_6). Note the peak-to-peak width of 140 Hz and the signal-to-noise ratio $(S/N)_{1\text{Hz}}$ of 40; b) comparison with the signal of CHFCIBr ($(37,1,37) \leftarrow (36,0,36)$ and $(37,0,37) \leftarrow (36,1,36)$ rovibrational line of $\text{CHF}^{37}\text{C}^{81}\text{Br}$ @ -12.892 GHz from the 9- μm band $R(24)$ CO_2 laser line) used for the test in 2000: peak-to-peak = 75 kHz, $(S/N)_{1\text{Hz}} = 1000$.

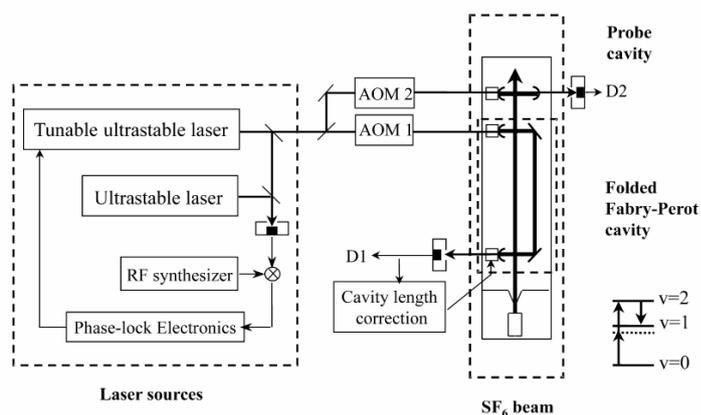


Figure 4. Experimental set-up for the Doppler-free two-photon experiment on a supersonic beam of SF_6 . (AOM: acousto-optic modulator) The molecular beam interacts with the two standing waves generated by a first Fabry–Perot cavity and in resonance with the two-photon transition between the vibrational levels $v=0$ and $v=2$. A probe laser beam detects the population in the $v=2$ level.

BiHBrF and BiHFI ^[69] but the stability and the absorption wavelengths of these molecules make them difficult to use without a totally renewed experiment. Active research is still under progress to find more convenient chiral molecules with a high PV effect, such as chiral compounds containing a heavy metal center, which yield energy shifts of up to $\Delta E_{\text{PV}} = 4.810 \cdot 10^{-14}$ a.u. (300 Hz) for compounds such as $[(\text{C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})\text{I}]$.^[70] In any case, a serious spectroscopic effort will have to be performed in the microwave and in the infrared regions to locate lines to be used for

Table 1. Calculated frequency difference ($\nu(R) - \nu(S)$) of the C–F stretching vibrational mode of a set of chiral fluorohalogenomethanes according to refs. [9, 12]; the differences are given in mHz

CHFCIBr	CFCIBrI	CHFCII	CHFBrl
1.7	11.7	23.7	50.8

the experiment. In fact, the synthesis and the resolution of these molecules is most challenging.

Resolution of New Fluorohalogenomethanes

Iodinated fluorohalogenomethanes seem to be more promising molecules for the observation of PV effects than CHBrClF. However, except CHBrClF, the resolution of other fluorohalogenomethanes is still not known. For this reason, we are now focused on the synthesis of iodinated halogenomethanes in a way that could enable us to obtain them enantiomerically enriched. Consequently, we were inspired by the synthesis of optically active **1** to perform the synthesis of racemic chlorofluoroiodomethane (\pm)-CHClFI (**2**). This compound was synthesized by Haszeldine in 1952,^[43] by using the Borodine–Hunsdiecker reaction, using I₂ on ClFHCCO₂H and more recently by Li and co-workers,^[71, 72] by action of HgF₂ on diiodochloromethane. In our turn, we could recently prepare (\pm)-**2** from chlorofluoroiodoacetic acid (**3**), by decarboxylation of its strychninium salt.^[73] ClFICCO₂H was synthesized in four steps from chlorotrifluoroethylene and then its strychninium salt was decarboxylated in triethyleneglycol (TEG) at 130 °C, giving (\pm)-**2** in 42% yield (Scheme 1). This synthesis opens up the possibility to resolve **3** by crystallization of the diastereomeric salts formed from a chiral amine (such as strychnine or others) and to subsequently decarboxylate the resolved ammonium salt to form optically active **1**. However, the low stability of these iodinated compounds will probably make the resolution step hazardous. Meanwhile, interesting results have been obtained concerning the chiral recognition of (\pm)-CHClFI with chiral cryptophanes such as cryptophane-E-(SCH₃)₆^[74] (see Figure 6). Following the procedure described above for CHBrClF with cryptophane-C, diastereomeric complexes [(+)-CHClFI, (+)-cryptophane] and [(–)-CHClFI, (+)-cryptophane] or their respective enantiomers, were characterized by ¹⁹F NMR. Figure 6 shows that the cryptophane can be used as an NMR chiral shift reagent,

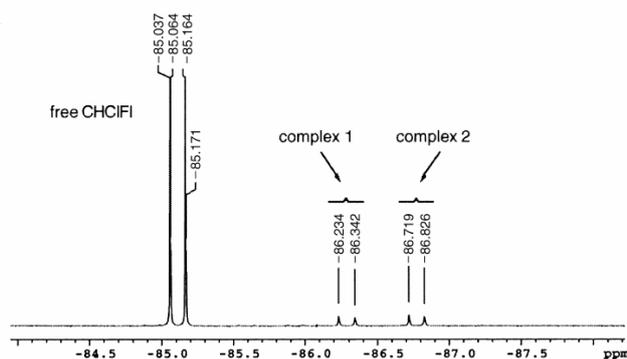
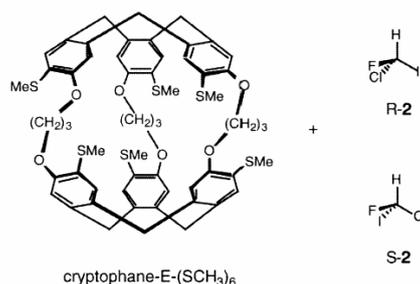


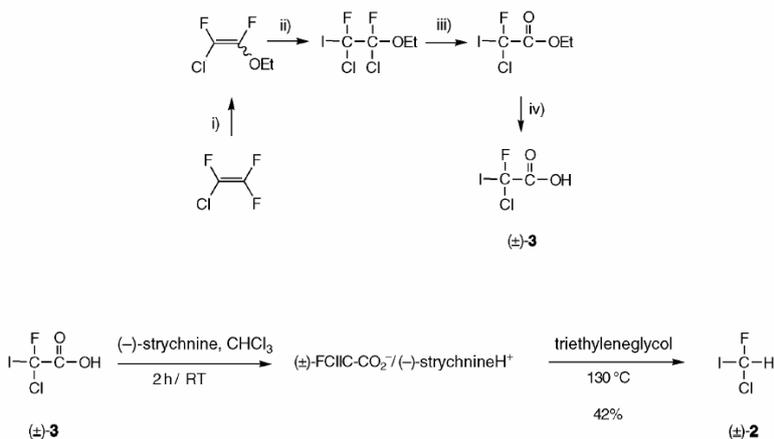
Figure 6. ¹⁹F NMR spectrum of (\pm)-CHClFI with cryptophane-E-(SCH₃)₆ at 471 MHz, in C₂D₂Cl₄ at 298 K.

which will be useful for the determination of the enantiomeric purity of resolved samples of CHClFI.

Conclusions and Perspectives

The almost 30-years-old dream of observing a parity-violation effect in the spectra of chiral molecules is still not a reality. However, since the proposal of Letokhov to use chiral fluorohalogenomethanes to observe such an effect, and after two decades with no experimental attempt, several steps have been cleared during the last period. The efficient resolution of CHBrClF was achieved and the first series of experiments pushed the relative sensitivity of the frequency difference for the two enantiomers to the level of 10⁻¹³. In parallel, this progress stimulated several ab initio calculations of the PV effect, corresponding precisely to the kind of experiments that we can perform.

This conjunction of efforts of physicists and chemists, experimentalists and theoreticians during these recent years, although it did not lead to the observation of a PV effect in molecules, highly clarified the horizon. We developed an experimental method with the highest sensitivity (10⁻¹³) ever reached for this problem. In



Scheme 1. Synthesis of racemic CHClFI. i) EtONa, Et₂O; ii) ICl, CH₂Cl₂; iii) conc. H₂SO₄; iv) aq. NaOH then H₂SO₄.

addition, we identified clearly the sources of limitation and proposed an experiment of second generation which should overcome the uncertainties due to the residual impurity of the samples. By contrast to some proposals (Mössbauer and NMR spectroscopy), the experimental situation corresponds to isolated molecules. This simplifies the theoretical analysis. In fact, the spectacular progresses of the quantum chemistry calculations, partly stimulated by this work, can now provide probably reliable predictions for various molecules with heavy atoms, which should be of great help before preparing such a heavy experimental program.

The observation of an unambiguous parity-violation effect in the spectrum of molecules has become now accessible. Beyond the sum of taken up challenges that would represent such a success, measuring a parity violation effect by a spectroscopic method would be a première. We can expect several fallouts of such an observation: a test of the molecular Hamiltonian, first of all the PNC Hamiltonian but also the hyperfine Hamiltonian which has strong similarities. Even if this is a longer-term and still uncertain objective, this may open an alternative route for testing the electroweak force. A relative precision on the PV frequency difference of 1% has to be reached for this purpose. Fortunately, the methods of frequency measurements, which lead to the most precise experiments in physics, keep being improved and new significant progress from the present stage should be made in the near future. The second main condition is the knowledge of the molecular Hamiltonian. The present PV ab initio relativistic calculations are performed with a conservative 10–20% uncertainty.^[75] To obtain even higher accuracy at the theoretical level needs some major program coding and a few years of effort to reach the precision of atomic physics. Such a theoretical investment could be stimulated by precise experimental results.

Finally, from the chemical point of view, the study of fluorohalogenomethanes deals with many other aspects of chirality: the resolution of small chiral molecules, their enantioselective recognition with chiral hosts, the determination of their absolute configuration, and the study of their chiroptical properties are the most important.

Let us remind the readers that Ch. J. Bordé initiated preliminary spectroscopic work on CHFCIBr and CHFCII in 1980 in Villetaneuse, although the resolution of the enantiomers was not successful at that time, which blocked the project for 15 years. We thank also T. Marrel and A. Amy-Klein for their contributions at the beginning of this project. We thank Peter Schwerdtfeger for fruitful exchanges during the preparation of this paper and the referees for helping us in improving it.

- [1] J. Crassous, A. Collet, *Enantiomer* **2000**, *5*, 429–438.
 [2] M. Quack, *Angew. Chem.* **2002**, *114*, 4812–4825; *Angew. Chem. Int. Ed.* **2002**, *41*, 4618–4630.
 [3] F. Swarts, *Bull. Acad. R. Belg.* **1893**, *26*, 102–106.
 [4] T. R. Doyle, O. Vogl, *J. Am. Chem. Soc.* **1989**, *111*, 8510–8511.
 [5] J. Costante-Crassous, T. J. Marrone, J. M. Briggs, J. A. McCammon, A. Collet, *J. Am. Chem. Soc.* **1997**, *119*, 3818–3823.

- [6] O. N. Kompanets, A. R. Kukudzhanov, V. S. Letokhov, L. L. Gervits, *Opt. Comm.* **1976**, *19*, 414–416.
 [7] M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, *Tetrahedron Asymmetry* **2000**, *11*, 2845–2874.
 [8] M. Quack, J. Stohner, *Phys. Rev. Lett.* **2000**, *84*, 3807–3810.
 [9] J. K. Laerdahl, P. Schwerdtfeger, H. M. Quiney, *Phys. Rev. Lett.* **2000**, *84*, 3811–3814.
 [10] M. Quack, J. Stohner, *Zeit. Phys. Chem.* **2000**, *214*, 675–703.
 [11] R. G. Viglione, R. Zanasi, P. Lazzeretti, A. Ligabue, *Phys. Rev. A* **2000**, *62*, 052516/052511–052515.
 [12] P. Schwerdtfeger, J. K. Laerdahl, C. Chardonnet, *Phys. Rev. A* **2002**, *65*, 0425081–0425087.
 [13] T. D. Lee, C. N. Yang, *Phys. Rev.* **1956**, *104*, 254–258.
 [14] C. S. Wu, E. Ambler, R. W. Hayward, D. D. Hoppes, R. P. Hudson, *Phys. Rev.* **1957**, *105*, 1413–1415.
 [15] M. A. Bouchiat, C. C. Bouchiat, *Phys. Lett.* **1974**, *48B*, 111–114.
 [16] L. M. Barkov, M. S. Zolotarev, *JETP* **1980**, *52*, 360–376.
 [17] M. A. Bouchiat, C. C. Bouchiat, *Rep. Prog. Phys.* **1997**, *60*, 1351–1396.
 [18] C. S. Wood, S. C. Bennett, D. Cho, B. P. Masterson, J. L. Roberts, C. E. Tanner, C. E. Wieman, *Science* **1997**, *275*, 1759–1763.
 [19] Y. Yamagata, *J. Theoret. Biol.* **1966**, *11*, 495–498.
 [20] D. W. Rein, *J. Mol. Evol.* **1974**, *4*, 15–22.
 [21] E. Gajzago, G. Marx, *Atomki Kozlemenkev* **1974**, *Suppl. 16/2*, 177–184.
 [22] S. F. Mason, *Nature* **1984**, *311*, 19–23.
 [23] D. K. Kondepudi, G. W. Nelson, *Nature* **1985**, *314*, 438–441.
 [24] W. Bonner, *Chirality* **2000**, *12*, 114–126.
 [25] B. Y. Zel'dovich, D. B. Saakyan, I. I. Sobel'man, *JETP Lett.* **1977**, *25*, 94–97.
 [26] G. E. Tranter, *Mol. Phys.* **1985**, *56(4)*, 825–838.
 [27] G. E. Tranter, A. J. MacDermott, R. E. Overill, P. J. Speers, *Proc. R. Soc. Lond. A* **1992**, *436*, 603–615.
 [28] M. Quack, *J. Mol. Struct.* **1993**, *292*, 171–195.
 [29] A. Bakasov, T.-K. Ha, M. Quack, in *Proceedings of 4th Trieste Conference, Trieste, 1995*, (Eds. J. Chela-Flores, F. Raulin) Kluwer, Dordrecht, Trieste, **1995**, pp. 287–296.
 [30] P. Lazzeretti, R. Zanasi, *Chem. Phys. Lett.* **1997**, *279*, 349–354.
 [31] A. Bakasov, T.-K. Ha, M. Quack, *J. Chem. Phys.* **1998**, *109*, 7263–7285.
 [32] J. K. Laerdahl, P. Schwerdtfeger, *Phys. Rev. A* **1999**, *60*, 4439–4453.
 [33] A. C. Hennum, T. Helgaker, W. Klopper, *Chem. Phys. Lett.* **2002**, *354*, 274–282.
 [34] V. S. Letokhov, *Phys. Lett.* **1975**, *53A*, 275–277.
 [35] E. Arimondo, P. Glorieux, T. Oka, *Opt. Comm.* **1977**, *23*, 369–372.
 [36] P. Schwerdtfeger, A. Kühn, R. Bast, J. K. Laerdahl, F. Faglioni, P. Lazzeretti, unpublished results.
 [37] A. L. Barra, J. B. Robert, L. Wiesenfeld, *Phys. Lett. A* **1986**, *115*, 443–447.
 [38] A. L. Barra, J. B. Robert, *Mol. Phys.* **1996**, *88*, 875–886.
 [39] A. S. Lahamer, S. M. Mahurin, R. N. Compton, D. House, J. K. Laerdahl, M. Lein, P. Schwerdtfeger, *Phys. Rev. Lett.* **2000**, *85*, 4470–4473.
 [40] M. Quack, *Phys. Lett.* **1986**, *132*, 147–153.
 [41] F. Swarts, *Bull. Acad. R. Belg.* **1896**, *31*, 25–28.
 [42] F. Swarts, *Mémoires Couronnés* **1896**, *54*, 1–26.
 [43] R. N. Haszeldine, *J. Chem. Soc.* **1952**, 4259–4267.
 [44] J. Canceill, L. Lacombe, A. Collet, *J. Am. Chem. Soc.* **1985**, *107*, 6993–6996.
 [45] M. K. Hargreaves, B. Modarai, *J. Chem. Soc. C* **1971**, 1013–1015.
 [46] M. K. Hargreaves, B. Modarai, *J. Chem. Soc. D* **1969**, *16*, 458.
 [47] S. H. Wilen, K. A. Bunding, C. M. Kascheres, M. J. Wieder, *J. Am. Chem. Soc.* **1985**, *107*, 6997–6998.
 [48] For more details about the chirality of cryptophanes see: J. Canceill, A. Collet, G. Gottarelli, P. Palmieri, *J. Am. Chem. Soc.* **1987**, *109*, 6454–6464.
 [49] T. R. Doyle, O. Vogl, *Polymer* **1991**, *32*, 751–760.
 [50] J. Costante, L. Hecht, P. L. Polavarapu, A. Collet, L. D. Barron, *Angew. Chem.* **1997**, *109*, 917–919; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 885–887.
 [51] P. L. Polavarapu, *Angew. Chem.* **2002**, *114*, 4544–4546; *Angew. Chem. Int. Ed.* **2002**, *41*, 4544–4546.
 [52] T. P. Radhakrishnan, S. Topiol, P. U. Biedermann, S. Garten, I. Agranat, *Chem. Commun.* **2002**, 2664–2665.
 [53] J. Costante, N. Ehlinger, M. Perrin, A. Collet, *Enantiomer* **1996**, *1*, 377–386.
 [54] V. Schurig, M. Juza, B. J. Green, J. Horakh, A. Simon, *Angew. Chem.* **1996**, *108*, 1814–1816; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1680–1682.
 [55] A. Beil, D. Luckhaus, R. Marquardt, M. Quack, *Faraday Discuss.* **1994**, *99*, 49–76.

