

Structures et propriétés d'agrégats de silicium dopés avec des alcalins

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Introduction

Un sujet d'intérêt: microélectronique

Un sujet actuel: les études d'agrégat silicium-métaux
(plusieurs centaines de publications depuis 2004)

Si_n-alcalin: Exp PI(Si_nNa_p), Kaya et al., *J. Chem. Phys.*, **1997**,
107, 3056.

Le but: • l'étude de la géométrie des petits agrégats silicium-
alcalin (neutres et cations) de type Si_nM_p ($n \leq 6$, $p \leq 2$)
et pour les agrégats plus gros de type cage Si_nM
($10 \leq n \leq 20$) ;

- la stabilité et les propriétés électroniques et
structurales.

M=Li, Na ou K

Sommaire

Méthode

Les résultats

I. Petits agrégats

1. Les structures optimisées

2. Les propriétés physico-chimiques

- ❖ Transfert de charge
- ❖ Potentiel d'ionisation
- ❖ Énergie de liaison
- ❖ Moment dipolaire

II. Cages: Les structures optimisées - stabilité et propriétés

Conclusions

Perspectives

Approche théorique

Méthodes de calculs envisagées: MP2 et DFT

• Tests sur les diatomiques Si_2 , SiM ...



- ✓ Distances internucléaires d'équilibre: $R_e(\text{\AA})$
- ✓ Potentiel d'ionisation: $PI(\text{eV})$
- ✓ Énergie de liaison: $E_b(\text{eV})$

Approche théorique

| $R_e(\text{Å})$ | | | | | |
|--|----------------|-----------------|-----------------|------------------|--------------|
| <i>Molécule</i> | MP2/6-311+G(d) | BPW91/6-31+G(d) | B3LYP/6-31+G(d) | B3LYP/6-311+G(d) | Exp. |
| Si ₂ (³ Σ _g ⁻) | 2.164 | 2.303 | 2.171 | 2.166 | 2.246 |
| Li ₂ (¹ Σ _g ⁺) | 2.747 | 2.771 | 2.725 | 2.705 | 2.673 |
| SiNa (⁴ Σ ⁻) | 2.708 | 2.903 | 2.724 | 2.725 | 2.70 2.68 |
| $PI_v(eV)$ | | | | | |
| <i>Molécule</i> | MP2/6-311+G(d) | BPW91/6-31+G(d) | B3LYP/6-31+G(d) | B3LYP/6-311+G(d) | Exp. |
| Si ₂ (³ Σ _g ⁻) | 10.164 | 7.834 | 7.856 | 7.882 | 7.9 |
| Li ₂ (¹ Σ _g ⁺) | 4.335 | 5.133 | 5.254 | 5.322 | 5.113 |
| $E_b(eV)$ | | | | | |
| <i>Molécule</i> | MP2/6-311+G(d) | BPW91/6-31+G(d) | B3LYP/6-31+G(d) | B3LYP/6-311+G(d) | Exp. |
| SiLi (⁴ Σ _g ⁻) | 1.689 | | 1.57 | 1.580 | 1.539 |
| SiLi ⁺ (¹ Σ _g ⁺) | 1.15 | | 0.75 | 0.716 | 0.73 |
| SiNa (⁴ Σ ⁻) | | | 1.19 | 1.11 | 1.45 |

Le compromis acceptable entre précision et coût du calcul
B3LYP/6-31G(d)

Outils

Les calculs ab initio avec GAUSSIAN 98 et GABEDIT (interface graphique)

The screenshot displays the GABEDIT graphical user interface. The main window shows the output of a Gaussian 98 calculation. The output text includes:

```
Integral derivatives from F0D11, F12K(0)F17.  
Symmetry not used in FoFDir.  
MinBra= 0 MaxBra= 2 Meth= 1.  
IRaf=      0 NMat=  1 IRICut=      1 DoRegI=T DoRafI=F ISym2E= 0 J  
Leave Link 703 at Tue Jun 14 20:36:30 2005, MaxMem= 6291456 cpu:  
(Enter /data/logiciels/Gaussian/g98/1716.exe)  
Dipole      =-3.40812564D-03-3.28864175D+00-8.83778078D-02  
Polarizability= 2.10170289D+02 1.07587529D-01 1.84455317D+02  
                2.17782566D-01-5.88721651D-01 1.94010425D+02  
Full mass-weighted force constant matrix:  
Low frequencies --- -8.4839  0.0012  0.0021  0.0029  1.7859  
Low frequencies ---  9.3040 16.0324 35.4459  
***** 1 imaginary frequencies (negative Signs) *****  
Harmonic frequencies (cm**-1), IR intensities (KM/Mole),  
Raman scattering activities (A**4/AMU), Raman depolarizat  
reduced masses (AMU), force constants (mDyne/A) and norma  
                1                2  
                ?A                ?A  
Frequencies -- -5.4340                15.2421  
Red. masses -- 29.8463                31.7823  
Frc consts --  0.0005                0.0044  
IR Inten  --  0.0465                11.4361
```

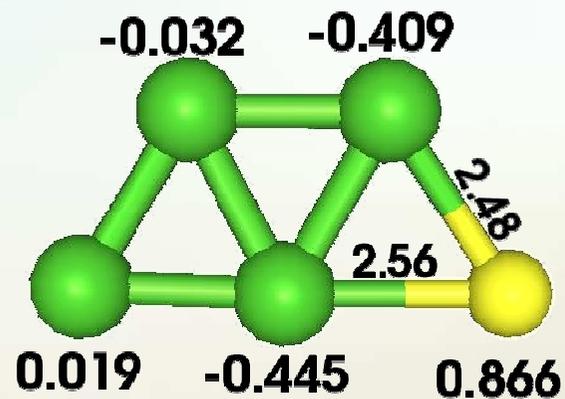
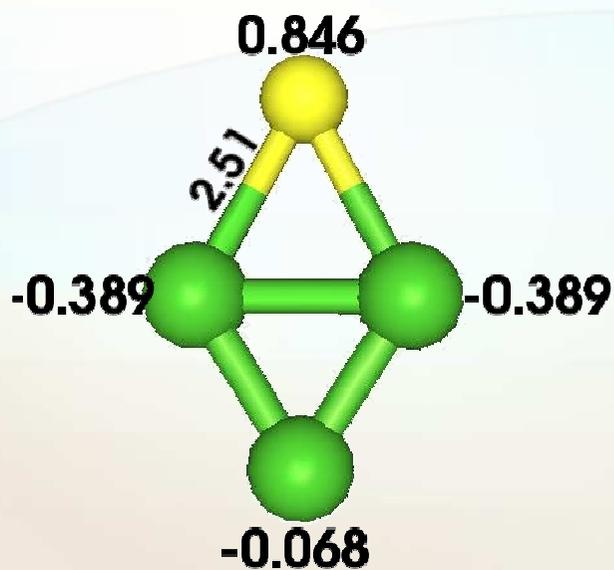
The interface also features a 'Recent Projects' list on the left, a 'Location' and 'Remote' section at the bottom, and a 3D molecular model in the bottom right corner. The molecular model shows a cluster of atoms, with orange spheres representing oxygen and green spheres representing carbon, connected by bonds.