- [56] H. Grosenick, V. Schurig, J. Costante, A. Collet, *Tetrahedron Asymmetry* **1995**, *6*, 87–88.
- [57] A. Beil, D. Luckhaus, M. Quack, *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 1853–1875.
- [58] M. Diem, D. F. Burow, *J. Chem. Phys.* **1976**, *64*, 5179–5185.
- [59] A. Bauder, A. Beil, D. Luckhaus, F. Müller, M. Quack, *J. Chem. Phys.* **1997**, *106*, 7558–7570.
- [60] T. Marrel, M. Ziskind, C. Daussy, C. Chardonnet, *J. Mol. Struct.* **2001**, *599*, 195–209.
- [61] C. Chardonnet, C. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, C. J. Bordé, in *Parity violation in atomic physics and electron scattering*, (Eds.: B. Frois, M. A. Bouchiat), World Scientific, New York, **1999**, pp. 325–355.
- [62] C. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, C. J. Bordé, C. Chardonnet, *Phys. Rev. Lett.* **1999**, *83*, 1554–1557.
- [63] C. Chardonnet, T. Marrel, M. Ziskind, C. Daussy, A. Amy-Klein, C. J. Bordé, *J. Phys. IV (France)* **2000**, *10-Pr8*, 45–54.
- [64] M. Ziskind, T. Marrel, C. Daussy, C. Chardonnet, *Eur. Phys. J. D* **2002**, *20*, 219–225.
- [65] A. Amy-Klein, L. F. Constantin, R. J. Butcher, G. Charton, C. Chardonnet, *Phys. Rev. A* **2000**, *63*, 0134041–0134048.
- [66] A. Shelkovich, C. Grain, C. T. Nguyen, R. J. Butcher, A. Amy-Klein, C. Chardonnet, *Appl. Phys. B* **2001**, *73*, 93–98.
- [67] J. Thyssen, J. K. Laerdahl, P. Schwerdtfeger, *Phys. Rev. Lett.* **2000**, *85*, 3105–3108.
- [68] R. A. Hegstrom, D. W. Rein, P. G. H. Sandars, *J. Chem. Phys.* **1980**, *73*, 2329–2341.
- [69] F. Faglioni, P. Lazzeretti, to appear in *Phys. Rev. A* **2003** *67*, 032101-1-4.
- [70] P. Schwerdtfeger, J. Gierlich, T. Bollwein, *Angew. Chem.* **2003**, *115*, 1331–1334; *Angew. Chem. Int. Ed.* **2003**, *42*, 1293–1296.
- [71] I. Novak, D. B. Li, A. W. Potts, *J. Phys. Chem. A* **2002**, *106*, 465–468.
- [72] D. B. Li, S. C. Ng, I. Novak, *Tetrahedron* **2002**, *58*, 5923–5926.
- [73] The strychninium salt of chlorofluoroiodoacetic acid (3.3 g, 5.8 mmol) was decarboxylated by heating at 130 °C in triethyleneglycol (18 mL) for 3 h. (\pm)-**2** was collected as a colorless liquid in a cold trap at –78 °C (0.473 g, 42%). ¹H NMR (200 MHz, 298 K, CDCl₃) δ = 7.62 (d, ²J_{HF} = 50.2 Hz); ¹³C NMR (50.4 MHz, 298 K, CDCl₃) δ = 55.04 (d, ¹J_{CF} = 308.4 Hz); ¹⁹F NMR (188.2 MHz, 298 K, CDCl₃; CFCl₃ as internal reference) δ = –86.99 (d, ²J_{HF} = 50.2 Hz); ¹⁹F NMR (188.2 MHz, 298 K, CDCl₃; CF₃CO₂H as internal reference) δ = –11.03 (d, ²J_{HF} = 50.3 Hz).
- [74] C. Garcia, D. Humilière, N. Riva, A. Collet, J.-P. Dutasta, *Org. Biomol. Chem.* **2003**, in press.
- [75] P. Schwerdtfeger, *personal communication* **2002**.

Received: October 11, 2002 [M536]

Revised: February 19, 2003

A. AMY-KLEIN^{1,✉}
 A. GONCHAROV^{1,*}
 C. DAUSSY¹
 C. GRAIN¹
 O. LOPEZ¹
 G. SANTARELLI²
 C. CHARDONNET¹

Absolute frequency measurement in the 28-THz spectral region with a femtosecond laser comb and a long-distance optical link to a primary standard

¹ LPL, Laboratoire de Physique des Lasers, UMR 7538 CNRS, Université Paris 13, 99, avenue J.-B. Clément, 93430 Villetaneuse, France

² BNM-SYRTE, UMR 8630 CNRS, Observatoire de Paris, 61 avenue de l'Observatoire, 75014 Paris, France

Received: 13 May 2003/Revised version: 17 September 2003
 Published online: 18 November 2003 • © Springer-Verlag 2003

ABSTRACT A new frequency chain was demonstrated to measure an optical frequency standard based on a rovibrational molecular transition in the 28-THz spectral region accessible to a CO₂ laser. It uses a femtosecond-laser frequency comb generator and two laser diodes at 852 nm and 788 nm as intermediate oscillators, with their frequency difference phase locked to the CO₂ laser. The rf repetition rate of the femtosecond laser was compared with a 100-MHz signal from a hydrogen maser, located at BNM-SYRTE. The 100-MHz signal is transmitted by amplitude modulation of a 1.55- μ m laser diode through a 43-km telecommunication optical fibre. As a first example, the absolute measurement of a saturation line of OsO₄ in the vicinity of the P(16) laser line of CO₂ is reported with a relative uncertainty of 10⁻¹², limited by the CO₂/OsO₄ frequency day-to-day reproducibility. The current limit on the stability of the frequency measurement is 4 \times 10⁻¹³ at 1 s.

PACS 06.20.-f; 42.62.Eh; 06.30.Ft

1 Introduction

Until recently, the measurement of the absolute frequency of an optical frequency standard required a complex and expensive set-up, as developed in only a few specialised metrological laboratories. In 1999, for the first time, a femtosecond laser comb generator was used for an absolute frequency measurement [1]. This much simpler technique is very attractive and saw a large development in many laboratories all around the world (see for instance the review articles [2–4]). A primary frequency standard is still needed for these measurements: a Cs clock, a Rb clock or a H maser, the frequency of which is compared to TAI (Temps Atomique International or International Atomic Time).

Here we describe the first absolute frequency measurement performed with a femtosecond laser and using a reference-frequency signal transmitted from the BNM-SYRTE laboratory at the Paris Observatory. This signal is

transmitted from SYRTE to LPL through a standard telecommunication optical fibre of length 43 km. It is controlled with the H maser and the Cs fountain from SYRTE. Also, for the first time, a 28-THz optical frequency is measured with the direct 25-THz-wide (FWHM) comb of a Ti:Sa laser. This requires nonlinear optical generation to transfer this frequency to the near-infrared region. This new measurement method gives us the possibility to reach a relative accuracy much better than can be obtained with a GPS receiver or a Rb clock for an averaging time as short as a few s.

The first application consisted in measuring the CO₂ laser at 10 μ m locked to a saturated absorption line of the molecule OsO₄. Since 1997, a set of CO₂/OsO₄ secondary standards are recommended for the 'mise en pratique du mètre' [5]. They had a preferential role in frequency measurement, because such infrared frequencies are intermediate between the Cs-clock primary standard and the visible optical clocks. They were used as references for many optical measurements, which could now be usefully verified with this new method. CO₂/OsO₄ frequency standards can also be used to calibrate a large variety of molecular spectra: for example the widely used frequency grid of CO₂ laser lines has been partly obtained from frequency measurement with respect to the OsO₄ lines [6].

2 The CO₂/OsO₄ frequency standard

The CO₂/OsO₄ stabilisation set-up was developed a few years ago for high-resolution molecular spectroscopy, high-precision measurement and fundamental physics. Figure 1 displays the OsO₄ frequency stabilisation system, which was already described in detail in [7]. It consists in a CO₂ laser stabilised onto a saturation signal detected in transmission of a Fabry–Perot cavity filled with OsO₄ [8]. A crucial component of the stabilisation scheme is a broadband CdTe electro-optic modulator (EOM), which generates sidebands, one of which is tuned into resonance with the molecular line. Efficient and pure frequency modulations can then be applied to the sidebands simply by modulating the frequency of the synthesiser, which drives the EOM. The cavity resonance is locked to the sideband frequency and a second servo-loop then locks the EOM sideband to the molecular line. Standard conditions for the detection of the OsO₄ saturated absorp-

✉ Fax: +33-(0)1-49-40-32-00, E-mail: amy@galileo.univ-paris13.fr

*Permanent address: Institute of Laser Physics, Novosibirsk, Russia, Fax: +7-3832-33-20-67

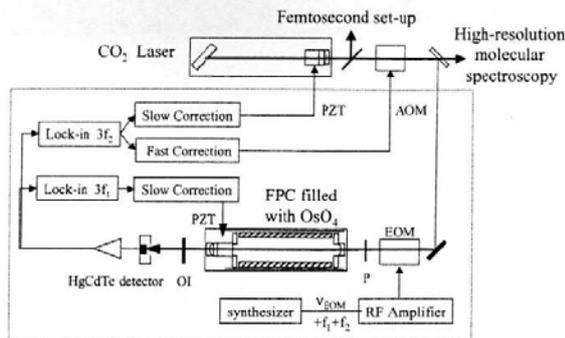


FIGURE 1 Experimental arrangement for the CO_2/OsO_4 stabilisation, OI: optical isolator, P: polariser, FPC: Fabry-Perot cavity, PZT: piezoelectric transducer, AOM: acousto-optic modulator

tion signal are a pressure of 0.04 Pa and a laser power of $50 \mu\text{W}$ inside the cavity. In this regime, the third harmonic of the molecular signal has a peak-to-peak line width of about 20 kHz and the signal-to-noise ratio is 500 in a bandwidth of 1 kHz. Two equivalent and independent systems have been developed to characterise the frequency stability. By stabilising both lasers onto the same strong $P(46) A_1^2(-) \text{OsO}_4$ line in coincidence with the $P(14) \text{CO}_2$ laser line we obtained an Allan deviation of $3.5 \times 10^{-14} \tau^{-1/2}$ for an integration time between 1 and 100 s, and a reproducibility of a few tens of Hz.

3 The optical link between LPL and BNM-SYRTE

The LPL is located in the surroundings of Paris, whereas in the centre of Paris the SYRTE develops cold atoms frequency standards in the microwave domain. Their Cs atomic fountain has a demonstrated accuracy of 10^{-15} and a frequency stability of $5 \times 10^{-14} \tau^{-1/2}$ [9]. They have developed an internal reference signal at 100 MHz, which is distributed around their whole laboratory for various metrological experiments. Its stability is given by a H maser, Allan deviation in Fig. 3, and the accuracy is controlled either with the Cs fountains or with a comparison to the local time scale and with GPS. Typical accuracy of the 100-MHz signal is below 10^{-14} .

It was very attractive to take advantage of this excellent reference for our measurements. Following what was done on the 3 km between SYRTE and Laboratoire Kastler-Brossel (LKB) [10], two optical links have been developed to transmit the 100-MHz signal from SYRTE to LPL. Interconnecting many different sections of existing standard single-mode optical fibres results in two close optical links of 43 km, which is much larger than the physical distance between the two laboratories of 13 km. At the few tens of network interconnection points the fibres were fused to ensure the continuity of the link. Optical time domain reflectometry measurement of one of the two link fibres has been performed, giving a one-way attenuation of about 10 dB at 1.55- μm wavelength.

The complete optical link includes a distributed feedback (DFB) semiconductor laser, emitting at 1.55 μm , and a p-i-n photodiode. The current of the laser is modulated at 100 MHz directly controlled by the H maser. The amplitude modula-

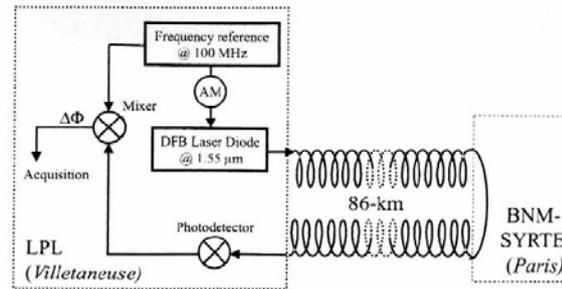


FIGURE 2 Experimental set-up for the characterisation of the phase noise of the optical link. LPL and BNM-SYRTE are the two laboratories involved in this experiment, AM: amplitude modulation; DFB: distributed feedback

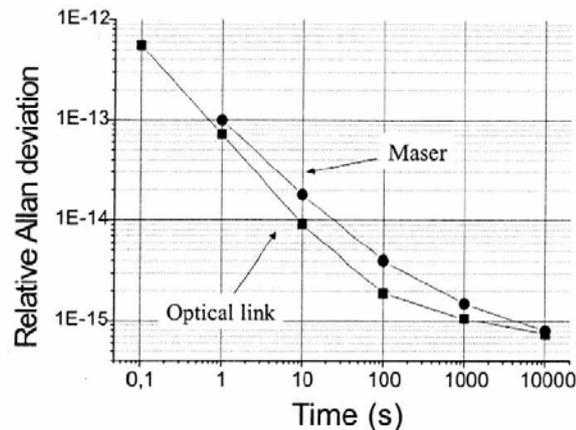


FIGURE 3 Allan deviation for the maser (circles) and the round-trip optical link (squares), as recorded along a period of 5 d

tion is then converted back into the electrical domain by the photodetector at the output of the link [11].

This optical link must not degrade the spectral quality of the metrological signal, while the background noise could impact on the 100-MHz stability along the 43-km propagation. The fibres are sensitive to both the mechanical stress and the temperature variations. The first affects the phase noise performances of the link and the short-term frequency stability; the second is a slow change of the optical length of the fibre, and impacts on the long-term stability. The metrological features of this link were measured by a complete round trip (86 km) of the 100-MHz signal as shown in Fig. 2. The phase difference between the input and return signals was detected and its variation was analysed in terms of frequency fluctuations. The Allan deviation (square root of the Allan variance) is reported in Fig. 3. This gives an upper limit for the Allan deviation for a one-way pass¹. On the same graph is depicted the Allan deviation of the H maser, which exhibits greater deviation. This demonstrates that the optical link does not degrade the perform-

¹ The time scale of Fig. 3 is larger than the round-trip propagation time of 0.5 ms, and the corresponding phase fluctuations for the two ways are thus strongly correlated. If phase noise is dominant against amplitude noise, the one-way Allan deviation can be deduced as half of the two-way pass.

ance characteristics of the H-maser reference frequency for measurement times below 10 000 s. A complete characterisation of the phase noise introduced by the optical link is in progress.

This signal is then used at LPL to phase lock a low phase noise quartz oscillator at 5 MHz with an Allan deviation of 5×10^{-13} from 1 to 100 s. The servo bandwidth is a few Hz, in order to filter out the high-frequency phase noise of the optical link. The quartz second harmonic at 10 MHz is then distributed through the laboratory and is used as an external reference clock for all the rf synthesisers and the counter involved in the frequency measurements. This 10-MHz signal reproduces the frequency stability of the 100-MHz received signal for an integration time longer than 1 s. Its frequency stability is estimated as a few 10^{-13} for 1 s.

4 Comparison of the 28-THz CO₂/OsO₄ standard and the primary standard with a fs laser comb

4.1 Principle of the frequency measurement

The principle of frequency measurements with a femtosecond laser comb has already been widely described [3, 4]. The emission spectrum of a mode-locked femtosecond laser is composed of modes which are spaced by the laser repetition rate f_r (around 1 GHz in our case). It has been demonstrated that this space f_r is constant from one side to the other side of the spectrum at a level better than 3×10^{-17} [3]. This fundamental property permits us to use the femtosecond comb as a 'frequency ruler'. The comb width is proportional to the inverse of the pulse duration. The frequency of one mode is of the form: $f_n = n \times f_r + f_0$, where n is an integer and f_0 the offset of the frequency comb. A first method of measurement consists in recording the beat note between this comb and the optical frequency f to be measured: $b = f - f_n = f - (n \times f_r + f_0)$. Accurate measurements of f_r and f_0 , and the determination of n , are needed to complete the frequency measurement.

Here we proceed in a quite different way because no direct beat note can be observed between the CO₂ laser emitting at 10 μm , that is at 28 THz, and the frequency comb centred at 800 nm. We take advantage of the fact that the comb frequency width is larger than the CO₂ frequency. Then the CO₂ frequency can be compared to the frequency difference $(n - m) f_r$ between two modes. This method avoids any measurement of f_0 , which simplifies the experimental arrangement [4]. The CO₂-laser frequency must just be transferred to the spectral range of the comb. A similar way is used in [12] to build up a scheme to measure the frequency of a He-Ne/CH₄ standard.

The measurement set-up is depicted in Fig. 4. Two laser diodes emit at 852 nm and 788 nm and their frequency difference is phase locked to the CO₂ laser with an offset Δ_0 : $f(\text{CO}_2/\text{OsO}_4) + \Delta_0 = f(788 \text{ nm}) - f(852 \text{ nm})$. Then, the beat notes Δ_1 and Δ_2 of these intermediate oscillators with the lower and upper parts of the femtosecond laser comb are detected and controlled. In fact, a very high harmonic of the repetition rate (about the 28 000th) is phase locked to the CO₂-laser frequency: $f(\text{CO}_2/\text{OsO}_4) + \Delta_0 - \Delta_1 - \Delta_2 = p \times f_r$. Finally, the repetition rate is measured with respect to the H-

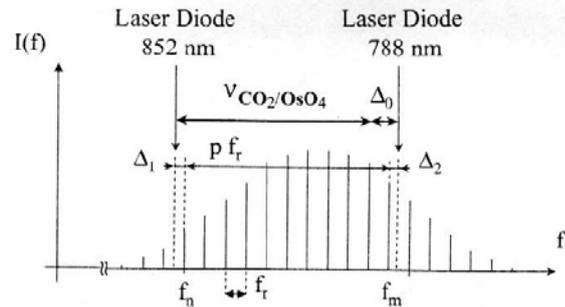


FIGURE 4 Principle of the frequency measurement

maser reference signal and the CO₂/OsO₄ absolute frequency is deduced.

4.2 Experimental set-up

A scheme of the experimental set-up is displayed in Fig. 5.

The femtosecond Ti:Sa laser (GigaJet from GigaOptics) has a repetition rate of ~ 1 GHz and emits 550 mW around 800 nm for 5 W of pumping power. Its emission spectrum spans 25 THz (FWHM) from 775 nm to 825 nm.

The laser diodes LD1 and LD2 emit respectively at 852 nm and 788 nm, and are in an extended cavity configuration. LD1 is tuned to the Cs D₂ resonance transition, for a simple and easy check of its frequency. An AgGaS₂ crystal is used to generate the sum-frequency (SF) of the CO₂ laser and LD1, in a type I angular phase-matching scheme [13]. By coupling 20 mW at 852 nm and 80 mW at 10 μm , about 1.5 μW of sum-frequency radiation at 788 nm is obtained (efficiency $\approx 1 \text{ mW/W}^2$). Since this power is very small, LD2 is used as an optical tracking oscillator: the SF radiation is separated from the incident beams with a polarisation beam splitter and mixed with the output of LD2. The frequency of LD2 is set to the sum-frequency with the help of a lambda meter.

Finally, the two beat notes Δ_1 and Δ_2 of LD1 and LD2 with the femtosecond laser comb are detected after spectral filtering with a 1200-line/mm grating. The signal-to-noise ratios are respectively 35 dB (LD1) and 45 dB (LD2) in a bandwidth of 100 kHz.

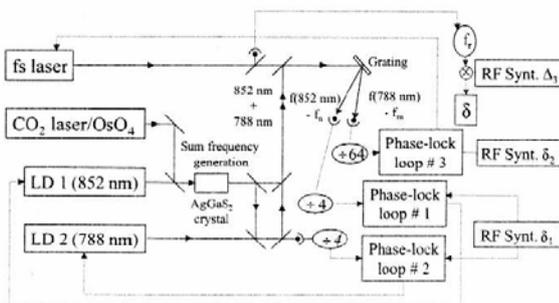


FIGURE 5 Experimental set-up. Optical beams are symbolised with solid lines, electronic connection with dotted lines. LD: laser diodes; RF synt.: radio-frequency synthesisers

4.3 Measurement procedure

The beat note between LD1 and the n th mode of the comb (frequency f_n) is phase locked to a rf synthesiser (phase-lock loop #1 in Fig. 5): $f_n - f(\text{LD1}) = \pm\Delta_1$. Corrections are applied both to the laser diode current and to a PZT controlling the length of the extended cavity. Then the beat note between the SF and LD2 is phase locked to the same rf synthesiser and corrections are applied to LD2 (phase-lock loop #2): $f(\text{LD2}) - f(\text{SF}) = \pm\Delta_0 \equiv \mp\Delta_1$. Finally, the beat note between LD2 and the comb (the m th mode) is phase locked to a second rf synthesiser (phase-lock loop #3) and corrections are applied to the femtosecond laser cavity length via a PZT: $f(\text{LD2}) - f_m = \pm\Delta_2$.