***Structures optimisées
de petits agrégats Si_nM
($n= 1-6$)***

Structures optimisées de Si_nLi



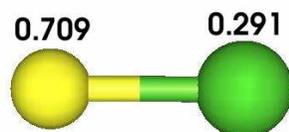
Transfert de charge



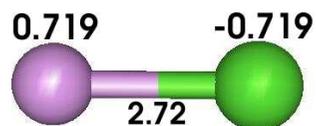
La structure électronique correspond à $Si_n^- + Li^+$

Structures optimisées de Si_nM ; $n=1, 2, 3$;

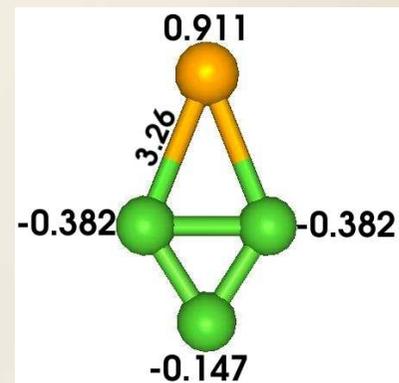
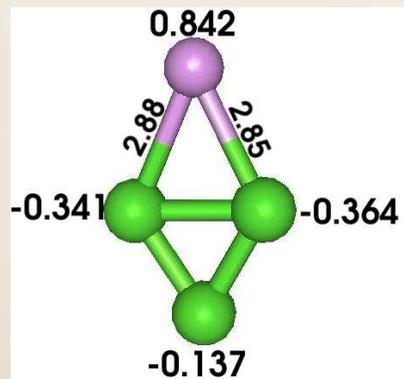
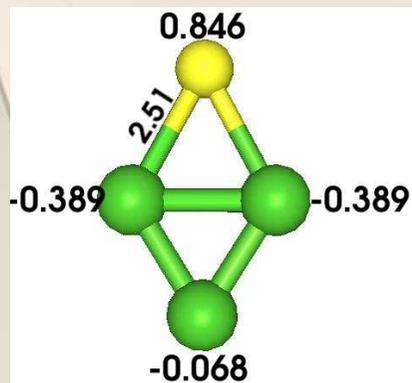
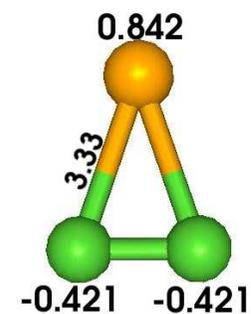
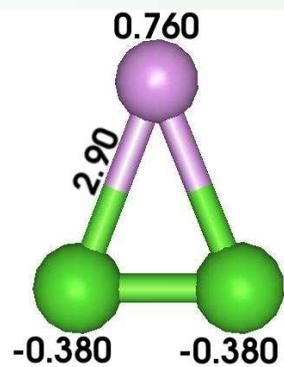
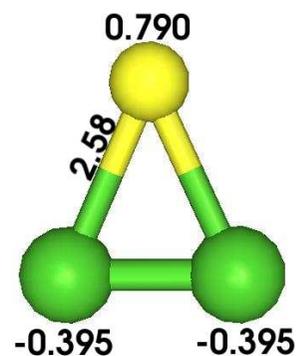
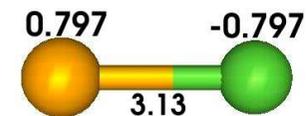
Si_nLi



Si_nNa

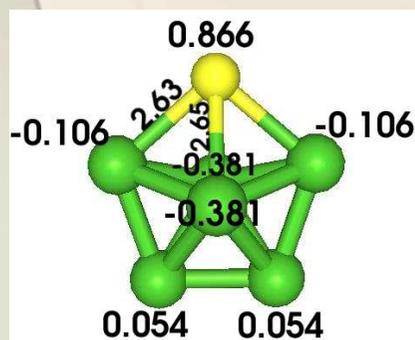
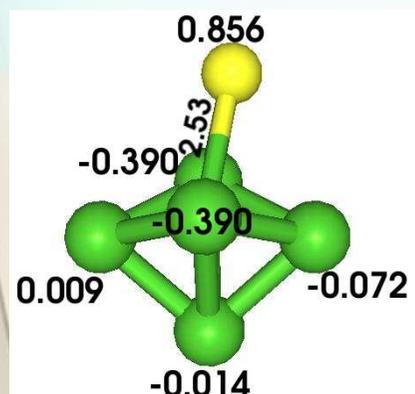
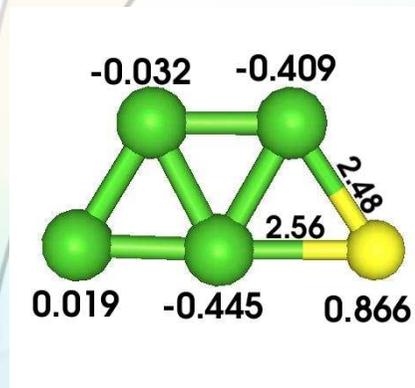


Si_nK

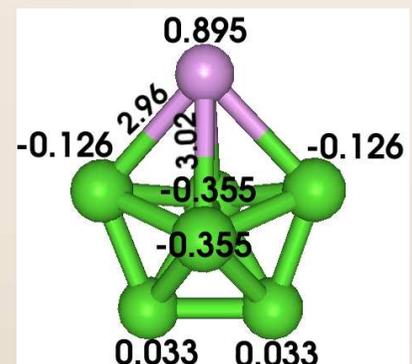
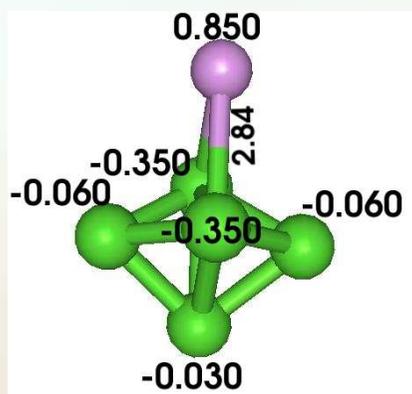
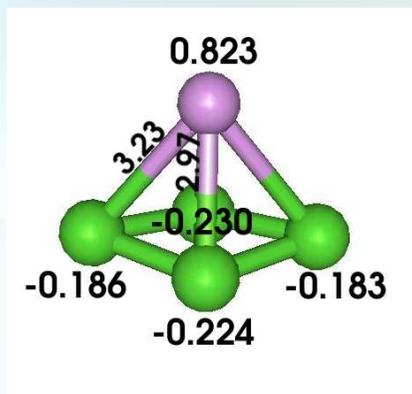


Structures optimisées de Si_nM ; $n=4, 5, 6$

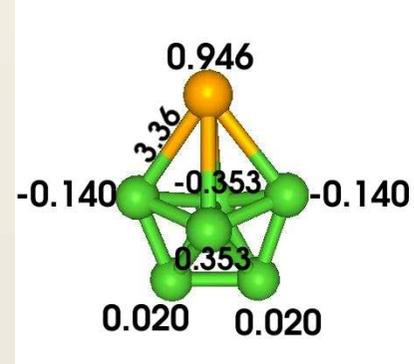
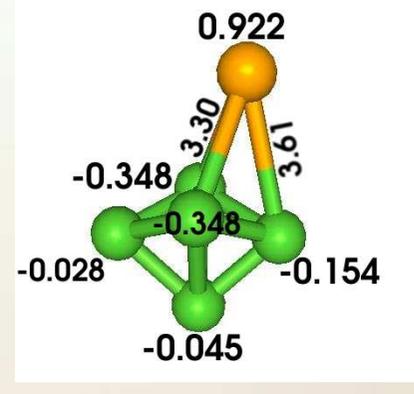
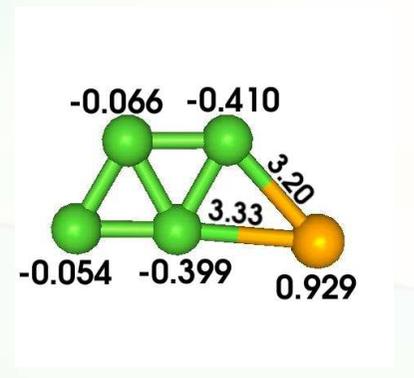
Si_nLi



Si_nNa

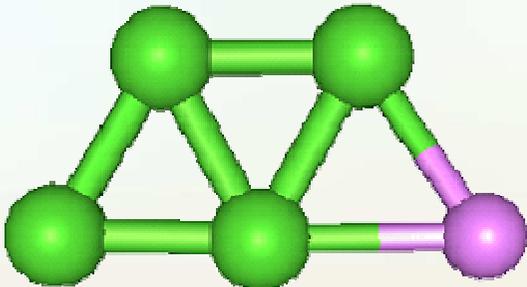
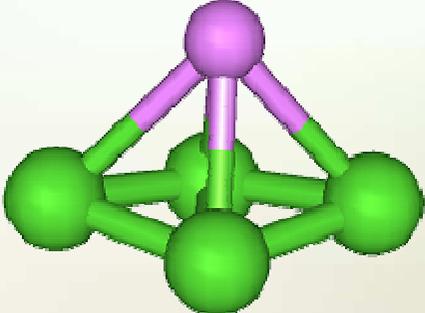


Si_nK

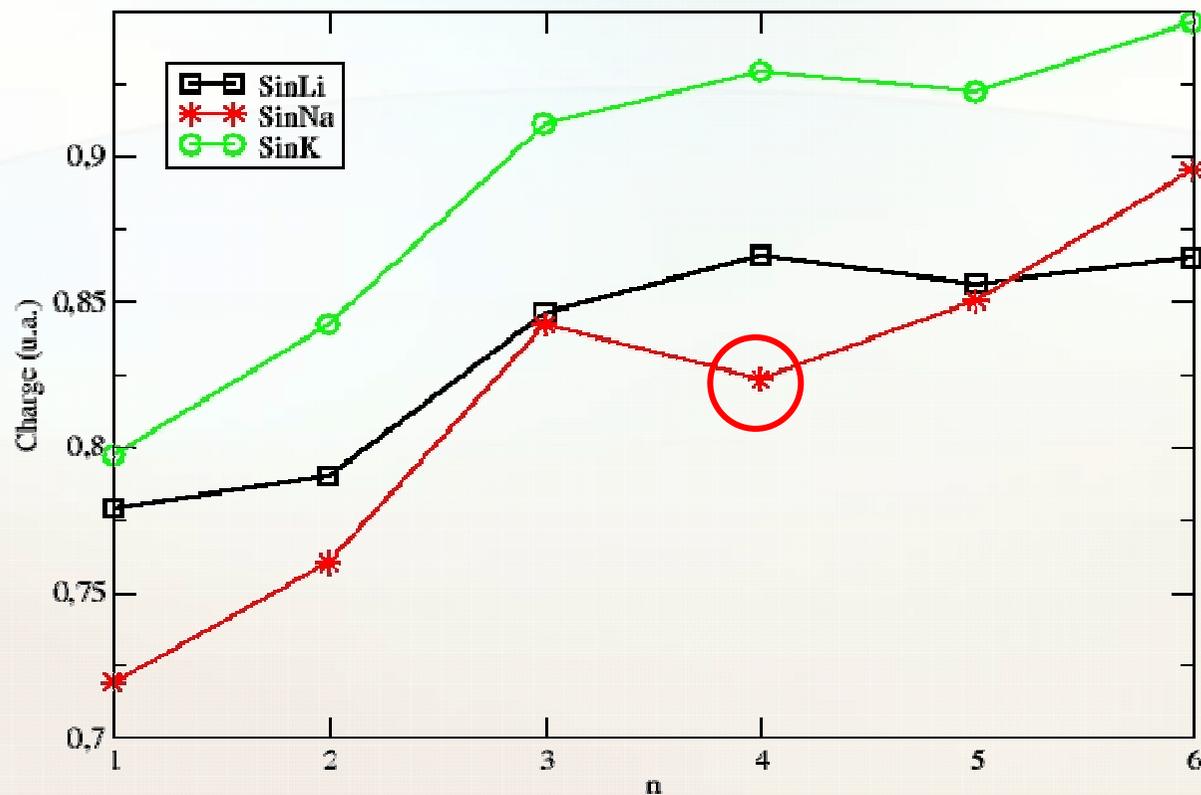


Position relative des isomères pour la taille $n=4$

Tests CCSD(T)

| Agrégat | Méthode |  |  |
|--------------------|---------|--|---|
| Si ₄ Li | B3LYP | 0.00 | +0.024 |
| | CCSD(T) | 0.00 | +0.042 |
| Si ₄ Na | B3LYP | +0.041 | 0.00 |
| | CCSD(T) | +0.042 | 0.00 |
| Si ₄ K | B3LYP | 0.00 | +0.027 |
| | CCSD(T) | 0.00 | +0.016 |

Transfert de charge

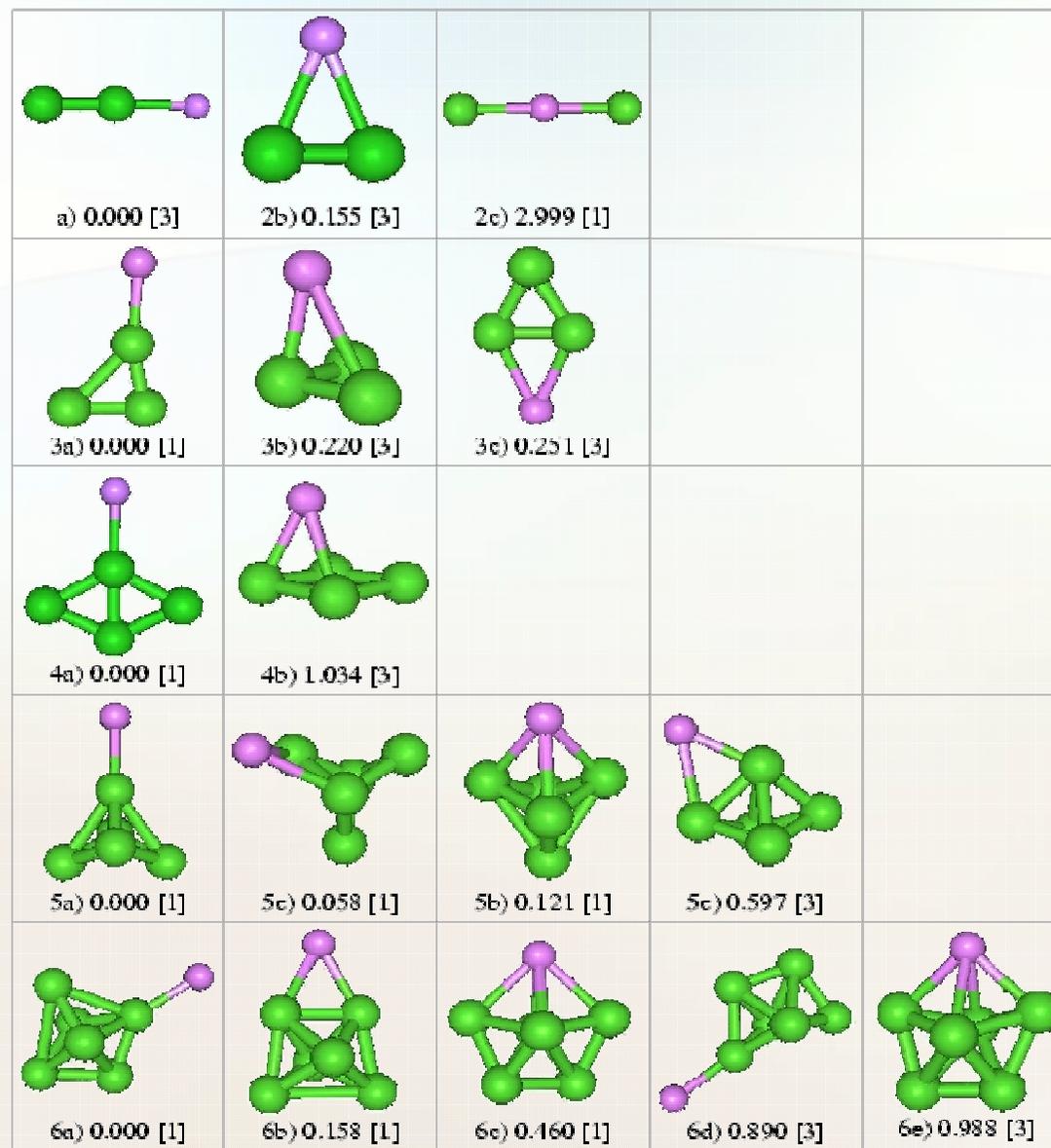


$$Q(\text{Li}) < Q(\text{K}) \Leftrightarrow \text{PI}(\text{Li}) \approx \text{PI}(\text{Na}) > \text{PI}(\text{K})$$