To increase the dynamic range of the different phase-lock loops, the beat notes are divided by 4 for loops #1 and #2, and by 64 for loop #3. The synthesisers' frequencies are then respectively $\Delta_1/4 = \delta_1$ and $\Delta_2/64 = \delta_2$. For the loops of the laser diodes bandwidths of 1 MHz are obtained and error signals do not exceed $\pi/50$, but the bandwidth of the servo-loop for the repetition rate is limited to a few kHz.

The combination of these frequency relations with $f(\text{CO}_2/\text{OsO}_4) + f(\text{LD1}) = f(\text{SF})$ gives²:

$$\begin{aligned} f(\text{CO}_2/\text{OsO}_4) &= f_m - f_n \pm 4\delta_1 \pm 4\delta_1 \pm 64\delta_2 \\ &= pf_r \pm 4\delta_1 \pm 4\delta_1 \pm 64\delta_2. \end{aligned} \quad (1)$$

The integer p is around 28 378 ($\approx 28 \text{ THz}/1 \text{ GHz}$), and is determined unambiguously from the existing OsO₄ frequency grid. Finally, $f(\text{CO}_2/\text{OsO}_4)$ is obtained by measuring f_r . It is detected with a fast photodiode, mixed with the output of a rf synthesiser Δ_3 to translate the difference frequency δ typically below 100 kHz: $f_r = \Delta_3 \pm \delta$, and finally δ is measured with a high-resolution reciprocal counter (Agilent 53132a) at a rate of one sample per s. The Allan deviation for longer time is then evaluated by averaging these 1-s measurements.

The uncertainty in $f(\text{CO}_2/\text{OsO}_4)$ measurements depends mainly on the f_r measurement because it is multiplied by $p \approx 28\,378$. Thus, the key point is to reduce the uncertainty in the f_r measurement as much as possible. This is less than 10^{-14} , using the BNM-SYRTE 100-MHz reference signal.

The measurement could be performed in a different way. The repetition rate could be first controlled with the SYRTE reference signal and then the beat note between LD2 and the comb measured to deduce the CO₂/OsO₄ frequency. But, for technical reasons, this method is less favourable in terms of noise performance. Moreover, with the present technique, an optical clock is actually demonstrated in the sense that the rf repetition rate frequency is controlled with the CO₂/OsO₄ frequency standard. The stability of the infrared standard is transferred to the femtosecond laser, and f_r may ideally reach the optimal stability of 3×10^{-14} at 1 s of the CO₂/OsO₄ frequency standard [7, 8], even if there is no possibility to measure this performance yet. This is better than the current short-term stability of the hydrogen maser, and is a motivation to develop an infrared optical clock.

² Changing the signs of the phase-lock loops increases the capture range of the whole system.

5 Results and discussion

Various OsO₄ frequencies, in the vicinity of the different CO₂ laser lines, have been measured in the past with classical frequency chains with an uncertainty in the range 20–60 Hz [14, 15]. For the demonstration of the method, we focus our attention on a $P(55)$ line of ¹⁹⁰OsO₄ near the $P(16)$ CO₂ laser line, the frequency of which is already well known. It is located at 59.070 MHz from the CO₂ line centre and was recently used as a reference for the measurement of a two-photon absorption line in SF₆ [16]. Its absolute frequency $\nu_{\text{ref}} = 28\,412\,648\,819\,596$ (45) Hz is calculated from two independent measurements. First, the absolute frequency of the line located at 33.379 MHz from the CO₂ line centre, which is an unidentified line belonging to the OsO₄ frequency grid, is well known [5, 17]. Its frequency was recently re-measured by conventional frequency-chain techniques with an uncertainty of 40 Hz [15]. Second, the frequency difference between the $P(55)$ line and the grid line was measured at the LPL with an uncertainty of 20 Hz [14].

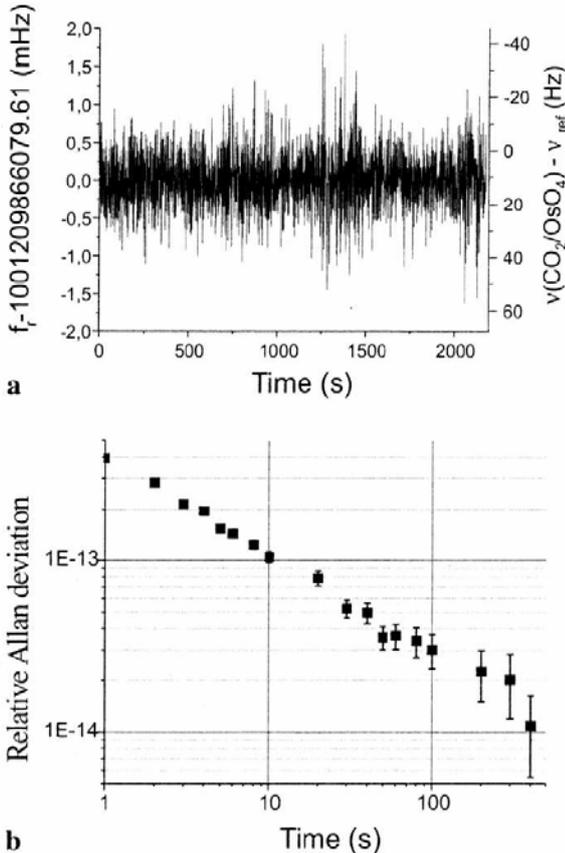


FIGURE 6 a Repetition rate of the femtosecond laser versus time when its 28 378th harmonic is locked to the CO₂/OsO₄ frequency standard. *Right-hand scale* is the corresponding scale for the CO₂/OsO₄ frequency, obtained with $p = 28\,378$, $\delta_1 = 51 \text{ MHz}$, $\delta_2 = 2.49 \text{ MHz}$ and $\Delta_3 = 1.00123 \text{ GHz}$ leading to a mean value of $\delta = 20.13392039 \text{ kHz}$. b Corresponding Allan deviation

Figure 6a displays the repetition-rate measurement and the associated OsO₄ frequency, deduced from the relation (1) above. Figure 6b gives the corresponding relative Allan deviation, which is 4×10^{-13} for a time of 1 s. This is due to the stability of the rf synthesiser's frequency Δ_3 , involved in the f_r measurement. The noise comes both from the imperfect 10 MHz to $\Delta_3 \approx 1$ GHz frequency synthesis, and from the 10 MHz itself (see Sect. 3). We measured the Allan variance of the beat note of two synthesisers referenced to the 10-MHz signal. It is 3×10^{-13} for a 1-s integration time and this gives a limit for the CO₂/OsO₄ Allan variance. A direct 100 MHz to 1 GHz synthesis is being currently developed in order to improve this short-term stability.

Measurements were performed over a period of nine months and are displayed in Fig. 7. Each point gives the statistical mean over three to nine measurements performed the same day, and the error bars are the 1σ deviation of these measurements. The day-to-day change in the error bars is related to the variation in the experimental conditions: the alignment of the Fabry–Perot cavity, the EOM's frequency or the adjustment of the baseline of the OsO₄ error signal. The main limitation for the total uncertainty is the day-to-day repeatability.

Finally, the mean value of the nine measurements is calculated: $\nu - \nu_{\text{ref}} = -16.5 \pm 58$ Hz, where the uncertainty is the 1σ deviation of the data of Fig. 7. This result compares within less than 1σ with the previous measurements [14, 15], which were performed however with a conventional frequency chain, and with a slightly different CO₂/OsO₄ stabilisation set-up [18]. This reproducibility is probably limited by systematic shifts connected with the use of a Fabry–Perot cavity for the reference saturated absorption line. The influence of the absorption and collisions on the central frequency, and the diaphragm effects across the cavity mirrors [19], are indeed not well known yet. Previous measurements on a more favourable line and with a very well optimised optical set-up gave a repeatability a few times better [7].

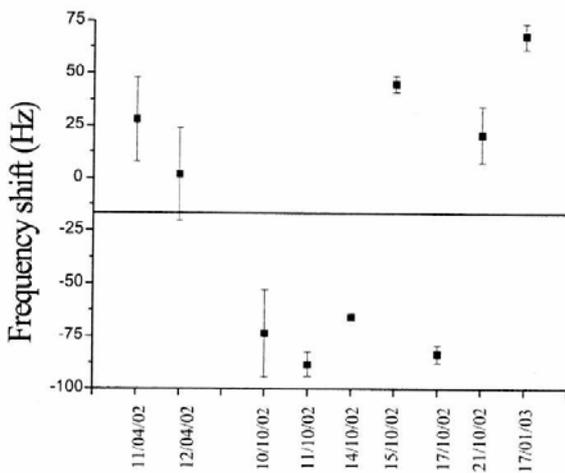


FIGURE 7 Frequency shift to ν_{ref} of the CO₂/OsO₄ standard

6 Conclusion

In this paper, the absolute frequency measurement of the CO₂/OsO₄ frequency standard using a femtosecond laser frequency comb is reported. Although the He–Ne/CH₄ infrared standard has already been measured using a frequency chain involving a femtosecond laser [20] as part of a more complicated scheme [21], this is the first frequency measurement of an infrared standard where the femtosecond laser with two flywheel oscillators forms the entire frequency chain. It requires that the frequency to be measured is less than the width of the femtosecond laser comb, and with the femtosecond laser this method could be extended to frequencies up to 60 THz. To reach higher frequency, the spectrum has to be broadened in a photonic crystal fibre [12, 22, 23]. It is also the first time that the primary standard reference frequency has been transmitted from another laboratory through a 43-km optical fibre.

The measurement agrees within less than 10^{-12} with the previous value deduced from a measurement [15] performed with a conventional frequency chain. The 2×10^{-12} uncertainty of this measurement is limited by the reproducibility of the frequency standard [19], and does not correspond, by far, to the present performance of this new frequency chain. With a connection to the SYRTE Cs fountains an accuracy of about 10^{-15} after 1000 s should be reached.

The short-term stability performance of this new ‘frequency chain’ is now limited by the absolute reference frequency. So far, the transmission along the optical fibre does not degrade the stability performance of the 100-MHz signal coming from SYRTE. But this 100 MHz does not exhibit yet the best frequency-stability performance. A cryogenic oscillator will be used soon for short-term stabilisation [24], which will set the relative Allan deviation to less than 10^{-14} between 1 and 1000 s. With the present set-up, this stability will be degraded through the optical link. Thus a correction system for the phase noise is currently under development, to improve its performance. The other crucial point is the direct synthesis from the 100-MHz signal of the 1-GHz frequency (Δ_3), which is necessary for the f_r measurement. Preliminary phase noise evaluation indicates that a stability of a few 10^{-14} for 1 s could be reached.

This new frequency chain is currently being more severely tested through the measurement of the metrological performance of a potential new frequency standard at 28 THz, studied for several years at LPL [25]. It consists of a two-photon resonance of the SF₆ molecule, detected in a Ramsey set-up with two zones separated by 1 m. It leads to a peak-to-peak width of 100 Hz, which is two orders of magnitude narrower than the width of the CO₂/OsO₄ reference line, and a S/N of 15 in a 1-Hz bandwidth. Thus one can expect to gain two orders of magnitude for the long-term stability and accuracy of this CO₂/SF₆ system compared to CO₂/OsO₄. With the femtosecond laser comb, we shall be able to measure the expected repeatability better than 1 Hz, by a direct comparison with a primary standard of SYRTE.

Finally, this frequency chain permits ultra-precise frequency comparison between a hyperfine transition in a Cs atom and a rovibrational frequency of a molecule. Repeated measurements then offer the possibility to test for variations

of fundamental constants over time [26]. These fundamental constants are not involved in the same way in these different quantum systems and this will provide an alternative test to the ones performed only with atoms. This is one of the most exciting fields of investigation offered by this new facility.

ACKNOWLEDGEMENTS The authors would like to thank members of the SYRTE for technical support and useful advice: O. Acef, S. Bize, A. Clairon, M. Lours, F. Narbonneau and D. Rovera. The authors would also like to thank the Ministère de la Recherche and the CNRS for specific funds. A. G. would like to thank University Paris 13 for its hospitality and financial support.

NOTE ADDED IN PROOFS After this paper was submitted, a paper concerning an optical fiber link was published: J. Ye, J.-L. Peng, R.J. Jones, K.W. Holman, J.L. Hall, D.J. Jones, S.A. Diddams, J. Kitching, S. Bize, J.C. Bergquist, L.W. Hollberg, L. Robertsson, L.-S. Ma: *J. Opt. Soc. Am. B* **20**, 1459 (2003).

REFERENCES

- 1 Th. Udem, J. Reichert, R. Holzwarth, T.W. Hänsch: *Phys. Rev. Lett.* **82**, 3568 (1999)
- 2 S.T. Cundiff, J. Ye, J.L. Hall: *Rev. Sci. Instrum.* **72**, 3749 (2001)
- 3 J. Reichert, R. Holzwarth, T. Udem, T.W. Hänsch: *Opt. Comm.* **172**, 59 (1999)
- 4 D.J. Jones, S.A. Diddams, J.K. Ranka, A. Stentz, R.S. Windeler, J.L. Hall, S.T. Cundiff: *Science* **288**, 635 (2000)
- 5 T.J. Quinn: *Metrologia* **36**, 211 (1999)
- 6 V. Bernard, G. Noguez, Ch. Daussy, L.F. Constantin, Ch. Chardonnet: *Metrologia* **34**, 314 (1997)
- 7 V. Bernard, C. Daussy, G. Noguez, L. Constantin, P.E. Durand, A. Amy-Klein, A. van Lerberghe, Ch. Chardonnet: *IEEE J. Quant. Electron.* **QE-33**, 1282 (1997)
- 8 O. Acef: *IEEE Trans. Instrum. Meas.* **46**, 162 (1997)
- 9 G. Santarelli, Ph. Laurent, P. Lemonde, A. Clairon, A.G. Mann, S. Chang, A.N. Luiten, C. Salomon: *Phys. Rev. Lett.* **82**, 4619 (1999)
- 10 B. de Beauvoir, F. Nez, L. Hilico, L. Julien, F. Biraben, B. Cagnac, J.-J. Zondy, D. Touahri, O. Acef, A. Clairon: *Eur. Phys. J. D* **1**, 227 (1998)
- 11 K. Sato, T. Hara, S. Kuji, K. Asari, M. Nishio, N. Kawano: *IEEE Trans. Instrum. Meas.* **49**, 19 (2000)
- 12 S.N. Bagayev, S.V. Chepurov, V.M. Klementyev, D.B. Kolker, S.A. Kuznetsov, Yu.A. Matyugin, V.S. Pivtsov, V.F. Zakharyash: *Laser Phys.* **11**, 1094 (2001)
- 13 D. Touahri, O. Acef, J.-J. Zondy: *Opt. Lett.* **21**, 213 (1996)
- 14 Ch. Chardonnet, Ch.J. Bordé: *J. Mol. Spectrosc.* **167**, 71 (1994)
- 15 O. Acef, F. Michaud, G.V. Rovera: *IEEE Trans. Instrum. Meas.* **48**, 567 (1999)
- 16 A. Shelkovnikov, Ch. Grain, C.T. Nguyen, R.J. Butcher, A. Amy-Klein, Ch. Chardonnet: *Appl. Phys. B* **73**, 93 (2001)
- 17 A. Clairon, A. van Lerberghe, C. Salomon, M. Ouhayoun, Ch.J. Bordé: *Opt. Commun.* **35**, 368 (1980)
- 18 O. Acef: *Opt. Commun.* **134**, 479 (1997)
- 19 V.A. Alekseev, D.D. Krylova, O. Acef: *Opt. Commun.* **174**, 163 (2000)
- 20 P.V. Pokasov, R. Holzwarth, Th. Udem, M. Zimmerman, J. Reichert, M. Niering, T.W. Hänsch, A.K. Dmitriyev, S.N. Bagayev, P. Lemonde, G. Santarelli, P. Laurent, M. Abgrall, A. Clairon: in *Proc. 6th Frequency Standards and Metrology Symp.*, ed. by P. Gill (World Scientific, Singapore 2002) p. 510
- 21 J. Reichert, M. Niering, R. Holzwarth, M. Weitz, Th. Udem, T.W. Hänsch: *Phys. Rev. Lett.* **84**, 3232 (2000)
- 22 T.A. Birks, J.C. Knight, P.St.J. Russel: *Opt. Lett.* **22**, 961 (1997)
- 23 J.K. Ranka, R.S. Windeler, A.J. Stentz: *Opt. Lett.* **25**, 25 (2000)
- 24 P. Wolf, S. Bize, A. Clairon, A.N. Luiten, G. Santarelli, M.E. Tobar: *Phys. Rev. Lett.* **6**, 9006 (2003)
- 25 C. Grain, A. Shelkovnikov, A. Amy-Klein, R.J. Butcher, C. Chardonnet: *IEEE J. Quant. Electron.* **QE-38**, 1406 (2002)
- 26 S.G. Karshenboim: *Can. J. Phys.* **78**, 639 (2000)

Long-Distance Frequency Dissemination with a Resolution of 10^{-17} C. Daussy, O. Lopez, A. Amy-Klein,^{*} A. Goncharov,[†] M. Guinet, and C. Chardonnet*LPL, Laboratoire de Physique des Lasers, UMR 7538 C.N.R.S., Université Paris 13, 99, avenue J.-B. Clément, 93430 Villetaneuse, France*

F. Narbonneau, M. Lours, D. Chambon, S. Bize, A. Clairon, and G. Santarelli

SYRTE, Systèmes de Référence Temps Espace, UMR 8630 CNRS, Observatoire de Paris, 61 avenue de l'Observatoire, 75014 Paris, France

M. E. Tobar and A. N. Luiten

School of Physics, University of Western Australia, 35 Stirling Highway, Crawley, Western Australia, Australia

(Received 22 December 2004; published 24 May 2005)

We use a new technique to disseminate microwave reference signals along ordinary optical fiber. The fractional frequency resolution of a link of 86 km in length is 10^{-17} for a one day integration time, a resolution higher than the stability of the best microwave or optical clocks. We use the link to compare the microwave reference and a CO_2/OsO_4 frequency standard that stabilizes a femtosecond laser frequency comb. This demonstrates a resolution of 3×10^{-14} at 1 s. An upper value of the instability introduced by the femtosecond laser-based synthesizer is estimated as 1×10^{-14} at 1 s.

DOI: 10.1103/PhysRevLett.94.203904

PACS numbers: 42.62.Eh, 06.20.-f, 06.30.Ft

Significant progress has been made in the past few years with the development of atomic and ion optical frequency standards. For example, clocks are presently being built based on Hg^+ [1] and Yb^+ ions [2], as well as Ca [3] or Sr [4] atoms. These projects are aiming to reach an accuracy in the range of 10^{-17} – 10^{-18} in the near future. In this context the precise comparison of distant frequency standards becomes a crucial issue, since a typical optical clock is not portable. Such systems will also be extremely important for those future tests of fundamental physics that are based on accurate time and frequency comparisons. Examples of this include the search for possible time variations of fundamental constants [5] and tests of Lorentz invariance [6].

Distant clock comparisons can be performed using a satellite link, such as a global positioning system (GPS), giving a resolution at one day of a few 10^{-14} with a commercial receiver, or a few 10^{-15} using a geodesic receiver, or two-way satellite time transfer systems (TWSTT). Alternatively, clock comparisons can be made indirectly using transportable clocks as transfer oscillators between fixed high-stability clocks. However, in all but a few cases the performance of transportable clocks is significantly worse than the best available frequency standards, which are complex devices that are difficult to move from their laboratories. Presently the best of the transportable clocks show an accuracy of slightly below 10^{-15} for the Cs fountain [7], 2×10^{-13} for a transportable CH_4 standard [8,9], and 1.3×10^{-12} for a Ca transportable standard [10]. For more distant laboratories optical fibers can be used to disseminate the rf signal of the primary standard, or directly distribute the optical frequency signal, as demonstrated for the 3.5 km link between NIST and

JILA, with a resolution of 4×10^{-14} at 1 s [11]. In addition, the advent of femtosecond (fs) laser-based optical frequency synthesizers has greatly simplified the frequency comparison of different optical frequency signals. For instance, a resolution of 7×10^{-15} at 1 s was recently obtained for a frequency comparison between Hg^+ and Ca standard [12]. It was also established that the fractional frequency uncertainty introduced by the fs laser synthesizer can be in the 10^{-17} domain at 1 s and is approaching the 10^{-19} domain after 100 s [13] when comparing two optical signals. However, the sensitivity and accuracy of optical-microwave frequency comparisons is often limited by noise processes which occur in the microwave frequency domain. For instance, the upper limit of the instability of a fs laser-based synthesizer that connects the microwave and optical domains has been reported to 2×10^{-14} at 1 s [14].

In this Letter we demonstrate, for the first time, that two standards can be compared over a distance of 43 km, using a standard telecommunication optical link, with a resolution of 8×10^{-15} at 1 s, and 10^{-17} at one day integration time. As an application, we measured the frequency of a stabilized CO_2 laser at Laboratoire de Physique des Lasers (LPL) against the primary frequency standard of the Systèmes de Référence Temps Espace (SYRTE), with a resolution of 3×10^{-14} at 1 s integration time, limited by the CO_2 laser frequency stability. From this measurement, the instabilities of the fs laser-based synthesizer connecting the microwave and optical domains can be estimated to be less than 1×10^{-14} at 1 s.

The LPL, located on the outskirts of Paris, develops optical frequency standards in the mid infrared. The SYRTE, in the center of Paris, develops Cs atomic foun-

tains with an accuracy of 7×10^{-16} , and a frequency stability of $1.6 \times 10^{-14} \tau^{-1/2}$ [15]. A 100 MHz high-stability flywheel oscillator has been developed at SYRTE, which is based on a combination of a cryogenic sapphire oscillator (CSO), an H-maser, and a set of low noise microwave synthesizers [16]. The conventional means of characterizing the frequency stability of an oscillator is the Allan frequency deviation [17]. It is given by $\sigma_y(\tau) = \sqrt{\frac{1}{2} \langle (\bar{y}_n - \bar{y}_{n+1})^2 \rangle}$, where y_n is the n th measurement of the fractional average frequency of the oscillator measured over an integration time, τ . The flywheel oscillator shows a frequency stability slightly below $10^{-14} \times \tau^{-1}$ in the range 1–10 s, and $(1-2) \times 10^{-15}$ from 10 to 10^5 s (see the Allan deviation as a dashed line in Fig. 1). The frequency of this signal is steered by the H-maser in the long term, and monitored by the Cs atomic fountain.

Two parallel optical links have been used to transmit the reference signal between SYRTE and LPL [18]. A few sections of standard $1.55 \mu\text{m}$ telecommunication single mode optical fibers have been interconnected by splicing leading to a total length of 43 km. The optical link is fed with a distributed feedback semiconductor laser emitting at $1.55 \mu\text{m}$. The junction current of the diode is modulated with the 100 MHz reference signal, which generates synchronous intensity modulation of its output light. The intensity modulation is then detected at the distant end of the optical link. The fibers are sensitive to both acoustic noise and temperature variations. A preliminary measurement of the metrological features of this link was made by redirecting the output signal from one fiber back into the second fiber leading to a complete round trip (86 km) of the 100 MHz signal [18]. The phase difference between the input and return signal was detected and analyzed in terms of frequency fluctuations. In a second experiment, the same

100 MHz signal was sent in both fibers, and the two output signals were compared. Their phase noise fluctuations were found to be of a few 10^{-15} at 1 s, which is 10 times less than the noise seen on a single fiber. This demonstrates that the phase fluctuations arising in both fibers are strongly correlated, and that the Allan frequency deviation for a one-way pass can be deduced by dividing by 2 the Allan deviation of the round trip, at least on time scales longer than 1 s. The Allan deviation for a complete round trip in a single fiber is reported in Fig. 1 (up triangles). The typical short-term noise is 3×10^{-14} at 1 s, while the long-term noise is dominated by diurnal temperature variations of about $(3-5) \times 10^{-15}$. This performance, remarkable for a nondedicated fiber, is occasionally degraded by noise bursts. For precise metrological applications, one must implement a method for compensation of the fiber phase noise.

In order to fully characterize the frequency transfer, we have implemented two independent correction systems on the two fibers. Figure 2 displays a schematic of the measurement setup. A first compensation system is used to correct the perturbation introduced on the rf reference signal through the optical link from SYRTE to LPL. The corrected signal received at LPL is sent back to SYRTE for evaluation via the second fiber. This transfer requires a second correction system. By comparing the reference with the return signal, a complete stability analysis can be done.

The first compensation system implemented at SYRTE is based on rf signal processing and is very similar to the design used at the Jet Propulsion Laboratory for the Deep Space Network distribution [19]. The rf signal detected at SYRTE after one round trip in the same fiber is compared to the reference signal. The perturbation value is extracted and used to compensate one-path perturbations by phase shifting the 100 MHz signal in the opposite sense in order to get a corrected 100 MHz signal at LPL.

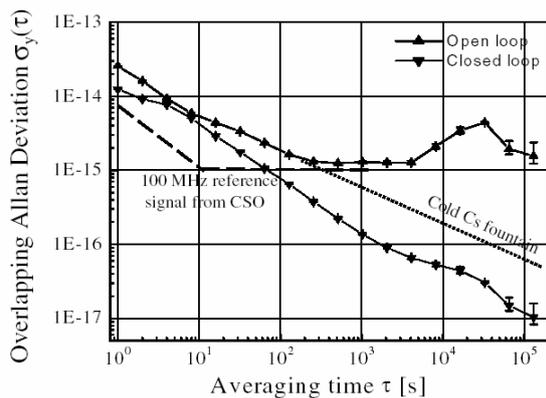


FIG. 1. Allan deviation for the round-trip optical link, 86 km, in open loop (\blacktriangle) and closed loop (\blacktriangledown), as calculated from phase measurement with 1 s sample time. Dashed line indicates the fractional frequency instability of the 100 MHz reference signal from the CSO, and dotted line the fractional frequency instability of the Cs fountain FO2.

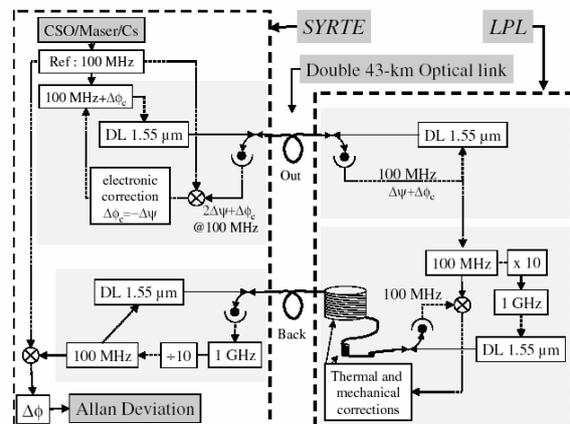


FIG. 2. Schematic of the optical link compensation.

The second correction system, implemented at LPL, acts directly on the optical path. A correction signal is generated by comparing the phase of the 100 MHz arriving from SYRTE and the 100 MHz modulation after one round trip in the second fiber. Fast fluctuations are compensated by stressing a 15 m optical fiber wrapped around a cylindrical piezoelectric actuator, which is implemented at the input of the second optical fiber. Slow perturbations are compensated by heating a 1 km optical fiber spool. In order to increase isolation between channels, the forward and return beams are modulated at different frequencies, 1 GHz and 100 MHz, respectively. In this case both the one-way and the round-trip signals are corrected.

These two correction systems present very similar performance and are interchangeable. The control bandwidth, about 300 Hz is mainly limited by round-trip delay (0.4 ms). The spectral density of the residual phase fluctuations is -120 dB (rad²/Hz) at 1 Hz, which limits the 1 s frequency stability to about 8×10^{-15} . The phase instability of the link without the benefits of the control system (open loop) can be simultaneously measured by slightly modulating the signal transmitted in the electronically controlled link at a frequency (270 MHz) that is different from the operating 100 MHz frequency. Thus both open and closed loop stabilities can be simultaneously recorded. The results relating to the 86 km round-trip link are displayed in Fig. 1: the fractional frequency stability is 1.2×10^{-14} at 1 s, and 1×10^{-17} for one day integration time. A stability of 8×10^{-15} at 1 s for the one-way transfer can be deduced, since the compensation systems are independent. The long-term fluctuations, due to the daily temperature variations are reduced by 2 orders of magnitude. Finally, the stability performance of the Cs fountain can be retrieved with no degradation at the output of the link. The 100 MHz signal short-term stability performance is slightly degraded by the optical link, but with no impact as far as frequency measurements are concerned.

As a first application of the compensated optical link, we measured the absolute frequency of a molecular optical clock. A CO₂ laser emitting about 30 THz is locked onto a saturated absorption line of the OsO₄ molecule. We chose the very strong R(42) A₃³(-) line of ¹⁹²OsO₄ as it is coincident with the R(12) CO₂ laser line. Two equivalent and independent CO₂/OsO₄ stabilization systems have been developed [20]. An Allan deviation of 4.2×10^{-14} at 1 s was obtained for the beat note between these two lasers (that is, 3×10^{-14} for a single laser). The principle of frequency measurements at 30 THz using a fs laser comb has been described elsewhere [18]. The CO₂ laser frequency is smaller than the span of the modes of the fs laser, and this can be exploited so that the CO₂ laser controls the separation between two of these modes. The stability of the CO₂/OsO₄ system is thus transferred to the repetition rate f_r of the fs laser, and we can dispense with any need for controlling the offset frequency of the fs laser. Two laser diodes at 852 and 788 nm are used as intermedi-

ate oscillators, their frequency difference being phase locked to the CO₂ laser frequency. Finally, $f(\text{CO}_2) = qf_r \pm \Delta$, where Δ corresponds to the offsets of the phase-lock loops, and the integer q is about 29 100. The CO₂ frequency is deduced from the measurement of the repetition rate f_r , which is detected with a fast photodiode. A schematic view of the experimental apparatus is given in Fig. 3. The SYRTE reference signal is used to synchronize all the synthesizers and counter at LPL, and to synthesize a 1 GHz signal, which is mixed with the repetition rate signal. The resulting beat note signal, at about 5 MHz, is further shifted to 68 Hz, filtered (10 Hz bandwidth) and counted.

Figure 4 displays the fractional Allan deviation associated with the repetition rate measurement. It is 3×10^{-14} for 1 s, which demonstrates that the Allan deviation is limited by the stability of the CO₂/OsO₄ system. If we consider the Allan deviations at 1 s of, respectively, 8×10^{-15} for the optical link, 8×10^{-15} for the 100 MHz SYRTE reference signal (from the CSO), and 3×10^{-14} for the CO₂/OsO₄ stabilized laser, we can derive a conservative upper limit of 1×10^{-14} for the Allan deviation at 1 s integration time, for the equipment comparing the CO₂/OsO₄ signal with the microwave signal including fs laser, phase-lock loops, and detection electronics. This level of uncertainty reflects a significant advance in the direct measurement of the instabilities of a fs laser-based synthesizer connecting microwave and optical domains. It compares very well with the noise level of 2×10^{-14} at 1 s measured with a microwave beat note of two fs lasers driven by the same optical frequency standard [14].

The optical link to the primary standard of SYRTE allows an absolute frequency measurement, without any need for long integration time. It is remarkable indeed that the resolution of the CO₂/OsO₄ frequency measurement is 3×10^{-14} after only 1 s integration time. The absolute frequency measurement of the R(42) line of OsO₄ was performed by repeating the CO₂/OsO₄ frequency measurement a few times. The mean value is $\nu - \nu_{\text{ref}} = 3.9 \pm 10$ Hz, where the uncertainty is the $1 - \sigma$ deviation of the data and ν_{ref} is deduced from [21,22]. The uncertainty is

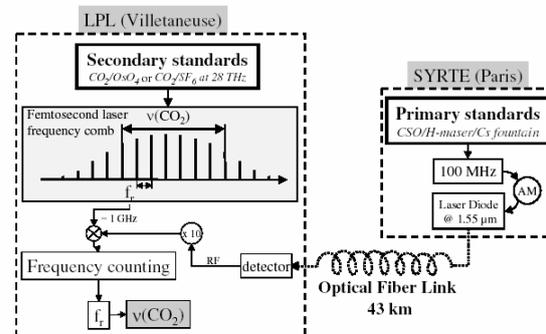


FIG. 3. Schematic of the whole measurement setup.

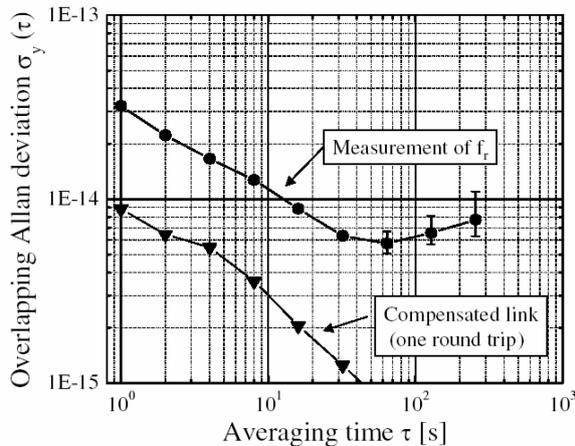


FIG. 4. Fractional CO_2/OsO_4 frequency stability as given by the Allan deviation (\bullet) of the repetition rate f_r of the fs comb calculated from a series of 1 s gate measurement. The noise due to the optical link is negligible (\blacktriangledown).

limited by the reproducibility of the CO_2/OsO_4 stabilization [18,20].

We have demonstrated a transfer of the stability of a primary standard along a 43 km optical link of telecommunication network with a resolution of 8×10^{-15} at 1 s and 10^{-17} for one day. As a demonstration, the transferred signal of a cryogenic oscillator was used to measure a CO_2/OsO_4 optical frequency standard, with a resolution of 3×10^{-14} at 1 s limited by the CO_2 laser fluctuations. The long-term frequency fluctuations of this optical link are 2 orders of magnitude lower than that obtainable with a GPS-based transfer system, and the short-term fluctuations are 1 order of magnitude lower than the stability of a H-maser. It appears that this type of approach could provide a better frequency reference than the use of conventional local time standards.

Our next development will increase the reference frequency from 100 MHz to 1 GHz. An improvement by a factor of 3 should then be obtained for the short-term resolution of the optical link. For transmission between more distant laboratories, both the fiber attenuation and the higher noise can degrade the signal transfer. Optical amplification and the use of more powerful laser diodes can overcome this attenuation, extending the performance of our compensated link for distances up to 200 km. For more distant laboratories, a scaled up version of this link using a few repeaters could further extend the range of an optical distribution system. In fact, in the present arrangement the stabilization system at LPL is acting as a repeater at the midway point of the round trip.

A very attractive application of the present work concerns the search for possible time variations of the fundamental constants [5]. Recent measurements [1,2,23,24] have shown no time dependence of the fine structure

constant at the limit of about $10^{-15}/\text{yr}$, which is approaching the sensitivity needed to give quantitative results for the theoretical models. For the next generation of optical clocks, an even higher resolution will be needed for the frequency comparison. The present performance of our frequency dissemination system, or its extension to a continental basis, could be fully exploited in such a program. It would also allow comparison between a larger set of clocks, and thus enable discrimination between the variations of different constants [2].

The authors thank the Ministère de la Recherche, the CNRS, the Bureau National de Métrologie, and the European Space Agency for specific funds.

*Corresponding author.

Electronic address: amy@galilee.univ-paris13.fr

†Permanent address: Institute of Laser Physics, Novosibirsk, Russia.

- [1] S. Bize *et al.*, Phys. Rev. Lett. **90**, 150802 (2003).
- [2] E. Peik *et al.*, Phys. Rev. Lett. **93**, 170801 (2004).
- [3] U. Sterr *et al.*, C.R. Physique **5**, 845 (2004).
- [4] M. Takamoto and H. Katori, Phys. Rev. Lett. **91**, 223001 (2003).
- [5] S. G. Karshenboim, Can. J. Phys. **78**, 639 (2000).
- [6] F. Cane *et al.*, Phys. Rev. Lett. **93**, 230801 (2004); D. F. Phillips *et al.*, Phys. Rev. D **63**, 111101(R) (2001); M. A. Humphrey *et al.*, Phys. Rev. A **68**, 063807 (2003); P. Wolf *et al.*, Phys. Rev. D **70**, 051902(R) (2004); H. Müller *et al.*, Phys. Rev. Lett. **91**, 020401 (2003); J. Lipa, J. A. Nissen, S. Wang, D. A. Stricker, and D. Avaloff, Phys. Rev. Lett. **90**, 060403 (2003).
- [7] M. Niering *et al.*, Phys. Rev. Lett. **84**, 5496 (2000).
- [8] O. Acef *et al.*, in *Proceedings of the 1999 Joint Meeting of EFTF and IFCS* (IEEE, Piscataway, NJ, 1999), p. 742.
- [9] S. N. Bagayev, A. K. Dmitriyev, and P. V. Pokasov, Laser Phys. **7**, 989 (1997).
- [10] P. Kersten, F. Mensing, U. Sterr, and F. Riehle, Appl. Phys. B **68**, 27 (1999).
- [11] J. Ye *et al.*, J. Opt. Soc. Am. B **20**, 1459 (2003).
- [12] S. A. Diddams *et al.*, Science **293**, 825 (2001).
- [13] L. S. Ma *et al.*, Science **303**, 1843 (2004).
- [14] A. Bartels, S. A. Diddams, T. M. Ramond, and L. Hollberg, Opt. Lett. **28**, 663 (2003).
- [15] C. Vian *et al.*, IEEE Trans. Instrum. Meas. **54**, 833 (2005).
- [16] D. Chambon *et al.*, Rev. Sci. Instrum. (to be published).
- [17] D. W. Allan, Proc. IEEE **54**, 221 (1966).
- [18] A. Amy-Klein *et al.*, Appl. Phys. B **78**, 25 (2004).
- [19] R. T. Logan and G. F. Lutes, in *Proceedings of the IEEE Frequency Control Symposium* (IEEE, Piscataway, NJ, 1992), p. 310.
- [20] V. Bernard *et al.*, IEEE J. Quantum Electron. **QE-33**, 1282 (1997).
- [21] O. Acef, F. Michaud, and G. V. Rovera, IEEE Trans. Instrum. Meas. **48**, 567 (1999).
- [22] Ch. Chardonnet and Ch. J. Bordé, J. Mol. Spectrosc. **167**, 71 (1994).
- [23] H. Marion *et al.*, Phys. Rev. Lett. **90**, 150801 (2003).
- [24] M. Fischer *et al.*, Phys. Rev. Lett. **92**, 230802 (2004).