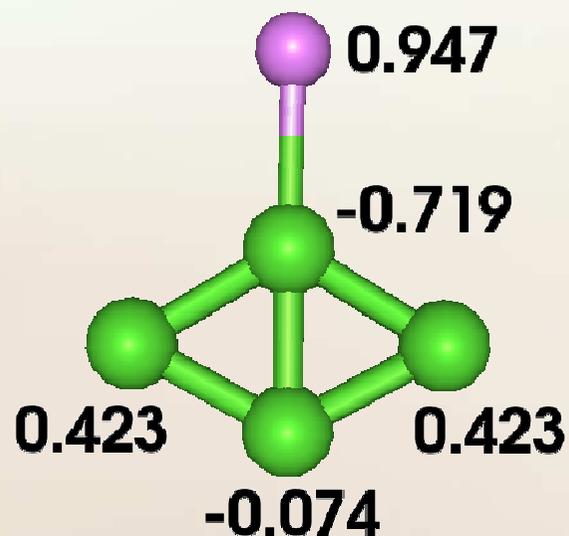
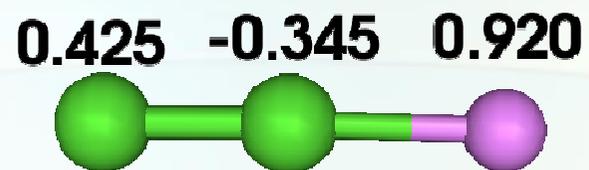
$$\text{PI}(\text{Li}) = 5.392 \text{ eV}; \quad \text{PI}(\text{Na}) = 5.139 \text{ eV}; \quad \text{PI}(\text{K}) = 4.341 \text{ eV}$$

***Structures optimisées
de petits agrégats $Si_nM^{(+)}$
($n= 1-6$)***

Structures optimisées de Si_nLi^+



Charges atomiques pour les systèmes Si_nLi^+



***Structures optimisées
d'agrégats Si_nM_2
($n= 1-6$)***

Structures optimisées de Si_nM_2 ; $n=1, 2, 3$

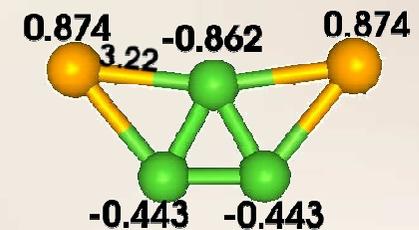
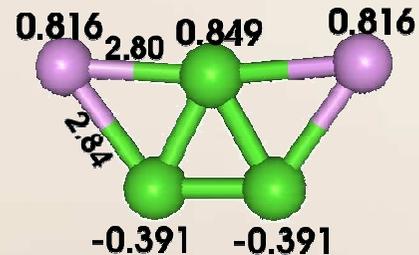
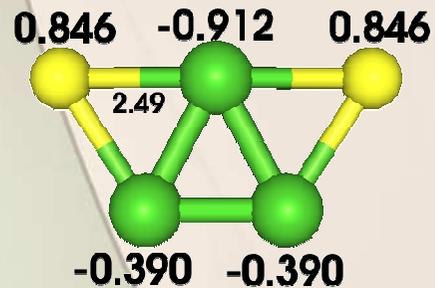
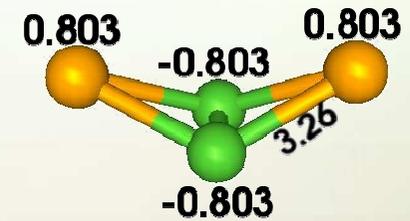
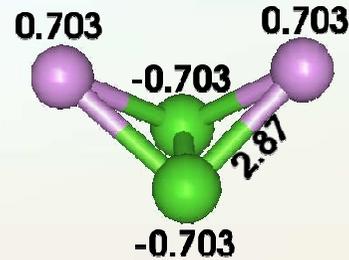
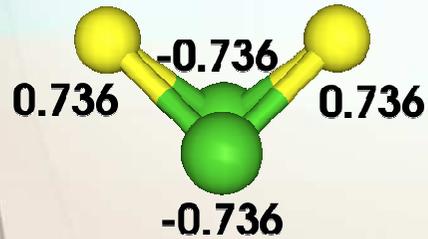
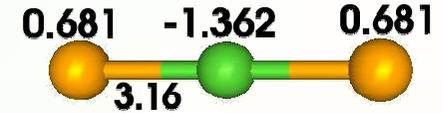
Si_nLi_2



Si_nNa_2

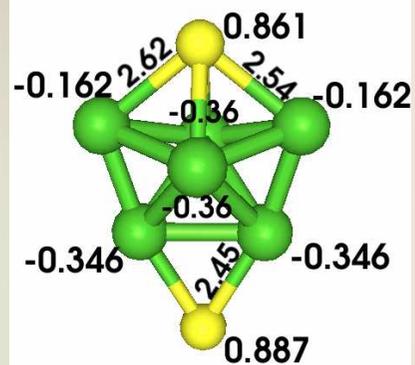
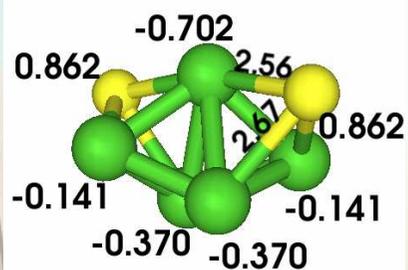
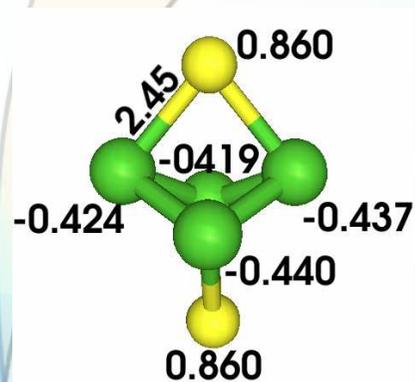


Si_nK_2

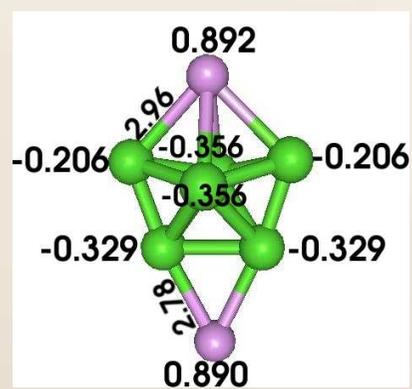
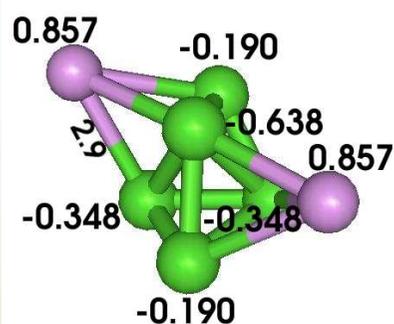
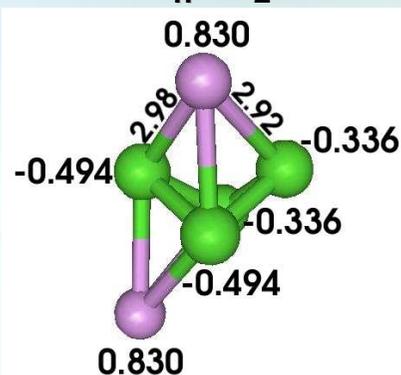


Structures optimisées de Si_nM_2 ; $n=4, 5, 6$

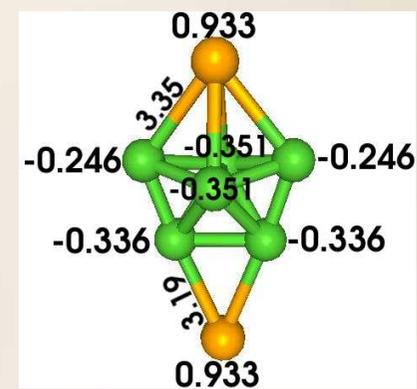
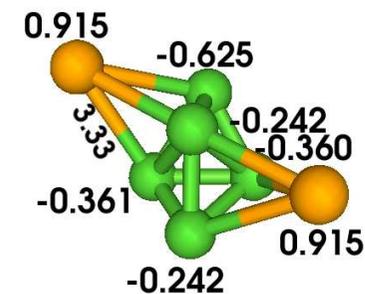
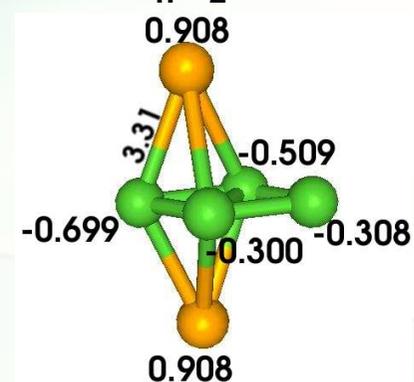
Si_nLi_2



Si_nNa_2



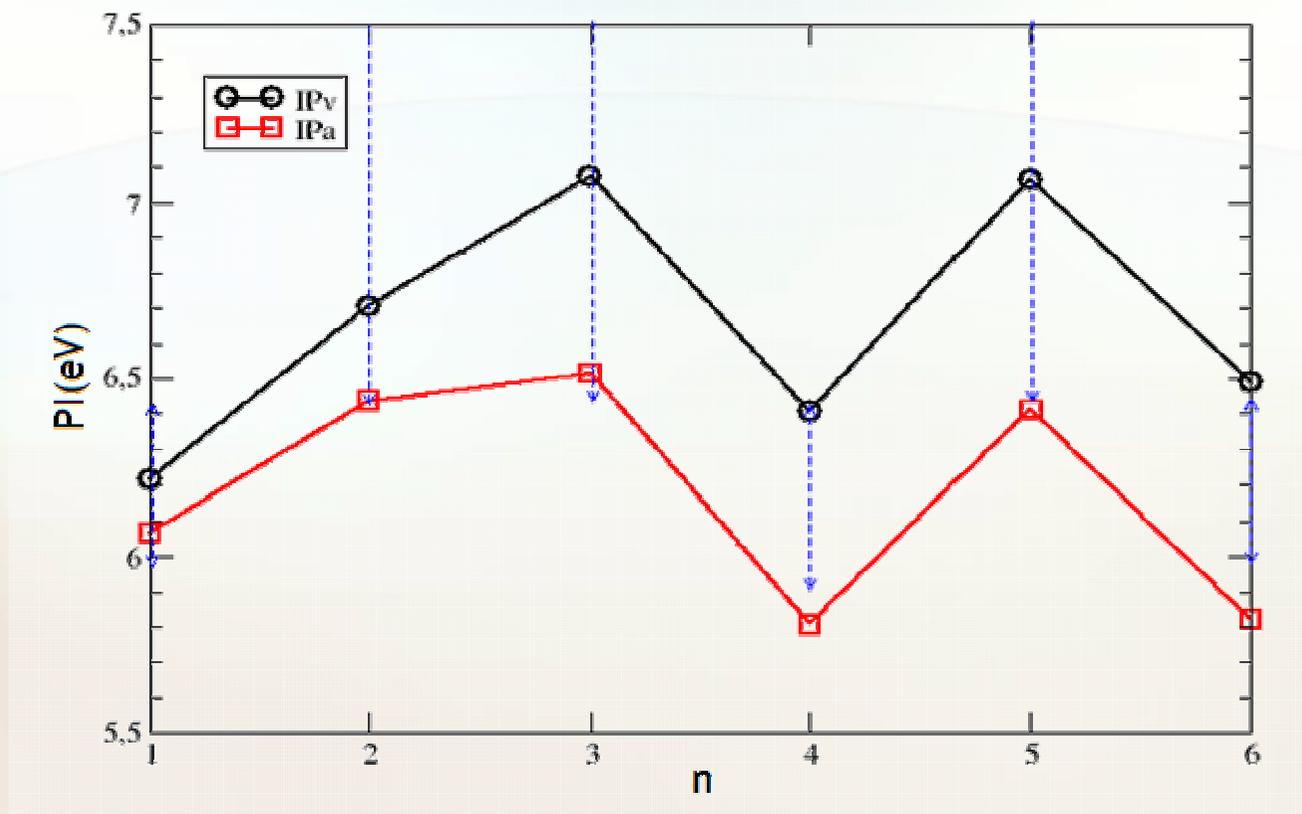
Si_nK_2



Propriétés électroniques

- Potentiel d'ionisation adiabatique et vertical
- Énergies de liaison
- Moment dipolaire

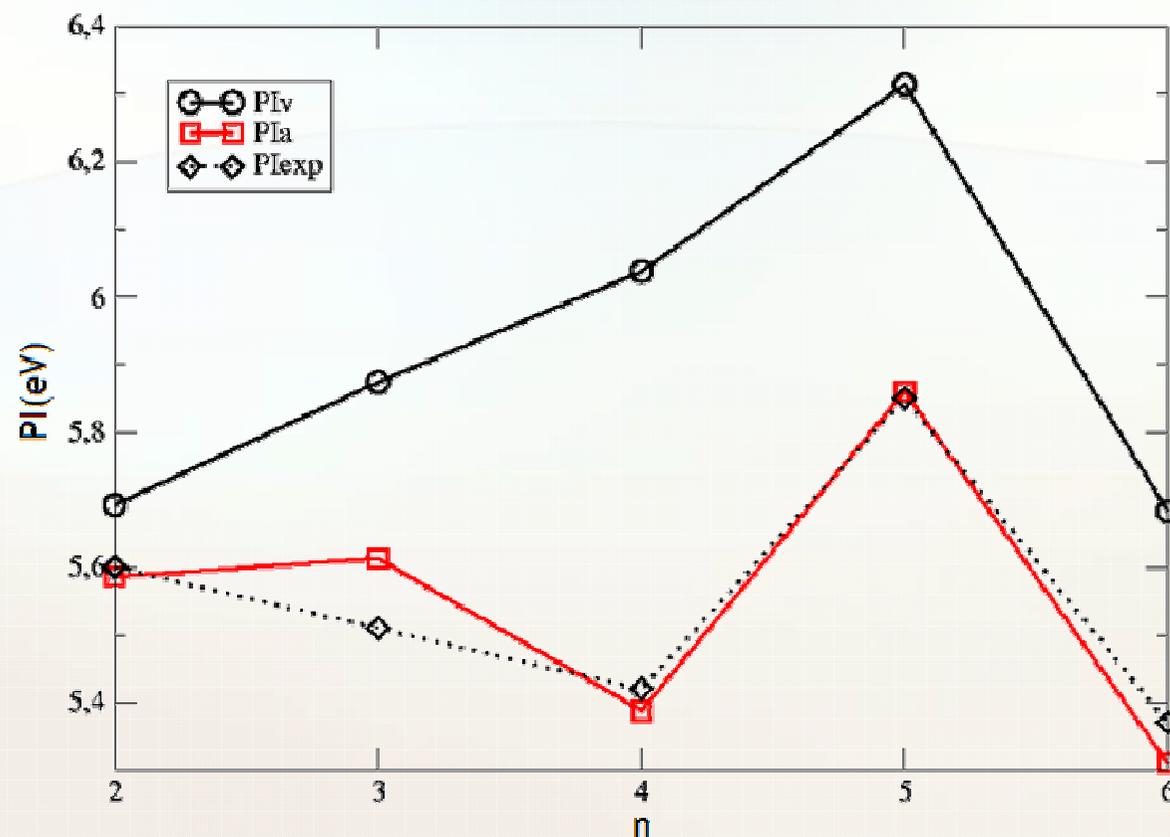
Potentiel d'ionisation adiabatique et vertical Si_nNa