Direct Determination of the Boltzmann Constant by an Optical Method

C. Daussy, M. Guinet, A. Amy-Klein, K. Djerroud, Y. Hermier,* S. Briauadeau,* Ch. J. Bordé, and C. Chardonnet

Laboratoire de Physique des Lasers, UMR CNRS 7538, Institut Galilée, Université Paris 13,

99, avenue J.-B. Clément, 93430 Villetaneuse, France

(Received 21 January 2007; published 18 June 2007)

We have recorded the Doppler profile of a well-isolated rovibrational line in the ν_2 band of $^{14}\text{NH}_3$. Ammonia gas was placed in an absorption cell thermalized by a water-ice bath. By extrapolating to zero pressure, we have deduced the Doppler width which gives a first measurement of the Boltzmann constant k_B by laser spectroscopy. A relative uncertainty of 2×10^{-4} has been obtained. The present determination should be significantly improved in the near future and contribute to a new definition of the kelvin.

DOI: 10.1103/PhysRevLett.98.250801

PACS numbers: 06.20.Jr, 33.20.Ea, 42.62.Fi

The tremendous progress in high precision measurements during recent decades will lead unavoidably to a complete renewal of fundamental metrology. There is a strong tendency to relate the base units to fundamental constants [1]. As an example, this was done in 1983 by fixing the velocity of light c and thus defining the length unit from the time unit, because the second is the fundamental unit which is realized, by far, with the best accuracy. The unit of temperature could follow the same line. Up to now, the kelvin was defined by the temperature (273.16 K) of the triple point of water (TPW) which implies a particular property of macroscopic matter. Instead, the temperature of a sample has a microscopic interpretation and can be related through the Boltzmann constant to the mean energy E per particle and per degree of freedom according to the well-known expression $E = 1/2 k_B T$. This energy may itself be related to a frequency via the Planck constant. This Letter presents a first accurate experiment which gives a direct measurement of such a frequency in a gas at a well-defined temperature. Fixing the value of k_B would connect temperature and time units. But, before fixing the value of the Boltzmann constant, it is necessary to verify precisely the consistency of the value of k_B in the present context. The accepted value in the CODATA [2] $k_B = 1.3806505(24) \times 10^{-23} \text{ JK}^{-1}$ is derived from the value of the ideal gas constant R and the Avogadro constant N_A by the relation $k_B = R/N_A$. The relative uncertainty of k_B is 1.8×10^{-6} and should come mostly from that for R because the uncertainty of N_A is 1.7×10^{-7} [2]. But there is presently an inconsistency at the level of 10^{-6} between the values of N_A derived from the Si sphere and from the watt balance experiment [3].

Very few experiments lead to an accurate determination of k_B or R [4]. Up to now, the accepted value of R has come from a single experiment by Moldover *et al.* [5] performed before 1988 by acoustic gas thermometry.

An alternative and indirect measurement of the Boltzmann constant was proposed along an approach based on the virial expansion of the Clausius-Mossotti equation [6]. This relates the permittivity of helium ϵ to its molar polarizability A_e , which implies a QED calculation.

Here we propose a direct determination of the Boltzmann constant by laser spectroscopy [1]. The principle consists in recording the linear absorption in a vapor phase and measuring the Doppler width of an atomic or molecular line in a cell in thermodynamic equilibrium. In the Doppler limit, the line shape is a Gaussian (for an optically thin medium) and $k_B T$ is given by

$$k_B T = \frac{m c^2}{2} \left(\frac{\Delta_D}{\nu} \right)^2.$$

Δ_D is the e -fold half-width, ν is the frequency of the molecular line, and m is the molecular mass. Δ_D and ν are determined experimentally. The probed atoms or molecules belong to a single quantum level of a well-defined isotopic species, which avoids uncertainties coming from macroscopic quantities as is the case in the schemes mentioned above. Strictly speaking, we are sensitive to the temperature of one translational degree of freedom of a subset of molecules. Since the temperature is measured on the walls of the cell containing the gas, the determination of k_B using different rovibrational lines can lead to a verification of the equipartition of energy principle. This experimental situation benefits from an analysis considerably more straightforward than other methods, as we will see.

Ion mass ratios can now be measured in Penning traps with 10^{-9} – 10^{-10} accuracies [7], and binding energies for a molecule can be easily calculated to keep the accuracy of the molecular mass expressed in atomic units at the same level. However, because of the definition of the kilogram, its absolute value implies the Avogadro constant N_A as in the previous experiments, but, since atom interferometry yields a direct determination of the quantity h/mc^2 [8], the present experiment gives directly the ratio k_B/h .

Experiment.—The experiment consists simply in recording an absorption line. The selected line for these first experiments is the ν_2 as $Q(6, 3)$ rovibrational line of the ammonia molecule $^{14}\text{NH}_3$ at the frequency $\nu = 28\,953\,694 \text{ MHz}$. The choice of the molecule is governed by two main reasons: a strong absorption band in the spectral region of 8–12 μm of the ultrastable spectrometer that we have developed over several years and a well-

isolated Doppler line to avoid any deformation of the line shape due to neighboring lines. Clearly, the conditions for such an experiment can be obtained with a wide set of molecules or even atoms in various spectral regions and also over a large range of temperatures. In our experiment, the gas pressure varies from 0.1 to 10 Pa. The 37 cm-long absorption cell is placed in a large thermostat filled with an ice-water mixture, fixing the temperature at 273.15 K. Several temperature probes based on 100Ω platinum resistors with a $0.39\Omega\text{ K}^{-1}$ dependency are firmly attached to the cell to follow the temperature changes or gradients. These probes were calibrated against a TPW. A conservative uncertainty of 20 mK (7×10^{-5}) was guaranteed in this experiment. This can be easily improved in the future. The laser source is based on a CO_2 laser stabilized on an absorption line of OsO_4 . The laser frequency control is a key point of the experiment: The laser spectral width is less than 10 Hz as measured by the beat note between two independent lasers, and the Allan deviation at 100 s can reach 0.1 Hz (3×10^{-15}) [9]. Recently, we have measured the absolute frequency of our laser source against the Cs fountain of SYRTE (Paris Observatory) through an optical fiber link connecting our two laboratories. The uncertainty of 1 Hz (3×10^{-14}) [10] shows that the relative accuracy of the frequency axis of the recorded Doppler profile (width of about 100 MHz) can reach 10^{-8} . This is 2 orders of magnitude better than the present accuracy of the Boltzmann constant and will not be a limitation. The tunability of the laser source is obtained with an 8–18 GHz electro-optic modulator (EOM) [11] which generates two weak sidebands (SB) (10^{-4} – 10^{-3} efficiency). The sideband, red-detuned by 13 GHz from the R(6) CO_2 laser carrier, is brought into resonance with the desired molecular transition. The full Doppler profile is scanned by detecting the light transmitted by the cell on a HgCdTe photodetector. The main difficulty in this experiment is our capability to record a signal which reflects perfectly the Doppler profile and to suppress any parasitic optical signal. For this, several precautions were added together, and the present setup is displayed on Fig. 1. A polarizer blocks 99.5% of the laser carrier and transmits the 2 cross-polarized sidebands. Then, a Fabry-Perot cavity (FPC) with a free spectral range of 1 GHz and a finesse of 150 is used to filter drastically the residual carrier and the unwanted sideband. For this purpose, the sidebands via the EOM are frequency modulated at $f = 8$ kHz with a depth of 38 kHz to lock the FPC on the useful sideband. However, when the EOM is tuned around the molecular line, resonance conditions can be reached accidentally by different transverse modes of the carrier or the other sideband. This problem may be strongly reduced by a careful choice of the laser frequency, which can be adjusted via a second EOM used for the laser stabilization (not represented in Fig. 1). To eliminate even more the laser carrier residuals, a 30% amplitude modulation at $f_1 = 17$ kHz is applied to the sidebands only via the 8–18 GHz EOM. With this successive filtering, the contrast of the selected

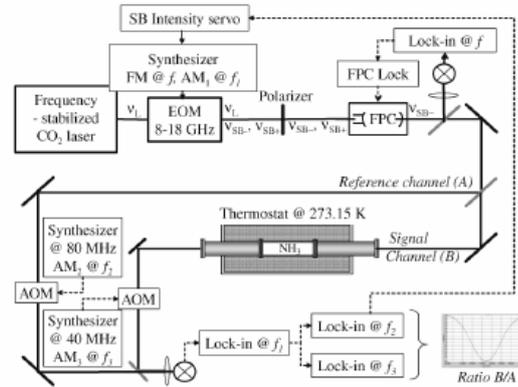


FIG. 1. Experimental setup. $f = 8$ kHz, $f_1 = 17$ kHz, $f_2 = 1.7$ kHz, $f_3 = 2.2$ kHz. Only the sideband ν_{SB} from the EOM is kept after filtering for recording the NH_3 absorption profile.

sideband against carrier and unwanted sideband is better than 1000. The next main concern is the stability of the laser intensity during the tuning range. In fact, the response of our EOM can vary by 20% over the 300 MHz range used for recording the molecular spectrum. To circumvent this unacceptable problem, we split the laser beam into two channels: The reference beam (A) is frequency shifted with an acousto-optic modulator (AOM) of 80 MHz and amplitude modulated at $f_2 = 1.7$ kHz; the probe beam (B) which traverses the absorption cell is also frequency shifted by an AOM of 40 MHz and amplitude modulated at $f_3 = 2.2$ kHz. The path lengths are adjusted to be equal, and the two beams are recombined to be directed to the same photodetector. The optical setup first provides demodulation of the combined signals at f_1 which eliminates any contribution of the laser carrier. Then each signal is recovered by demodulations at f_2 and f_3 . The reference signal reflects the sideband intensity and is used to apply a correction to the amplitude of the EOM signal to maintain it constant during the frequency scan. Thus, the signal detected at f_3 reflects exactly the absorption signal of the molecular gas recorded with a constant incident laser power. Starting from a laser carrier of 1.5 W, the available power in the cell can be chosen between 0.1 and 3 μW for a beam diameter of 11 mm. The Doppler profile of about 100 MHz width is recorded over 250 MHz by steps of 500 kHz with a time constant of 20 ms. However, the important frequency step which is also applied to the filtering cavity by the way of a servo loop imposes a time delay of about 200 ms between two points to prevent extra noise. The time for recording a spectrum is thus about 110 s, dominated by the waiting time. Figure 2 displays a series of spectra recorded at different pressures. The vertical axis is the relative transmission normalized by the incident laser power.

Methodology of the line shape analysis.—The theoretical description of this experiment corresponds to the well-

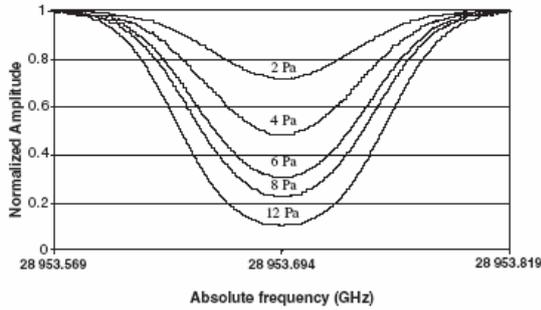


FIG. 2. Series of absorption spectra at different pressures.

established situation of the linear absorption of a sample in a cell at thermal and pressure equilibrium. However, an accurate determination of the linewidth requires a very accurate description of the line shape. In the case of an optically thick medium, the line shape is given by the Beer-Lambert law $\exp(-\alpha L)$, where L is the length of the absorption cell and where the absorption coefficient α has a Gaussian shape in the Doppler limit, as mentioned above. Experimentally, we have tried to work as close as possible to this regime. In practice, several causes of broadening must be taken into account. In the first place, the pressure broadening and the natural width are responsible for the homogeneous width γ_{hom} . In this case the line shape is a Voigt profile, that is, the convolution of a Gaussian and a Lorentzian. In linear absorption spectroscopy and for an isotropic velocity distribution, a detailed calculation of the line shape, taking into account all transit effects, shows that these effects are already included in the usual Doppler broadening [12]. Two other effects must be considered: the unresolved hyperfine structure of the transition and the modulations applied for experimental reasons which broaden the laser spectrum. In a first approach, these two effects act in the same way: In the first case, the line shape is exactly the sum of the individual hyperfine components, and, in the second case, the frequency comb of the laser spectrum due to the frequency modulation f_1 (which is the main effect here) generates absorption signals which reflect the laser spectrum (positions and relative intensities). We have checked that our experiments were performed in the low field limit, far from saturation. In order to derive the theoretical line shape, one can take into account exactly all of these effects. However, since experimentally we are very close to the Doppler limit, the actual line shape cannot be easily distinguished from the exponential of a broadened Gaussian. We have fitted the theoretical line shape with the exponential of a Gaussian and calculated numerically the relative broadening caused by the various effects mentioned above: For the homogeneous broadening, we found $0.484\gamma_{\text{hom}}/\Delta_D$; the hyperfine structure and the laser frequency modulation depth create respective broadenings equal to $0.254(\Delta_{\text{hyp}}/\Delta_D)^2$ and $(\text{depth}/\Delta_D)^2$, where Δ_{hyp} is the total width of the structure. The coefficient 0.254

corresponds to the less favorable case of a doublet of equal amplitude. The line under study has a 12 components hyperfine structure of the order of 150 kHz which can be calculated or measured by saturation spectroscopy [13]. Its contribution to the linewidth could be also precisely taken into account, reducing the associated uncertainty to a negligible level. Finally, at a relative uncertainty of 10^{-6} , only the homogeneous broadening, which ranges between 10^{-2} and $10^{-4} \Delta_D$ under our experimental conditions, contributes to the linewidth. The natural linewidth of the order of 1 Hz is negligible. The only parameter of importance is the relative pressure in the cell which is carefully measured, as explained below.

Finally, the experimental spectra have been fitted with the exponential of the Gaussian profile:

$$\alpha(\nu) = An_0 \exp\left(-\frac{(\nu - \nu_0)^2}{\Delta(n_0)^2}\right),$$

where n_0 is the population density in the considered lower level, a quantity proportional to the pressure, A is a constant specific to our transition, ν is the laser frequency, ν_0 is the resonance frequency, and $\Delta(n_0)$ is the $1/e$ -fold half-width of the Gaussian. The fit gives the two key parameters: the width of the Gaussian and the amplitude. As the pressure is decreased to zero, the width converges linearly to the Doppler width, and we have checked that the residuals become negligible. The amplitude An_0 determined by the fit is, in fact, a relative measurement of the pressure. This way to calibrate the pressure is much more precise than by a pressure gauge and is particularly appropriate for an extrapolation to zero pressure. However, this parameter is related to the pressure of the active gas, while the width of the Gaussian depends on the total pressure including the impurities in the cell which must be eliminated as much as possible for a correct extrapolation to zero pressure.

Results and discussion.—Figure 2 displays a series of absorption spectra at pressures between 0.2 and 10 Pa. To obtain a good signal-to-noise ratio, we operate with an absorption between 10% and 80%, and at the highest pressures the line shape clearly differs from a Gaussian. The absolute pressure is measured with a Baratron gauge, but this value is not used for the analysis of the results, as explained above. A typical signal-to-noise ratio (S/N) under the best conditions is 10^3 for a time constant of 20 ms. A set of 2000 spectra was recorded over more than one month. Figure 3 displays the linear regression which leads to the determination of the Doppler width by extrapolation to zero pressure. Experimental linewidths depart from the Doppler limit by less than 2%, which confirms that the profile is very close to the exponential of a Gaussian. The relative calibration of the pressure axis is systematically performed by the amplitude of the signal, as explained in the previous section. This uncertainty which is directly related to the S/N is negligible for the extrapolation. The resulting Doppler e -fold half-width is

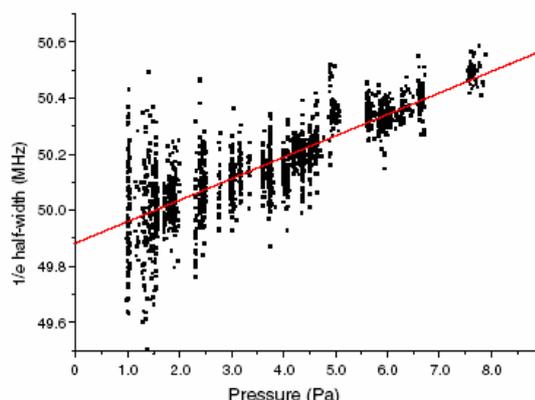


FIG. 3 (color online). Linear regression of the $1/e$ half-width of the absorption line which gives an extrapolated value at zero pressure: 49.883 1(47) MHz.

$$\Delta_D = 49.883\,1(47)\text{ MHz } (9.5 \times 10^{-5}).$$

This leads to the following determination of the Boltzmann constant:

$$k_B = 1.380\,65(26) \times 10^{-23}\text{ J K}^{-1} (1.9 \times 10^{-4}).$$

The uncertainty takes into account that of the temperature. This value is in agreement with the CODATA value. Attempts to observe systematic effects due to the modulation index, the size or the shape of the laser beam, and the laser power, including the nonlinearity of the photodetector, were unsuccessful, as expected from the analysis of the previous section. For the fit, a slope is added to the exponential of the Gaussian to take into account a hypothetical background optical signal. A careful analysis of the data revealed that, by suppressing the spectra which present a slight slope, the dispersion of the 500 remaining measurements was reduced, leading to the same result with the same uncertainty. On the other hand, regrouping data with a given slope gives a systematic shift. This is the only observation of a systematic effect and is probably due to parasitic light reaching the detector. For further experiments, this observation offers a method to avoid this very tiny systematic effect by adjustment of the optical alignment.

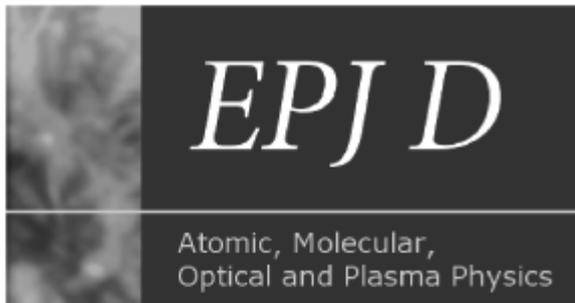
Conclusion and perspectives.—This demonstration experiment of an optical method for the measurement of the Boltzmann constant which reaches an uncertainty of 2×10^{-4} after a cumulative time of 61 hours is very promising, since obvious improvements can be made in the near future. Three kinds of progress will be implemented: a temperature control with a stability better than 10^{-6} obtained by using embedded thermostats, an absorption length 10 times larger in a multiple path cell will improve

the extrapolation to zero pressure, and changing the intensity stabilization scheme will reduce the dead time between data points by a factor of 10, thus reducing by almost the same factor the accumulation time of the spectra. These three straightforward directions of progress let us expect a gain of 2 orders of magnitude in the signal-to-noise ratio. These improvements will provide the signal-to-noise ratio needed to study quantitatively all systematic effects. Since no fundamental limitation has been identified at the 10^{-6} level, a potential accuracy comparable to that of the acoustic method should be possible. This method is very general and is a direct application of the first principles: the direct measurement of the thermal energy related to 1 degree of freedom of the system. In fact, the line profile reflects the velocity distribution along the laser beam axis for molecules in a given rovibrational level, while the measured temperature is that of the whole sample. Thus, the obtention of a common value by using various transitions and temperatures leads to a partial check of the equipartition principle. Moreover, our method can be easily applied to different physical systems, different molecules, and isotopes in a very large range of temperatures. One should also explore, especially at higher pressure, the influence of the adsorption energy on the walls, the nonideal character of the gas for a possible departure from a Maxwell-Boltzmann distribution. In addition, our experiment will open access to a detailed study of the Lamb-Dicke effect. Finally, the measurement of the Doppler width in gases will give an universal way to measure the absolute thermodynamical temperature.