R. Kishi, S. Iwata, A. Nakajima, K. Kaya, *J. Chem. Phys.* **107**, 3056 (1997).

C. Sporea, F. Rabilloud, A.R. Allouche, M. Frécon, *J. Phys. Chem. A*, **110** (2006) 6032.

Potentiel d'ionisation Si_nNa_2



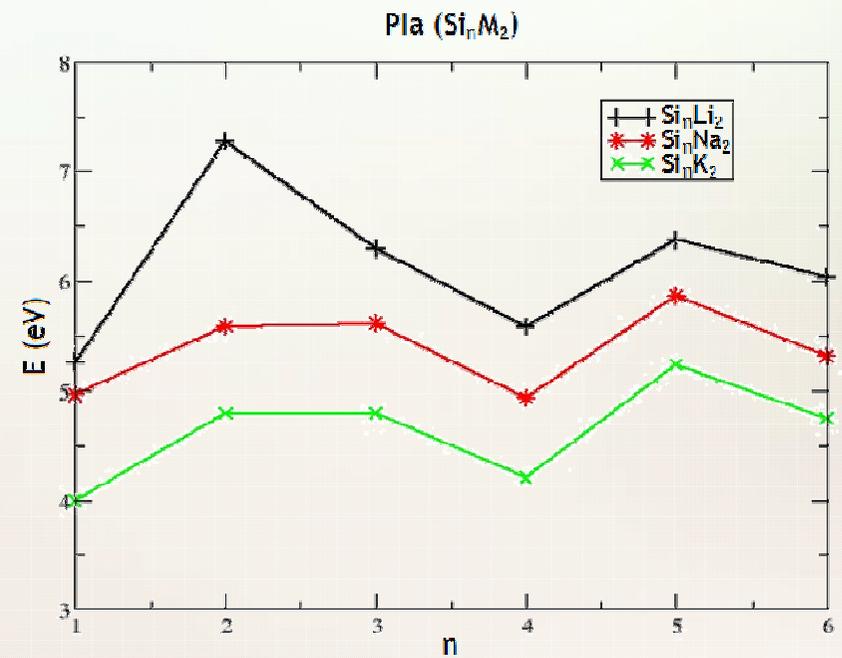
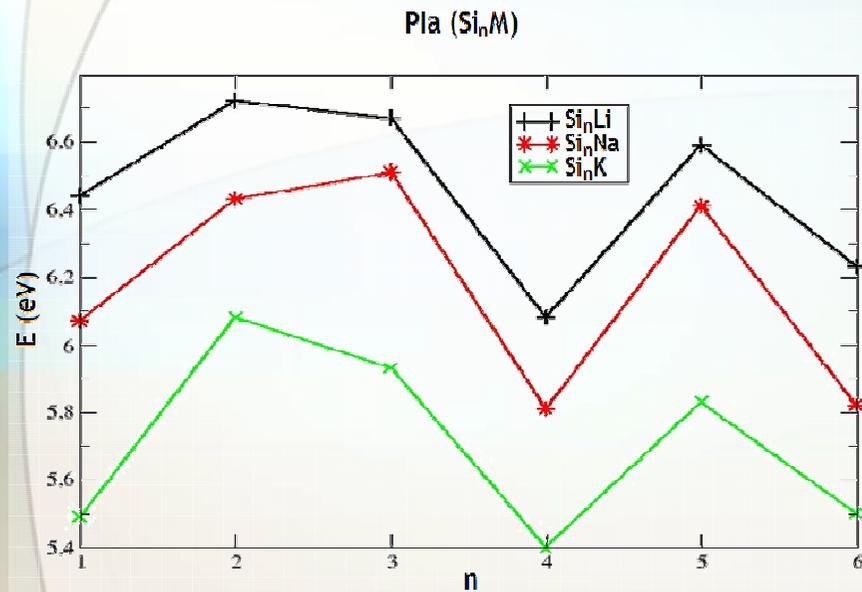
R. Kishi, S. Iwata, A. Nakajima, K. Kaya, *J. Chem. Phys.* **107**, 3056 (1997).

R. Kishi, A. Nakajima S. Iwata,, K. Kaya, *Chem. Phys.Lett.* **224**, 200 (1994).

S. Wei, R. N. Barnett, U. Landman, *Phys. Rev. B*, **55**, 7935, (1997)

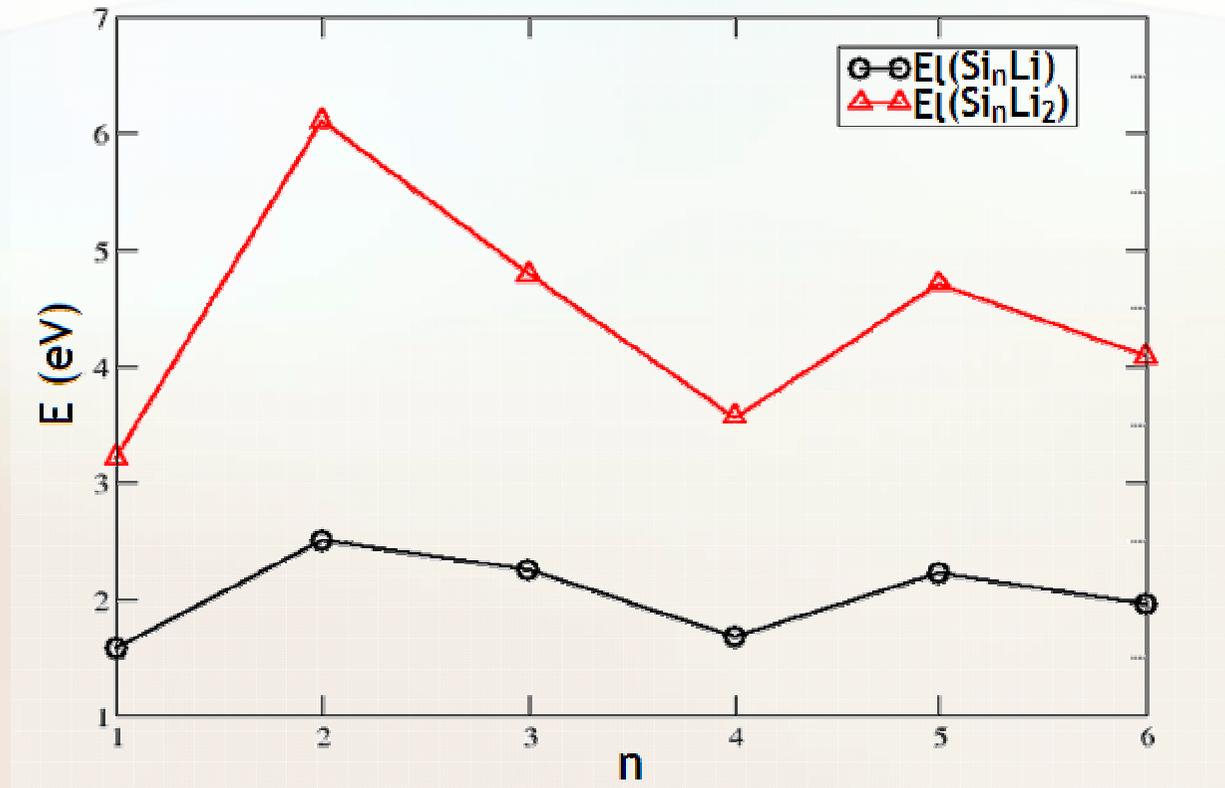
C. Sporea, F. Rabilloud, A.R. Allouche, M. Frécon, *J. Phys. Chem. A*, **110** (2006) 6032.

Comparaison de potentiel d'ionisation pour Si_nM_p



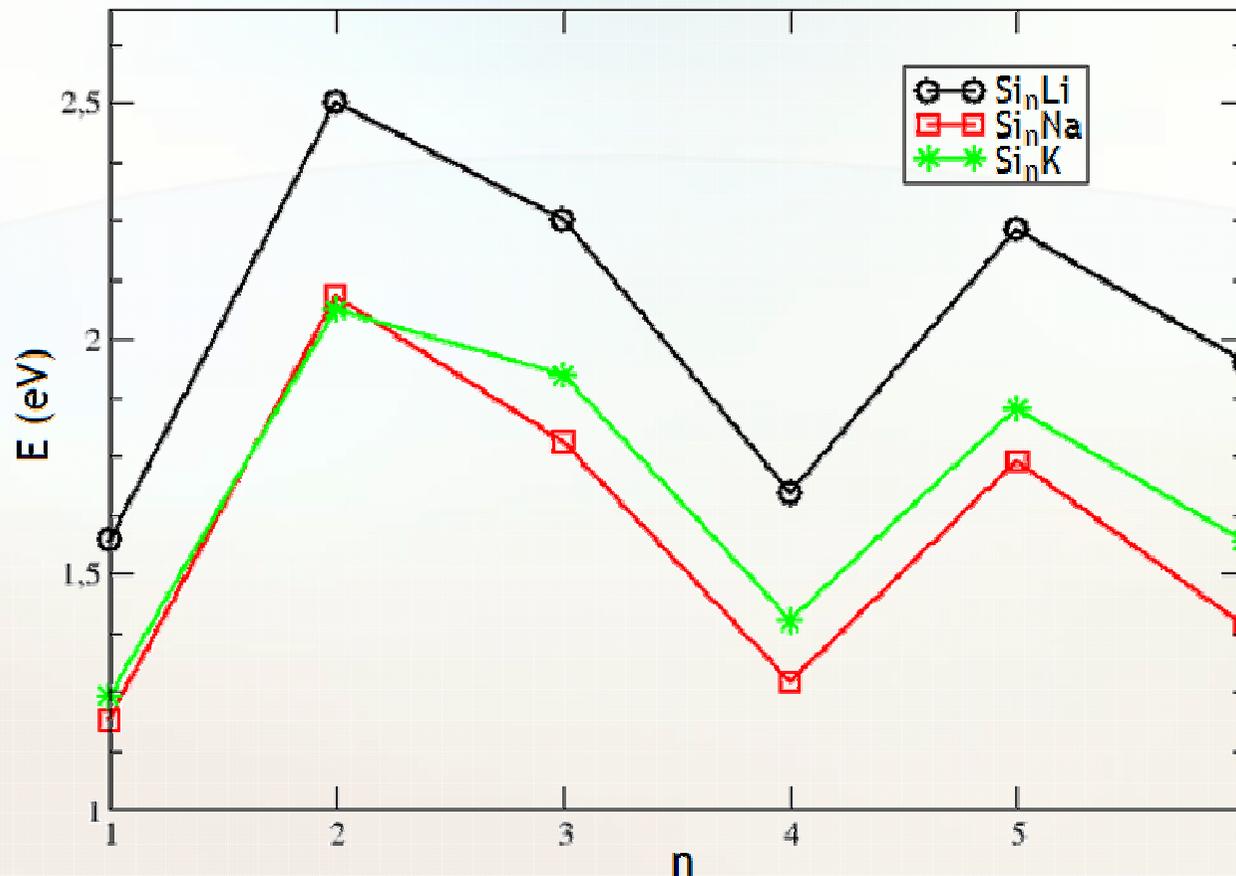
Énergie de liaison de l'alcalin dans Si_nLi_p

$$E_{liaison} = -[E(Si_nM_p) - E(Si_n) - p * E(M)]$$



$$E_{liaison}(Si_nLi_2) \approx 2 * E_{liaison}(Si_nLi)$$

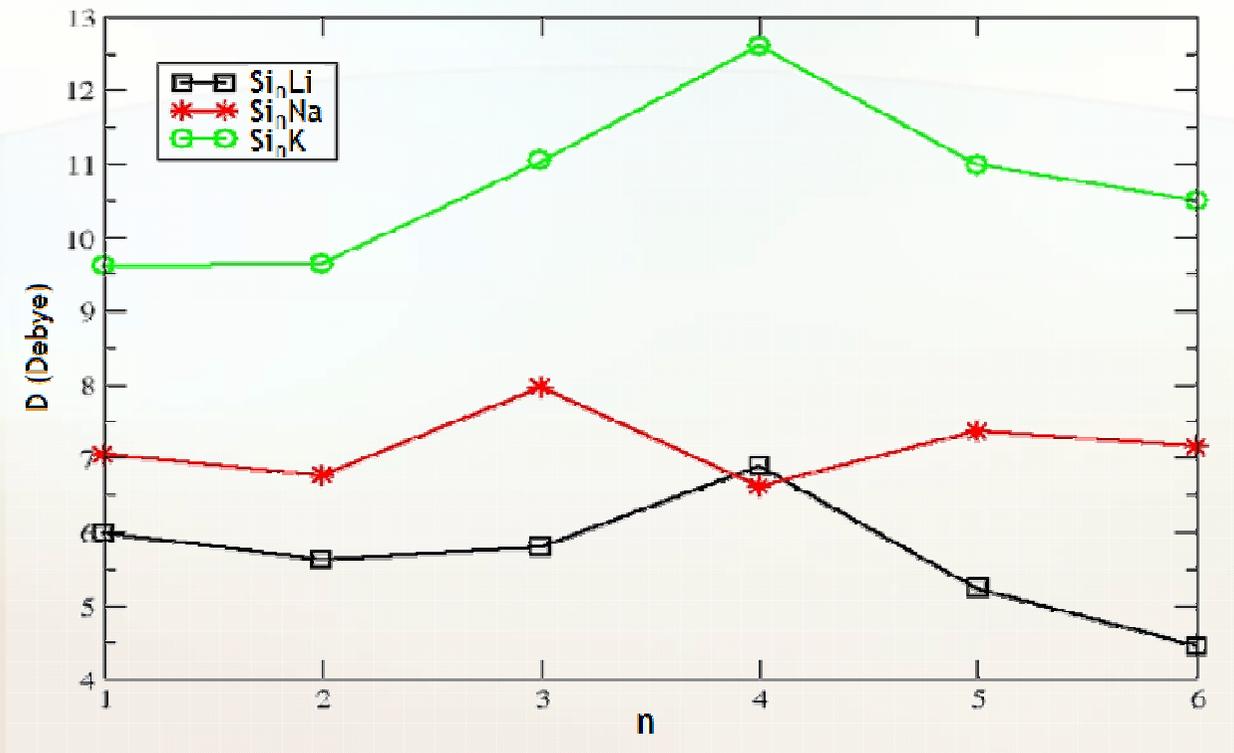
Énergie de liaison de l'alcalin dans Si_nM