This work is supported in part by the Laboratoire National de Métrologie et d'Essais.

*Permanent address: Institut National de Métrologie LNE-INM-CNAM, La Plaine Saint-Denis, France.

- [1] Ch. J. Bordé, *Phil. Trans. R. Soc. A* **363**, 2177 (2005).
- [2] P. J. Mohr and B. N. Taylor, *Rev. Mod. Phys.* **77**, 1 (2005); <http://www.codata.org/>.
- [3] K. Fujii *et al.*, *IEEE Trans. Instrum. Meas.* **54**, 854 (2005).
- [4] B. Fellmuth *et al.*, *Meas. Sci. Technol.* **17**, R145 (2006).
- [5] M. R. Moldover *et al.*, *Phys. Rev. Lett.* **60**, 249 (1988).
- [6] L. R. Pendrill, *J. Phys. B* **29**, 3581 (1996).
- [7] M. P. Bradley *et al.*, *Phys. Rev. Lett.* **83**, 4510 (1999).
- [8] A. Wicht *et al.*, *Phys. Scr.* **T102**, 82 (2002); P. Cladé *et al.*, *Phys. Rev. Lett.* **96**, 033001 (2006).
- [9] V. Bernard *et al.*, *IEEE J. Quantum Electron.* **33**, 1282 (1997).
- [10] C. Daussy *et al.*, *Phys. Rev. Lett.* **94**, 203904 (2005).
- [11] O. Pfister *et al.*, *J. Opt. Soc. Am. B* **10**, 1521 (1993).
- [12] C. J. Bordé (to be published).
- [13] M. Ouhayoun, Ch. J. Bordé, and J. Bordé, *Mol. Phys.* **33**, 597 (1977); Ch. J. Bordé *et al.*, in *Laser Spectroscopy VII*, edited by T. W. Hänsch and Y. R. Shen (Springer-Verlag, Berlin, 1985), p. 108.



www.epj.org

Eur. Phys. J. D **48**, 35–41 (2008)

DOI: [10.1140/epjd/e2008-00059-5](https://doi.org/10.1140/epjd/e2008-00059-5)

86-km optical link with a resolution of 2×10^{-18} for RF frequency transfer

O. Lopez, A. Amy-Klein, C. Daussy, C. Chardonnet, F. Narbonneau, M. Lours and G. Santarelli



86-km optical link with a resolution of 2×10^{-18} for RF frequency transfer

O. Lopez¹, A. Amy-Klein^{1,*}, C. Daussy¹, C. Chardonnet¹, F. Narbonne², M. Lours², and G. Santarelli²¹ Laboratoire de Physique des Lasers, UMR 7538 CNRS, Université Paris 13, 99 avenue J.-B. Clément, 93430 Villetaneuse, France² LNE-SYRTE, UMR 8630 CNRS, Observatoire de Paris, 61 avenue de l'Observatoire, 75014 Paris, France

Received 6 November 2007 / Received in final form 22 February 2008

Published online 4 April 2008 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2008

Abstract. RF frequency transfer over an urban 86 km fibre has been demonstrated with a resolution of 2×10^{-18} at one day measuring time using an optical compensator. This result is obtained with a reference carrier frequency of 1 GHz, and a rapid scrambling of the polarisation state of the input light in order to reduce the sensitivity to the polarisation mode dispersion in the fibre. The limitation due to the fibre chromatic dispersion associated with the laser frequency fluctuations is highlighted and analyzed. A preliminary test of an extended compensated link over 186 km using optical amplifiers gives a resolution below 10^{-17} at 1 day.

PACS. 42.62.Eh Metrological applications; optical frequency synthesizers for precision spectroscopy – 06.30.Ft Time and frequency – 42.81.Uv Fiber networks – 42.81.Gs Birefringence, polarization

1 Introduction

Besides the current developments of atomic clocks, high resolution frequency distribution and comparison have become a new challenge in the field of frequency metrology. Atomic clocks have improved to a fractional frequency accuracy in the range 10^{-15} – 10^{-16} (see for instance [1–4]) and fractional accuracies in the 10^{-17} range or better are under investigation by several groups. The comparison between collocated clocks has been greatly simplified by the recent development of optical synthesizer based on femtosecond laser frequency comb (see for instance [5]). On the other hand the comparison of distant RF or optical clocks is currently using satellite-based techniques and is limited at a level around 10^{-15} over one day of measurement. In the context of fundamental physics tests the development of long-distance high resolution frequency transfer is an important issue. From the comparison of atomic or molecular clocks the temporal variation of fundamental constants can be measured providing a test of the equivalence principle [6,7]. The development of such measurements for a large number of clocks with different atoms and molecules will allow discriminating the variations of the different constants and will improve the reliability of measurements in this controversial field. Astrophysics could also benefit from such frequency transfer development especially for large-base interferometers [8–12].

* e-mail: amy@univ-paris13.fr

Recent developments gave greater place to optical fibres for high resolution frequency transfer [13]. Progress has been reported in the dissemination of either a RF/microwave [10–12,14,15] or an optical reference frequency [16–18]. Optical transfer is promising and very attractive in the perspective of optical clocks comparison; alternatively a RF system can be easier to implement depending on the local laboratories facilities and the aimed applications.

We have already demonstrated the distribution of a reference signal in the RF domain at 100 MHz through an optical link of 43 km between two laboratories, LPL and LNE-SYRTE [15,19]. Since mechanical perturbation and temperature variation along the fibre slightly perturb the propagation delay on the link, a noise compensation set-up was implemented and described in [14,15]. Two types of noise compensator have been developed, both using a round trip phase correction technique. We will design as electronic compensator the one based on the phase conjugation method; it acts on the phase of the reference signal injected in the link [10]. The so-called optical compensator is based on an optomechanical actuator, which acts directly on the optical length of the fibre [8,11]. With this compensated link, two frequency standards from each laboratory, one in the IR domain (CO_2/OsO_4 at 30 THz) and the other in the microwave domain (CSO at 12 GHz) have been compared with a resolution of 3×10^{-14} at 1 s [15].

This paper is describing the improvement of the transfer resolution on the cascaded 86 km link using an

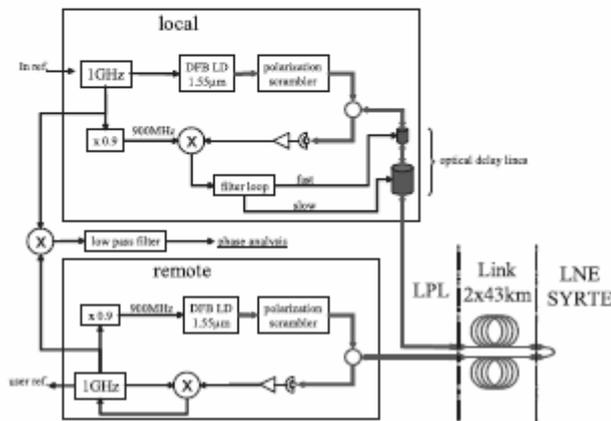


Fig. 1. Block diagram of the 86-km fibre link and the optical compensation system. Both local and remote functions are located in the same place. DFB LD: distributed feedback laser diode.

upgraded optical compensator. Two major developments have been implemented. To gain on the signal-to-noise ratio, the reference carrier frequency has been increased to 1 GHz. To reduce the sensitivity to polarisation mode dispersion (PMD) in the fibre, the polarisation state of the input light has been scrambled. The further limitation due to the fibre chromatic dispersion is highlighted and analyzed. A preliminary attempt to realize a compensated link over 186 km is also presented.

2 RF reference dissemination and noise optical compensation

The schematic of the optical link and its compensation system is shown in Figure 1. The link connecting LPL and LNE-SYRTE is composed of two parallel 43-km dark optical fibres, which have been obtained by splicing a few sections of SMF 28 single mode fibres from the standard telecommunication network. The 86 km link is obtained by cascading the two twin fibres between LPL and LNE-SYRTE. This way the two ends are collocated at LPL, one designated as Local, and the other as Remote.

The input RF signal at 1 GHz is modulating the intensity of a DFB laser diode which is feeding the optical link. The wavelength is about $1.55 \mu\text{m}$ and the maximum output optical power is 20 mW. After propagation along the link, the modulation is detected at the other end of the fibre with a fast photodiode, and used to synthesize a coherent RF signal at 900 MHz. This signal exhibits the phase fluctuations of the forward signal at the Remote end; it modulates the intensity of a second laser diode, which is feeding the link in the backward direction. Optical circulators are used at each fibre end to discriminate the forward and backward optical signals. The backward signal is detected at Local end with a second photodiode and exhibits phase fluctuations produced by one round trip. The phase comparison of this backward signal and

the input signal is realized at 900 MHz and gives a measurement of the round trip phase fluctuations.

The optical polarizations of both laser diodes are scrambled directly at each fibre end, as discussed below. Two different frequencies, 1 GHz and 900 MHz, are used for the forward and backward RF signals in order to eliminate the parasitic signals due to stray optical reflections on connectors and splicing along the link, which are adding noise to the error signal. The stimulated Brillouin back scattering (SBS) is also strongly attenuated by the 100 MHz shift between forward and backward signals, much larger than the SBS gain profile (<10 MHz).

The error signal is processed by a simple analog loop filter and applied to two delay lines, designed as fast and slow ones, at the Local input of the link in order to cancel out the variations of the propagation delay. The fast delay line is achieved with a 15 m length optical fibre that is wrapped around a cylindrical piezoelectrical transducer (PZT). Fast and small variation corrections are applied on the PZT voltage to stretch the fibre with a correction range of about 15 ps. The slow delay line is made of a 4 km optical fibre wrapped around a copper wheel; the slow corrections are applied by heating the whole spool with a sensitivity of $150 \text{ ps}/^\circ\text{C}$ and a total dynamic range of 6 ns. The loop bandwidth is limited by the roundtrip propagation delay (0.88 ms) to a few hundreds Hz. The relative stability of the compensated link is measured by analyzing the phase variation between the 1 GHz signals at both Local and Remote end. The phase signal is filtered with a low-pass filter (3 Hz bandwidth) then digitized and the overlapping Allan deviation of the measured phase samples is deduced.

3 Results and limitations

Figure 2 displays a sample of the phase fluctuation of the compensated link. The propagation delay fluctuation is

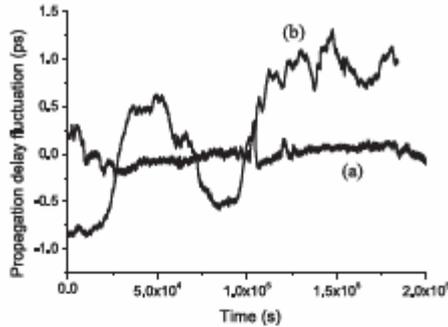


Fig. 2. Propagation delay fluctuation of the compensated link (a) with 2 scramblers and (b) with only one scrambler (see Sect. 4); it is obtained from the differential phase fluctuation of the 1 GHz signals at local and remote ends.

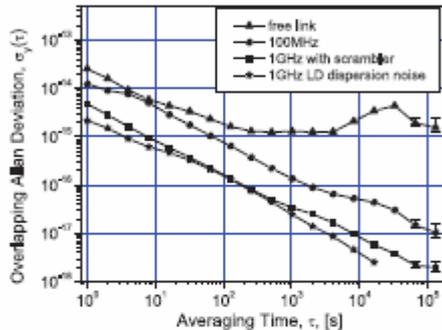


Fig. 3. Fractional frequency stability of the free 86-km link (triangles), the compensated link at 100 MHz (circles) and 1 GHz (squares) and dispersion noise due to the laser diodes frequency fluctuation (stars).

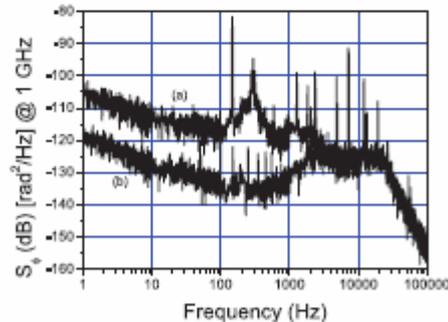


Fig. 4. Phase noise spectral density of the optical compensation system at 1 GHz in closed loop (a) with the 86-km optical fibre (b) with optical attenuators equivalent to the fibre attenuation.

around 1 ps over a few days. The fractional frequency stability of the link is displayed in Figure 3 (squares): it is 5×10^{-15} at 1 s integration time and 2×10^{-18} at one day integration time. For comparison, without any corrections, the stability is 3×10^{-14} at 1 s with a floor around 10^{-15} after 100 s (triangles in Fig. 3) limited by the diurnal temperature variations. The three orders of magnitude reduction of the long-term frequency fluctuations demonstrates the effectiveness of the compensation system. The stability at one day is 5 times better than previous implementation of the link at 100 MHz on 43 km (circles in Fig. 3) [15]. Moreover the average frequency offset between reference signal and transferred signal over the link is zero within the error bars. The better performance of the present system is directly related with the increased of the RF carrier frequency from 100 MHz to 1 GHz (900 MHz for the backward signal). The signal-to-noise ratio of the error signal driving the compensator is increased about a factor 9: fibre phase fluctuations are 9 times higher while detection noise is approximately the same.

The performance of this round trip compensation technique is limited by the parasitic noise on the error signal. Figure 4 shows the phase noise spectral density at 1 GHz of the compensator in closed loop with the 86 km link (upper trace) and with an equivalent optical attenuator instead of the link (lower trace). This last trace displays the noise of the compensation system, which is at the level of -120 dB at 1 Hz. It corresponds to an Allan deviation of 10^{-15} at 1 s integration time, which is the aimed stability for the compensated 86-km link. However the optical link degrades the noise by nearly 15 dB, leading to a noise of -105 dB at 1 Hz. The bump around 300 Hz is due to the bandwidth of the control loop.

This parasitic excess phase noise originates from the fact that the round trip phase fluctuations do not exactly correspond to twice the forward phase fluctuations due to an asymmetry of the phase noise in forward and backward propagation directions along the link. Due to the chromatic and polarization mode dispersions of the fibre the propagation delay is sensitive to the characteristics of the two optical signals injected in each direction at each end of the link. The two laser diodes have uncorrelated optical frequency fluctuations and polarizations state. We show in the next paragraph how the asymmetry due to the polarization mode dispersion (PMD) can be strongly reduced by scrambling the light polarization state at each end. Thus, in our set-up, the short-term frequency stability is limited by the chromatic dispersion and laser frequency fluctuations. The long-term frequency stability is restricted by the RF electronic components temperature sensitivity in the compensator.

4 Polarization effects

The propagation characteristics along the fibre depend on the polarization state through the polarization mode dispersion, PMD (see for instance [20]). The PMD is induced by the birefringence of the optical fibre due to the asymmetry of the core and is varying in time because of the

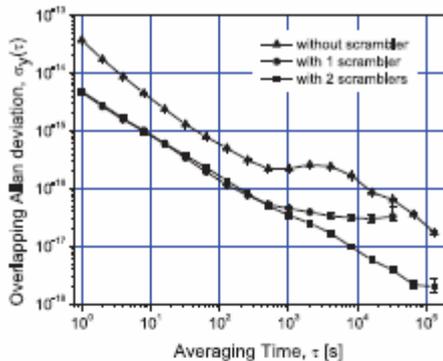


Fig. 5. Polarisation effects: fractional frequency stability of the 86-km compensated link without scramblers (and no fast delay line) (triangles), with only one scrambler at input end (circles), and with two scramblers (squares).

mechanical stress induced by vibrations or by temperature variations. Moreover the directions of both fast and slow axes of the link move randomly in time.

Due to PMD, the propagation delay along the link fluctuates. Since two independent laser diodes with different wavelengths and polarisation states are used at each fibre end, these propagation delay fluctuations are uncorrelated for the forward and backward signals along the link. This lack of symmetry of the propagation delay fluctuations degrades the effectiveness of the noise compensator, which can only correct the symmetrical phase fluctuations, since the error signal is the roundtrip phase fluctuations. The main effect is the degradation of the long term stability.

The polarisation related effects are enhanced by the optical compensator itself. Both delay lines induce a parasitic change of the polarization state of the signal injected in the 86-km link and thus introduce an unwanted variation in the propagation delay along the link. This variation is caused by the stretching of the correction fibres, and can be much faster than the typical slow variation of PMD.

As mentioned above, polarization effects can be significantly reduced by scrambling the polarization directly at each laser diode output, at a frequency higher than the cut off frequency of the stabilization loop. The polarization scrambling is obtained with a commercial three axes piezoelectric polarization scrambler. Each axis is excited with a low voltage sinusoidal signal tuned to a piezoelectric resonance. Among the possible resonance we chose the non-harmonically related ones (around 60, 100, and 130 kHz respectively). This fast polarisation modulation explores all the polarization states much faster than the propagation delay along the link [21]. In this case the differential group delay is averaged and the PMD effects are minimized.

In order to evaluate the limitations due to the PMD or the delay line induced polarisation effects, the following measurements have been performed. The phase fluctuations between the local and remote ends have been first

recorded without any scramblers and the corresponding Allan deviation is plot as triangles in Figure 5. In that case, the fast delay line is not used. In fact, we may notice that the delay lines are set directly at the input end of the link. They affect the polarisation from the input of the fibre, and their effect on the propagation delay fluctuations is then enhanced by the PMD. With the PZT fibre stretcher this effect is high enough to perturb the correction loop and prevent its use. Thus for time scale below 100 s there is no correction and the fractional frequency stability is that of the free link. For time scale above 100 s the stability is degraded by the polarisations effects about one order of magnitude. The bump between 10^3 and 10^4 s is due to the slow thermal compensator, which is also changing the polarisation. Since this Allan deviation is not typical from PMD effects, a second experiment has been performed with only one scrambler at the Local end (that is on the forward way) and no scrambler at the Remote end on the backward way. In that case, both delay lines are used and the polarisations effects due to the delay lines and PMD are minimized on the forward propagation delay. On the backward propagation way however, PMD effects are still effective but they are not enhanced by the delay line induced polarisation effects since the delay lines are at the output end of the backward way. With this scheme we aim to test the PMD of the 86-km fibre link alone. The phase fluctuations are displayed in Figure 2 together with the phase fluctuations of the compensated link with the two scramblers. Let us remind that the compensation system does not distinguish the forward and backward fluctuations and the delay lines are correcting on each way half the total round trip fluctuations. Since the PMD affects solely the backward phase fluctuations, only half of the PMD phase fluctuations can be corrected, and the phase data in closed loop still exhibits half the PMD phase fluctuations on the backward way. It amounts around 2 ps, and thus the effects of PMD on one way is about 4 ps. The Allan deviation plot of the phase data of Figure 2 is displayed as circles in Figure 5 and compared to the Allan deviation plot with two scramblers (squares). The PMD does not affect the short-term stability but diurnal temperature variations of the PMD degrade the long-term frequency stability to a few 10^{-17} .

Finally, when scrambling the polarization, the stability (squares in Figs. 3 or 5) reaches a value compatible with the laser dispersion noise level (see Sect. 5 below), which demonstrates that the polarization effects are strongly cancelled out.

5 Chromatic dispersion effects

The second source of parasitic noise limiting the compensation performance arises from the chromatic dispersion of the fibre associated with the frequency fluctuations of the laser diodes. An additional phase noise, that we will call dispersion noise, is induced along the fibre, and is not correlated in the forward and backward signals. This asymmetrical additional phase noise can not be corrected by our compensation system.

The laser current modulation induces both an amplitude and a frequency modulation (chirp), and the spectrum of both laser diodes is constituted by a carrier at the optical frequency and sidebands separated by the reference RF frequency $\frac{\Omega}{2\pi}$ ($= 0.9$ or 1 GHz) [22]. The detected signal at the RF frequency results from the beat notes between adjacent lines, which propagate at different velocities due to the dispersion. At first order, the propagation time of two adjacent lines differs from the quantity

$$\Delta t_d = -DL \left(\frac{\lambda_0 \Omega}{\omega_0} \right)$$

where $D = 17$ ps/kmnm is the dispersion of the fibre, L the fibre length (in km), λ_0 the laser wavelength (in nm) and $\frac{\omega_0}{2\pi}$ the laser frequency. In our case at 1 GHz, $\Delta t_d = -12.3$ ps for the 90-km fibre (including the link and the correction fibre spool). The phase detected at each end of the fibre at 1 GHz (respectively 900 MHz) is the contribution of two terms: $\Delta\varphi = \Omega t_0 + \omega_0 \Delta t_d$ where t_0 is the propagation time of the laser carrier along the fibre (see detailed calculation in Appendix). The fluctuation of t_0 in the first term gives the fibre noise that we want to correct. The second term gives the so-called dispersion noise resulting from the conversion of the laser frequency noise by the fibre chromatic dispersion. The resulting dispersion noise after one round trip is $(\delta\omega_{LD1} + \delta\omega_{LD2}) \Delta t_d$ where $\delta\omega_{LD1}$ and $\delta\omega_{LD2}$ are the uncorrelated frequency fluctuations of each laser diode. The dispersion noise degrades the system phase noise level of around 15 dB (see Fig. 4), leading to a noise of -105 dB at 1 Hz.

At the remote end, the remaining phase noise is

$$\delta\phi_d = \frac{(\delta\omega_{LD1} + \delta\omega_{LD2}) \Delta t_d}{2}$$

in closed loop. This additional phase noise can be evaluated by measuring the beat-note of the two laser diodes with a counter (Allan deviation ≈ 250 kHz at 1 s). The laser frequency fluctuations

$$\frac{\delta\omega_0}{2\pi} = \frac{\delta\omega_{LD1} + \delta\omega_{LD2}}{2\pi}$$

is then converted into the above RF phase noise $\delta\phi_d = \frac{\delta\omega_0}{2} \Delta t_d$. The Allan deviation floor (star plot) due to this effect is displayed in Figure 3 and is very close to the Allan deviation of the compensated link. The small difference partly arises from the additional thermal fluctuations induced by the compensator on the laser diodes. This demonstrates that the laser frequency noise associated with the dispersion of the fibre is presently the main limitation for the resolution of the compensation link. It is worth noting that this contribution to the noise scales linearly with the modulation frequency through Δt_d and, thus, cannot be reduced by increasing this value.

This limitation could be overcome with a stabilisation of the laser diodes frequencies. Extensive efforts had already been done to reduce the laser frequency fluctuations with a better control of the diode temperature and bias current. An active stabilisation is more efficient although

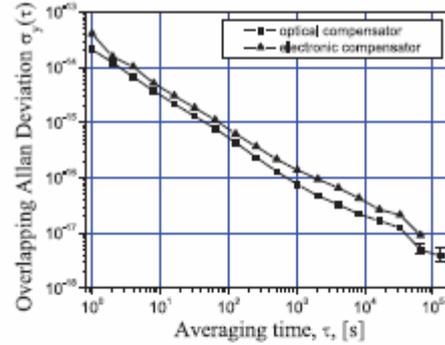


Fig. 6. Preliminary fractional frequency stability of the 186-km link. Triangles: electronic compensator; squares: optical compensator.

not straightforward to implement, especially at long-term. Laser frequency fluctuation of the order of 1 kHz at 1 s would lead to a negligible noise contribution (at the level of 10^{-17}). Finally a more simple solution would consist in adding a negative dispersion fibre of adequate length. This would compensate for the link chromatic dispersion, even if losses will be inserted.

6 Longer link: the problem of the attenuation

The above results demonstrate that an RF optical link can be used for metrological purposes to disseminate a RF reference signal between laboratories in the same area. We present a preliminary evaluation of this technique for longer distances, which has been tested by adding fibre spools to the existing 86-km link.

For a longer link, the performance of the noise compensator is still limited by the dispersion noise, which increases proportionally to the fibre length. Moreover the signal-to-noise ratio is further reduced by the attenuation of the fibre spool, which yields a reduction of 40 dB on the RF signal for each 100 km of additional fibre. This attenuation can not be compensated by increasing the laser diodes power, since the power in each sideband is already near the threshold of SBS. To overcome this limitation we use Erbium Doped Fibre Amplifiers (EDFA). A preliminary test was done with a 186-km link composed of the 86-km link and 100 km of fibre spools. Two standard telecom unidirectional amplifiers were connected with two optical circulators in order to obtain a full bidirectional configuration. This composite bidirectional EDFA was inserted at half distance of the link and the amplification level was adjusted to compensate the additional optical losses. For such an amplification level (around 20 dB), the EDFA's excess phase noise is equivalent to a few 10^{-18} frequency stability at 1 s, which is negligible compared to the chromatic dispersion noise.

Figure 6 shows preliminary results of the relative frequency stability of this 186 km link for two different set-ups, one using the optical compensator and the other an electronic compensator. For this alternative compensator described in [14], the correction is applied directly on the RF source signal. The two systems give about the same results. At short-term, the Allan deviation for the optical compensator is 2×10^{-14} at 1 s integration time, whereas the limit due to the laser dispersion is 1×10^{-14} at 1 s. This small difference could be attributed to any optical or electronic components which have not been carefully optimised for these measurements. The long term frequency stability is better than 10^{-17} at one day integration time.

This demonstrates the first realization of a RF frequency transfer below 10^{-17} level on distances above 100 km. The resolution is very close to the limit due to the dispersion noise, which demonstrates that EDFA's can be used to compensate for the attenuation. For longer distances the stability is degraded because the fibre phase fluctuations and the loop bandwidth are respectively increasing and reducing with the fibre length. For a 1000 km link around 10 EDFA's should be used to recover the signal, the control bandwidth is reduced to around 10 Hz, and the fibre noise could not be corrected by more than a factor of 10 at 1 s. However the present set-up demonstrates an elementary component which could act as a repeater for frequency dissemination over a multi-section optical link. By cascading a few such systems the stability of around 10^{-17} at one day could be maintained over distances up to 1000 km.

7 Conclusion

We have demonstrated a 86-km compensated link from an urban network with a frequency stability of 5×10^{-15} at one second and 2×10^{-18} at one day integration time. These results were obtained after the limiting effects were analyzed and two different AM frequencies used for each propagation direction and light polarization state scrambled. The dispersion of the fibre, associated with the laser frequency fluctuations, gives the present limit of our compensation set-up. This limitation can be overcome by the laser frequency stabilisation or by the cancelling of the chromatic dispersion with a negative dispersion fibre. In that case, an Allan deviation of 10^{-15} at 1 s is achievable, limited by the electronic noise of the compensator. For a longer link, the signal attenuation becomes critical. For 186-km, a stability below 10^{-17} at one day integration time has been measured using EDFA's and the short-term is limited by the fibre chromatic dispersion. This demonstrates a quite simple repeater for multi-section frequency dissemination over very long distances.

The compensator could be further improved by using a microwave frequency signal around 10 GHz instead of the present 1 GHz signal. The signal-to-noise ratio of the error signal is indeed proportional to the reference frequency. Thus the distance between repeaters for multi-section frequency transfer could be chosen with an additional tolerance of 50 km. The degradation of the error signal due

to the EDFA's and the electronic noise is also much less critical. However the set-up and compensator should be adapted to microwave modulation techniques and the stability improvement is not straightforward.

The present results give a new opportunity to compare distant frequency standards. Our compensation system constitutes a robust repeater with 100% duty cycle and a resolution below 10^{-17} at 1 day; it could be used for multi-section frequency transfer up to 1000 km distances. Further developments should render optical links a real alternative to satellite link.

This work was supported by Ministère de la Recherche and European Space Agency/ESOC.

Appendix

The laser field is given by

$$E = E_0 \sqrt{1 + m_i \cos \Omega t} e^{j(\omega_0 t + m \sin \Omega t)}$$

where m_i and m are respectively the amplitude and frequency modulation indexes. In our case, $m_i = 0.7$ and $m = 15$, due to the chirp coefficient of the laser diode estimated to $\eta = 375$ MHz/mA [20,22].

The field can be developed in Fourier series at the modulation frequency $\frac{\Omega}{2\pi}$. We note $J_n = J_n(m)$ the coefficients of the Fourier serie of the phase, and M_n the coefficients of the Fourier serie of the amplitude $\sqrt{1 + m_i \cos \Omega t} = \sum_{n=0}^{\infty} M_n \cos n \Omega t$.

One obtains an asymmetrical spectrum [22]:

$$E = E_0 e^{j\omega_0 t} \left(L_0 + \sum_{n=1}^{\infty} (L_{n+} e^{j n \Omega t} + L_{n-} e^{-j n \Omega t}) \right)$$

with

$$\begin{cases} L_0 = \sum_{a=0}^{\infty} M_{2a} J_{2a} \\ L_{n+} = \frac{1}{2} (M_0 J_n + J_0 M_n) \\ \quad + \frac{1}{2} \sum_{a=1}^{\infty} J_a \times (M_{|n-a|} + (-1)^a M_{n+a}) \\ L_{n-} = \frac{1}{2} ((-1)^n M_0 J_n + J_0 M_n) \\ \quad + \frac{1}{2} \sum_{a=1}^{\infty} J_a \times (M_{n+a} + (-1)^a M_{|n-a|}). \end{cases}$$

After propagation along the fibre, the Fourier components are dephased by the quantities φ_0 (for the fundamental) and φ_{n+} and φ_{n-} (for the $+n\Omega$ and $-n\Omega$ components respectively).

At low order (in term of chromatic dispersion), we have:

$$\begin{cases} \varphi_0 - \varphi_{1+} = -\omega_0 \Delta t_d - \Omega \Delta t_d - \Omega t_0 \\ \varphi_0 - \varphi_{1-} = \omega_0 \Delta t_d - \Omega \Delta t_d + \Omega t_0 \\ \varphi_{1+} - \varphi_{2+} = -\omega_0 \Delta t_d - 3\Omega \Delta t_d - \Omega t_0 \\ \varphi_{1-} - \varphi_{2-} = \omega_0 \Delta t_d - 3\Omega \Delta t_d + \Omega t_0 \\ \dots \end{cases}$$

The intensity is detected and filtered at $\frac{\Omega}{2\pi}$. One obtains:

$$S = 2 \sum_{n=0}^{\infty} (L_{n+} L_{(n+1)+} + L_{n-} L_{(n+1)-}) \cos((2n+1)\Omega \Delta t_d) \\ \times \cos(\Omega t - \omega_0 \Delta t_d - \Omega t_0) + 2 \sum_{n=0}^{\infty} (L_{n+} L_{(n+1)+} - L_{n-} L_{(n+1)-}) \\ \times \sin((2n+1)\Omega \Delta t_d) \sin(\Omega t - \omega_0 \Delta t_d - \Omega t_0).$$

The term in quadrature is resulting from the frequency modulation of the laser, which induces a non-symmetrical spectrum. Note also that the amplitude is depending from the differential time delay Δt_d . The amplitude is thus modulated with the fibre length.

References

1. C. Vian et al., *IEEE Trans. Instrum. Meas.* **54**, 833 (2005)
2. R. Le Targat et al., *Phys. Rev. Lett.* **97**, 130801 (2006)
3. M.M. Boyd et al., *Phys. Rev. Lett.* **98**, 083002 (2007)
4. W.H. Oskay et al., *Phys. Rev. Lett.* **97**, 020801 (2006)
5. S.T. Cundiff, J. Ye, J.L. Hall, *Rev. Sci. Instrum.* **72**, 3749 (2001)
6. S.G. Karshenboim, *Can. J. Phys.* **83**, 767 (2005)
7. V.V. Flambaum, *Phys. Rev. D* **69**, 115008 (2004)
8. B. Shillue, ALMA Memo No. 443 (2002), <http://www.alma.nrao.edu/nemos/>
9. M. Musha et al., *Appl. Phys. B* **82**, 555 (2006)
10. R.T. Logan, G.F. Lutes, *Proc. of IEEE Frequency Control Symposium* **310** (1992)
11. M. Calhoun, S. Huang, R.L. Tjoelker, *Proceedings of the IEEE, Special Issue on Technical Advances in Deep Space Communications & Tracking* **95** (2007)
12. K. Sato et al., *IEEE Trans. Instrum. Meas.* **49**, 19 (2000)
13. S. Foreman et al., *Rev. Sci. Instrum.* **78**, 021101 (2007)
14. F. Narbonne et al., *Rev. Sci. Instrum.* **77**, 064701 (2006)
15. C. Dausy et al., *Phys. Rev. Lett.* **94**, 203904 (2005)
16. N.R. Newbury, P.A. Williams, W.C. Swann, *Opt. Lett.* **32**, 3056 (2007)
17. S.M. Foreman et al., *Phys. Rev. Lett.* **99**, 153801 (2007)
18. G. Grosche et al., *CLEO Report No. CMK11* (2007)
19. A. Amy-Klein et al., *Appl. Phys. B* **78**, 25 (2004)
20. M.I. Joindot, *Les Télécommunications par fibres optiques* (Dunod and CNET-ENST, Paris, 1998)
21. R. Noe, H. Heidrich, D. Hoffmann, *J. Lightwave Technol.* **6**, 1199 (1988)
22. G.J. Meslener, *IEEE J. Quant. Electr.* **QE-20**, 1208 (1984)

Références

1. D.W. Rein, *Some remarks on parity violating effects of intramolecular interactions*, J. Mol. Evol. **4**, 15-22, 1974
2. V.S. Letokhov, *On difference of energy levels of left and right molecules due to weak interactions*, Phys. Lett. **53A**, 275, 1975
3. P. Franck et al., in *Chemistry for the 21st Century*, E.K.a.I.S. (ed.), Editor, Willey-VCH Germany, 173-208, 2001
4. D.K. Kondepudi et al., *Weak neutral currents and the origin of biomolecular chirality*, Nature **314**, 438-441, 1985
5. J.K. Laerdahl et al., *Theoretical analysis of parity-violating energy differences between the enantiomers of chiral molecules*, Phys. Rev. Lett. **84**, 3811-3814, 2000
6. R. Berger, *Parity-Violation Effects in Molecules*, in *Relativistic Electronic Structure Theory. Part 2: Applications*, P. Schwerdtfeger (ed.), Elsevier, Amsterdam, 188, 2004
7. C.J. Bordé, *Spectroscopie d'absorption saturée de diverses molécules au moyen des lasers à gaz carbonique et à protoxyde d'azote*, C. R. Acad. Sc. Paris **271B**, 371, 1970
8. O.N. Kompanets et al., *Narrow resonances of saturated absorption of the asymmetrical molecule CHFClBr and the possibility of weak current detection in molecular physics*, Opt. Comm. **19**, 414-416, 1976
9. E. Arimondo et al., *Observation of inverted infrared lamb dips in separated optical isomers*, Opt. Comm. **23**, 369-372, 1977
10. P. Schwerdtfeger et al., *The vibrational spectrum of camphor from ab initio and density functional theory and parity violation in the C-C*-CO bending mode*, Chem. Phys. Lett. **383**, 496, 2004
11. A.L. Barra et al., *Parity non-conservation and NMR parameters*, Mol. Phys. **88**, 875, 1996

12. M. Quack, *Structure and dynamics of chiral molecules*, Angew. Chem. Int. Ed. **28**, 571, 1989
13. R.A. Harris, L. Stodolsky, *Quantum beats in optical activity and weak interactions*, Phys. Lett. B **78**, 313, 1978
14. A.S. Lahamer et al., *Search for a parity-violating energy difference between enantiomers of a chiral iron complex*, Phys. Rev. Lett. **85** (21), 4470-4473, 2000
15. J. Costante-Crassous et al., *Absolute configuration of bromochlorofluoromethane from molecular dynamics simulation of its enantioselective complexation by cryptophane-C*, J. of the Am. Chem. Soc. **119**, 3818-3823, 1997
16. J. Crassous et al., *The bromochlorofluoromethane saga*, Enantiomer **5** (5), 429-438, 2000
17. V. Bernard et al., *CO₂ laser stabilization to 0.1-Hz level using external electrooptic modulation*, IEEE J. of Quant.Elec. **QE-33**, 1282-1287, 1997
18. V. Bernard et al., *CO₂ laser stabilized on narrow saturated absorption resonances of CO₂: improved absolute frequency measurements*, Metrologia **34**, 314-318, 1997
19. A. Bauder et al., *Combined high resolution infrared and microwave study of bromochlorofluoromethane*, J. of Chem. Phys. **106** (18), 7558-7570, 1997
20. C. Daussy et al., *Limit on the parity nonconserving energy difference between the enantiomers of a chiral molecule by laser spectroscopy*, Phys. Rev. Lett. **83**, 1554-1557, 1999
21. T. Marrel et al., *High precision rovibrational and hyperfine analysis of the $\nu_4=1$ level of bromochlorofluoromethane*, J. of Mol. Struct. **599**, 195-209, 2001
22. M. Ziskind et al., *Improved Sensitivity in the Search for a Parity-Violating Energy Difference in the Vibrational Spectrum of the Enantiomers of CHFClBr*, EPJ D **20**, 219-225, 2002

-
23. R.G. Viglione et al., *Theoretical determination of parity-violating vibrational frequency differences between the enantiomers of the CHFClBr molecule*, Phys. Rev. A **62** (5), 052516/1-5, 2000
 24. M. Quack et al., *On the influence of parity weak nuclear potentials on vibrational and rotational frequencies in chiral molecules*, Phys. Rev. Lett. **84**, 3807-3811, 2000
 25. P. Schwerdtfeger et al., *Relativistic Second-Order Many-Body and Density Functional Theory for the Parity-Violation Contribution to the C-F Stretching Mode in CHFClBr*, Phys. Rev. A **71**, 012103, 2005
 26. P. Schwerdtfeger et al., *Calculation of parity-violation effects for the C-F stretching mode of chiral methyl fluorides*, Phys. Rev. A **65** (4), 0425081-7, 2002
 27. J. Crassous et al., *Search for resolution of chiral fluorohalogenomethanes and parity-violation effects at the molecular level*, Chem. Phys. Chem. **4**, 541, 2003
 28. P. Schwerdtfeger et al., *Parity Violation Effects in the C-F stretching Mode of Heavy Atom Containing Methyl Fluorides*, Phys. Rev. Lett. **91**, 023001, 2003
 29. A. Shelkovernikov et al., *Two-photon Ramsey fringes at 30 THz referenced to an H Maser / Cs fountain via an optical frequency comb at the 1-Hz level*, IEEE J. of Quant. Elec. **40** (8), 1023-1029, 2004
 30. C. Daussy et al., *Long-distance frequency dissemination with a resolution of 10⁻¹⁷*, Phys. Rev. Lett. **94**, 203904, 2005
 31. A. Amy-Klein et al., *Absolute frequency measurement in the 28 THz spectral region with a femtosecond laser comb and a long-distance optical link to a primary standard*, Appl. Phys. B **78**, 25-30, 2004
 32. A. Amy-Klein et al., *Absolute frequency measurement of a SF₆ two-photon line by use of a femtosecond optical comb and sum-frequency generation*, Opt. Lett. **30** (24), 3320-3322, 2005

-
33. T. Marrel, *Le spectre à très haute résolution de la molécule chirale CHFClBr à 9,3 μm : test de violation de la parité et étude de la structure hyperfine*, Thèse de doctorat, Paris 13, Villetaneuse, 2000
 34. M. Ziskind, *Spectroscopie infrarouge à ultra-haute résolution appliquée à l'étude de symétries fondamentales dans les molécules polyatomiques: recherche d'un effet de violation de parité et test du postulat de symétrisation*, Thèse de doctorat, Paris 13, Villetaneuse, 2001
 35. C. Chardonnet et al., *Towards a first observation of molecular parity violation by laser spectroscopy*, Lecture Series on Computer and Computational Sciences **1**, 1-3, 2005
 36. J. Crassous et al., *Preparation of (+)-chlorofluoroiodomethane, determination of its enantiomeric excess and of its absolute configuration*, Tetrahedron Asymmetry **15**, 1995, 2004
 37. J. Crassous et al., *Gas-chromatographic separation of tri(hetero)halogenomethane enantiomers*, Chirality **17** (8), 488-493, 2005
 38. A. Cuisset et al., *The chiral molecule CHClFI: First determination of its molecular parameters by Fourier transform microwave and millimeter-wave spectroscopies supplemented by ab initio calculations*, J. Phys. Chem. A **109** (25), 5708-5716, 2005
 39. P. Soulard et al., *Chlorofluoroiodomethane as a potential candidate for parity violation measurements: supersonic beam spectroscopy and VCD in the gas phase. Preparation of its partially resolved enantiomers and enantioselective recognition by a chiral cryptophane*, Phys. Chem. Chem. Phys. **8** (1), 79-92, 2006
 40. P. Schwerdtfeger et al., *Large Parity Violation Effects in the Vibrational Spectrum of Organometallic Compounds*, J. Am. Chem. Soc. **126**, 1652, 2004
 41. J. Crassous et al., *Recent experimental and theoretical developments towards the observation of parity violation (PV) effects in molecules by spectroscopy*, Org. Biomol. Chem. **3** (13), 2005

-
42. J.W. Faller et al., *Diastereoselective Synthesis and Electronic Asymmetry of Chiral Nonracemic Rhenium(V) Oxo Complexes Containing the Hydrotris(1-pyrazolyl)borate Ligand*, *Organometallics* **19**, 3957, 2000
 43. M. Goubet et al., *Conformational analysis of urethane investigated by microwave and infrared spectroscopies and quantum chemical calculations*, en préparation,
 44. C. Vian et al., *BNM-SYRTE Fountains: Recent Results*, *IEEE Trans. Instrum. Meas.* **54** (2), 833-835, 2005
 45. T. Rosenband et al., *Frequency ratio of Al⁺ and Hg⁺ single-ion optical clocks; Metrology at the 17th decimal place*, *Science* **319** (5871), 1808-1812, 2008
 46. T. Udem et al., *Absolute Optical Frequency Measurement of the Cesium D₁ Line with a Mode-Locked Laser*, *Phys. Rev. Lett.* **82** (18), 3568-3571, 1999
 47. J. Reichert et al., *Measuring the frequency of light with mode-locked lasers*, *Opt.Comm.* **172** (1-6), 59-68, 1999
 48. D.J. Jones et al., *Carrier-envelope Phase Control of Femtosecond Mode-Locked Lasers and Direct Optical Frequency Synthesis*, *Science* **288**, 635-639, 2000
 49. S.T. Cundiff et al., *Optical frequency synthesis based on mode-locked lasers*, *Rev. of Sc. instr.* **72** (10), 3749-3771, 2001
 50. M. Musha et al., *Robust and precise length stabilization of a 25-km long optical fiber using an optical interferometric method with a digital phase-frequency discriminator*, *Appl. Phys. B* **82**, 555-559, 2006
 51. R.T. Logan et al., *Proc. of IEEE Freq. Contr.Symp.*, 310-316, 1992
 52. M. Calhoun et al., *Stable Photonic Links for Frequency and Time Transfer in the Deep-Space Network and Antenna Arrays*, *Proc. of the IEEE, Spec. Iss. on Tech. Adv. in Deep Space Comm. & Tracking* **95** (10), 2007
 53. K. Sato et al., *Development of an ultrastable fiber optic frequency distribution system using an optical delay control module*, *IEEE Trans. Instr. Meas.* **49** (1), 19-24, 2000

-
54. B.d. Beauvoir et al., *Transmission of an optical frequency through a 3 km long optical fiber*, EPJ D **1** (2), 227-229, 1998
 55. A. Amy-Klein, *Habilitation à Diriger des Recherches*, Université Paris 13, Villetaneuse, 2001
 56. F. Narbonne et al., *High Resolution Frequency Standard Dissemination via Optical Fibre Metropolitan Network.*, Rev. Sci. Instr. **77**, 064701, 2006
 57. M.e.I. Joindot, *Les Télécommunications par fibres optiques*, Dunod, Paris,
 58. O. Lopez et al., *86-km optical link with a resolution of 2×10^{-18} for RF frequency transfer*, EPJ D **48**, 35-41, 2008
 59. M. GUINET et al., *Mesure de la fréquence absolue d'une raie à deux photons de SF₆ en utilisant un peigne femtoseconde*, J. Phys. IV France (135), 183-184, 2006
 60. A. Goncharov et al., *Absolute frequency measurement of iodine-stabilized Ar⁺ laser at 514.6 nm using a femtosecond-laser-based optical clockwork.*, Appl. Phys. B **78**, 725-731, 2004
 61. A. Amy-Klein et al., *Absolute frequency measurement of ¹²C¹⁶O₂ laser lines with a femtosecond laser comb and new determination of the ¹²C¹⁶O₂ molecular constants and frequency grid*, J. of Mol. Spec. (228), 206-212, 2004
 62. A. Shelkovernikov et al., *Stability of the proton-to-electron mass ratio*, Phys. Rev. Lett. **100** (15), 150801, 2008
 63. F. Bielsa et al., *HCOOH High resolution spectroscopy in the 9.18 μm region*, J. Mol. Spec. **247**, 41-46, 2008
 64. J.P. Karr et al., *High-accuracy calculations in the H-2(+) molecular ion: towards a measurement of m(p)/m(e)*, Canadian J. of Phys. **85** (5), 497-507, 2007
 65. F. du Burck et al., *Frequency measurement of the Ar⁺ laser stabilized on narrow lines of molecular Iodine at 501.7 nm*, IEEE Trans. on Instr. and Meas, **54**, 754-758, 2005

-
66. C.J. Bordé, *Atomic clocks and inertial sensors*, *Metrologia* **39**, 435-463, 2002
 67. C.J. Bordé, *Métrieologie fondamentale: unités de base et constantes fondamentales*, *CRAS - Physique* **5** (8), 813-820, 2004
 68. C.J. Bordé, *Base units of the SI, fundamental constants and modern quantum physics*, *Phil. Trans. Roy. Soc A* **363**, 2177-2201, 2005
 69. P.J. Mohr et al., *CODATA recommended values of the fundamental physical constants: 2002*, *Rev. of mod. phys.* **77**, 1-107, 2005
 70. P.J. Mohr et al. *CODATA recommended values of the fundamental physical constants: 2006*, 2007 available from: <http://physics.nist.gov/constants>.
 71. J.W.G. Wignall, *Some comments on the definition of mass*, *Metrologia* **44**, 19-22, 2007
 72. B.N. Taylor et al., *On the redefinition of the kilogram*, *Metrologia* **36**, 63-64, 1999
 73. B.W. Petley, *The atomic units, the kilogram and the other proposed changes to the SI*, *Metrologia* **44**, 69-72, 2007
 74. I.M. Mills et al., *Redefinition of the kilogram: a decision whose time has come*, *Metrologia* **42**, 71-80, 2005
 75. I.M. Mills et al., *Redefinition of the kilogram, ampere, kelvin and mole: a proposed approach to implementing CIPM recommendation 1 (CI-2005)*, *Metrologia* **43(3)**, 227-246, 2006
 76. M. Stock et al., *CPEM 2006 round table discussion: Proposed changes to the SI*, *Metrologia* **43**, 583-587, 2006
 77. P. Becker et al., *Considerations on future redefinitions of the kilogram, the mole and other units*, *Metrologia* **44**, 1-14, 2007
 78. V.S. Tuninsky, *Unit system based on the fundamental constants*, *Metrologia* **36**, 9-14, 1999

-
79. B.P. Leonard, *On the role of the Avogadro constant in redefining SI units for mass and amount of substance*, Metrologia **44**, 82-86, 2007
 80. R. Rusby et al., *Review of methods for a redetermination of the Boltzmann constant*, NPL Report DEPC TH006, 2005
 81. B. Fellmuth et al., *Determination of the Boltzmann constant: status and prospects*, Meas. Sci. Technol **17**, R145-R159, 2006
 82. H. Nyquist, *Thermal agitation of electric charge in conductors*, Phys. Rev. **32**, 110-113, 1928
 83. L. Storm, *Precision measurements of the Boltzmann constant*, Metrologia **22** (3), 229-234, 1986
 84. D.R. White et al., *The status of Johnson noise thermometry*, Metrologia **33** (4), 325-335, 1996
 85. T.J. Quinn et al., *A radiometric determination of the Stefan-Boltzmann constant and thermodynamic temperature between -40°C and +100°C*, Phil. Trans. R. Soc. Lond. A **316**, 85-189, 1985
 86. J.E. Martin et al., *A Cryogenic Radiometer for Absolute Radiometric Measurements*, Metrologia **21**, 147-155, 1985
 87. N.P. Fox, *Radiometry with cryogenic radiometers and semiconductor photodiodes*, Metrologia **32**, 535-543, 1995/96
 88. M.R. Moldover et al., *Measurement of the universal gas constant R using a spherical acoustic resonator*, J. Res. Natl. Bur. Stand. **93**, 85, 1988
 89. M.R. Moldover, *Measurement of the universal gas constant-R using a spherical acoustic resonator*, Phys. Rev. Lett. **60**, 249-252, 1988
 90. A.R. Colclough et al., *Acoustic redetermination of the gas-constant*, Proc. R. Soc. London Ser. A **368** (1732), 125-139, 1979

-
91. M.-G. He et al., *Measurement of the universal gas constant R with a spherical resonator*, Acta Phys. Sin. (Chin. Ed.) **51** (5), 2002
 92. L. Pitre et al., *Acoustic thermometry: new results from 273 K to 77 K and progress towards 4 K*, Metrologia **43**, 142-162, 2006
 93. J.B. Mehl et al., *Designing quasi-spherical resonators for acoustic thermometry*, Metrologia **41**, 295-304, 2004
 94. L.R. Pendrill, *Macroscopic and microscopic polarizabilities of helium gas*, J. Phys. B **29** (16), 3581-3586, 1996
 95. Lach, *Radiative corrections to the polarizability of helium*, Phys. Rev. Lett. **92** (23), 233001, 2004
 96. J.W. Schmidt et al., *Polarizability of Helium and Gas Metrology*, Phys. Rev. Lett. **98**, 254504, 2007
 97. H. Luther et al., *Determination of thermodynamic temperature and ^4He virial coefficients between 4.2 K and 27.0 K by dielectric constant gas thermometry*, Metrologia **33** (4), 341-352, 1996
 98. K. Fujii et al, *Present State of the Avogadro Constant Determination From Silicon Crystals With Natural Isotopic Compositions*, IEEE Trans.on Instr. and Meas. **54** (2), 854-859, 2005
 99. A. Wicht et al., *A preliminary measurement of the fine structure constant based on atom interferometry*, PHYSICA SCRIPTA **T102**, 82-88, 2002
 100. P. Cladé et al., *Determination of the fine structure constant based on Bloch oscillations of ultracold atoms in a vertical optical lattice*, Phys. Rev. Lett. **96** (3), 033001, 2006
 101. C. Daussy et al., *Spectroscopic determination of the Boltzmann constant: first results*, in *Laser Spectroscopy*, World Scientific Publishing Co. Pte. Ltd., edited by Prof Ed Hinds, Prof Allister Ferguson and Dr Erling Riis, 2005

-
102. M. Guinet et al., *Premiers résultats de mesure optique de la constante de Boltzmann par métrologie des fréquences*, J. Phys. IV Fr. **135**, 181-182, 2006
103. J.M. Chevalier, *conception et réalisation de modulateurs hyperfréquences pour laser à CO₂. Application à la spectroscopie infra-rouge à haute résolution*, Thèse de doctorat, Université des sciences et techniques de Lille Flandres Artois, Lille, 1989
104. O. Pfister et al., *CO₂ laser sideband spectroscopy at ultra-high resolution*, J. Opt. Soc. Am. B **10**, 1521-1525, 1993
105. C. Daussy et al., *First direct determination of the Boltzmann constant by an optical method: towards a new definition of the Kelvin*, Phys. Rev. Lett. **98**, 250801, 2007
106. C. Daussy et al., *La constante de Boltzmann mesurée par spectroscopie laser*, Images de la Physique 2006, 80-85, 2007
107. W. Demtröder, *Laser Spectroscopy 2nd ed.*: Springer, 1996
108. J. Vanier et al., *The Quantum Physics of Atomic Frequency Standards*. Vol. 1: IOP Publishing Ltd, 1989
109. C.J. Bordé et al., *Saturated absorption line shape: Calculation of the transit-time broadening by a perturbation approach*, Phys. Rev. A **14** (1), 236-265, 1976
110. C.J. Bordé, *Density matrix equations and diagrams for high resolution non-linear laser spectroscopy: application to Ramsey fringes in the optical domain*, in *Advances in laser spectroscopy*, F.T. Arecchi, F. Strumia, and H. Walther, Editors, Plenum publishing corporation, 1-70, 1983
111. C.J. Bordé, *Private communication*,
112. R.H. Dicke, *The Effect of Collisions upon the Doppler Width of Spectral Lines*, Phys. Rev. **89** (2), 472-473, 1953
113. M. Ouhayoun et al., *Vibrational dependence of hyperfine quadrupole constant in (NH₃)-N-14 observed by saturated absorption spectroscopy*, Mol. Phys. **33** (2), 597-600, 1977

-
114. C.J. Bordé et al., *Internal Dynamics of simple molecules revealed by the superfine and hyperfine structures of their infrared spectra*, Laser Spectroscopy VII, 108-113, 1985
115. K. Djerroud et al., *Towards an optical measurement of the Boltzmann constant at the 10-5 level*, Ann. Phys. Fr. **32** (2-3), 175-178, 2007
116. K. Djerroud et al., *Towards an optical measurement of the Boltzmann constant at 1 ppm*, en préparation pour CRAS, 2009
117. L. Galatry, *Simultaneous Effect of Doppler and Foreign Gas Broadening on Spectral Lines*, Phys. Rev. **122** (4), 1218-1223, 1961
118. M. Nelkin et al., *Simple Binary Collision Model for Van Hove's $G_s(r,t)$* , Phys. Rev. A **135** (1A), 4-9, 1964
119. S.G. Rautian et al., Sov. Phy. Usp. **9**, 701-716, 1967
120. A.S. Pine et al., *N_2 , O_2 , Ar and He Broadening in the ν_1 bande of NH_3* , Quant. Spectrosc. Radiat. Transfer **50/4**, 337-348, 1993
121. C.E. Baker, *Temperature dependence of self-diffusion coefficients for gaseous ammonia*, NASA Technical Note **TN D-5574**, 1969
122. M. Guinet, *Première détermination de la constante de Boltzmann par une méthode optique*, thèse de doctorat, Université Paris 13, Villetaneuse, 2006
123. R. Berger et al., *Isotopic chirality and molecular parity violation*, Angew. Chem. Int. Ed. **44**, 3623-3626, 2005
124. M. Quack et al., *High-resolution spectroscopic studies and theory of parity violation in chiral molecules*, Annu. Rev. Phys. Chem. **59**, 741-769, 2008
125. P. O. Schmidt et al., *Spectroscopy Using Quantum Logic*, **309** (5735), 749 - 752, 2005
126. O.R. Asvany, O; Muller, HSP, et al., *High-resolution rotational spectroscopy in a cold ion trap: H_2D^+ and D_2H^+* , Phys. Rev. Lett. **100** (23), 233004, 2008

-
127. P. Milman et al., *Topologically decoherence-protected qubits with trapped ions*, Phys. Rev. Lett. **99** (2), 020503, 2007
128. A. Ostendorf et al., *Sympathetic cooling of complex molecular ions to millikelvin temperatures*, Phys. Rev. Lett. **97** (100), 243005, 2006
129. S. Schiller et al., *Tests of time independence of the electron and nuclear masses with ultracold molecules*, Phys. Rev. A **71**, 032505, 2005
130. E.R. Hudson et al., *Cold molecule spectroscopy for constraining the evolution of the fine structure constant*, Phys. Rev. Lett. **96**, 143004, 2006
131. S.J.a.M.D. Anders Bertelsen, *The rotational temperature of polar molecular ions in Coulomb crystals*, J. Phys. B: At. Mol. Opt. Phys. **39** (5), L83-L89, 2006
132. J.C.J. Koelemeij et al., *Vibrational spectroscopy of HD^+ with 2-ppb accuracy*, Phys. Rev. Lett. **98**, 173002, 2007
133. S.Y.T. van de Meerakker et al., *Stark deceleration and trapping of OH radicals*, Annual Rev. Of Phys. Chem. **57**, 159-190, 2006
134. G. Casa et al., *Primary gas thermometry by means of laser-absorption spectroscopy: Determination of the Boltzmann constant*, Phys. Rev. Lett. **100** (20), 2008
135. K.M.T. Yamada et al., *high precision line profile measurements on ^{13}C acetylene using a near infrared frequency comb spectrometer*, J. Mol. Spec. **259**, 95-99, 2008

Résumé

Les travaux présentés ont été menés au sein de l'équipe HOTES (Horloges optiques et tests fondamentaux par spectroscopie et interférométrie atomique et moléculaire) du Laboratoire de Physique de Lasers (LPL) à Villetaneuse. La philosophie générale de l'équipe est de développer des expériences de très haute précision en spectroscopie moléculaire appliquées à des problèmes originaux de physique fondamentale.

La première partie de ce travail porte sur le développement d'une expérience de recherche d'un effet de non conservation de la parité dans des molécules chirales par spectroscopie laser. Cette expérience nous a conduit à un gain de près de 5 ordres de grandeur par rapport à la sensibilité de la précédente mesure publiée en 1977. Nous avons conclu au terme de ce travail à la nécessité de passer à une expérience en jet moléculaire pour aboutir à l'observation de l'effet. La sensibilité requise nécessite par ailleurs des sources lasers très bien contrôlées en terme de stabilité de fréquence et de reproductibilité. Nous avons donc développé un lien optique entre le LPL et le SYRTE (Paris) pour le transfert longue distance d'une fréquence d'horloge. Nous avons ensuite appliqué ce transfert à des expériences de métrologie au LPL au cours desquelles nous avons notamment démontré une amélioration significative du contrôle en fréquence de nos lasers à CO₂. Enfin depuis 4 ans, nous développons une nouvelle expérience de spectroscopie moléculaire avec pour objectif la première mesure de la constante de Boltzmann par spectroscopie laser à un niveau de quelques ppm. Le travail mené devrait prochainement nous permettre d'atteindre notre objectif. Cette nouvelle thématique nous conduit également à nous intéresser à des problèmes très fondamentaux sur les profils de raies en absorption linéaire.

Mots clés:

Métrologie des fréquences

Spectroscopie moléculaire à ultra haute résolution

Etalons de fréquence

Interaction faible

Constantes fondamentales