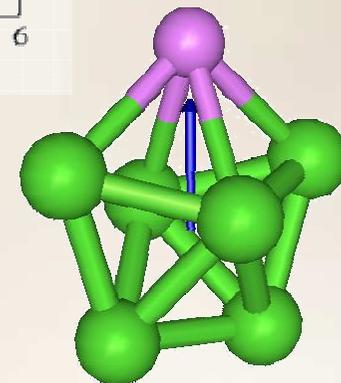
$E_{liaison}(Si_nLi) > E_{liaison}(Si_nNa, Si_nK) \Leftrightarrow d(Si-Li) < d(Si-Na, Si-K) \rightarrow$
l'interaction électrostatique entre Si_n^- et Li^+ est plus grande

Moment Dipolaire Électrique

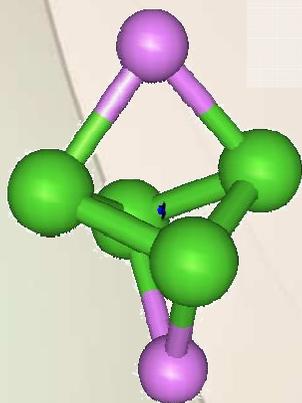
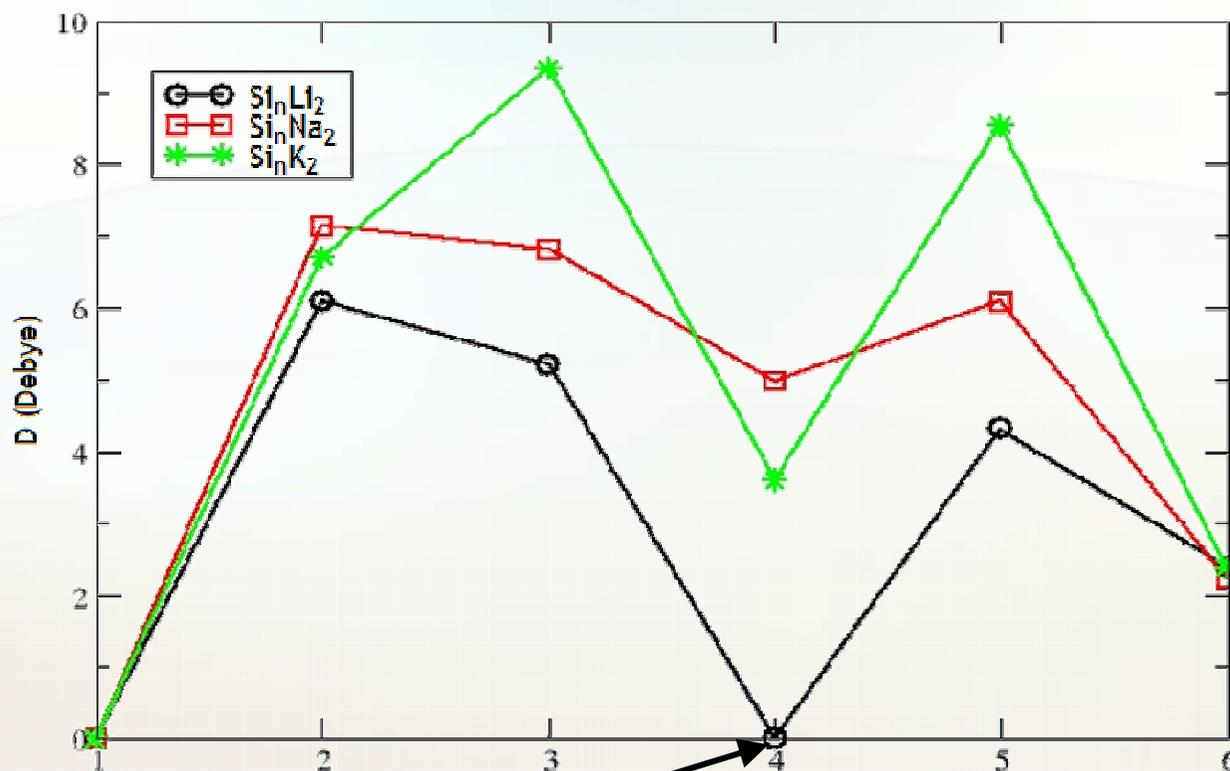
Le transfert de charge crée un moment dipolaire μ .



$$\mu(\text{Si}_n\text{K}_p) > \mu(\text{Si}_n\text{Na}_p) > \mu(\text{Si}_n\text{Li}_p)$$



Moment dipolaire Si_nM_2



$\mu(Si_nM) > \mu(Si_nM_2)$; $\mu(Si_nM^+) > \mu(Si_nM)$

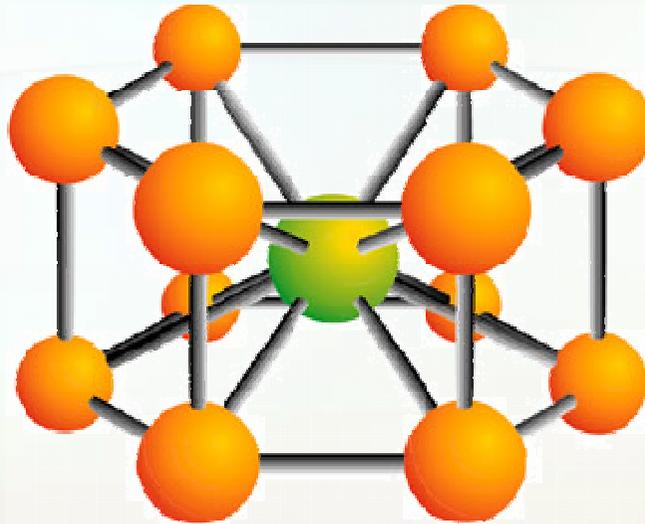
Petits agrégats Si_nM_p

Conclusion

- Si_n peu déformé et l'alcalin est adsorbé en surface
- Transfert de charge électronique de l'alcalin vers Si_n

Structures de type cage

$M@Si_n$ ($n=10-20$)



Prisme hexagonale avec W in centre

Référence:

- Hiura et al. PRL 86, 1733 (2001)
- Kumar et al., PRL 87, 045503 (2001)
- K. Jackson and B. Nellermoe, Chem. Phys. Lett. 254, 249 (1996)

Formation de $M@Si_n$ dans les expériences

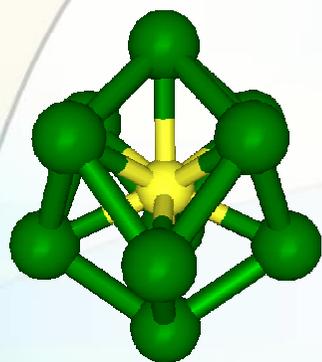
- ❖ E. Janssen, P. Gruene, G. Meijer, L. Wöste, P. Lievens, A. Fielicke, PRL, **99**, 063401, 2007.
- ❖ K. Koyasu, J. Atobe, M. Akutsu, M. Mitsui, and A. Nakajima, J. Phys. Chem. A **111**, 42 2007
- ❖ S. Neukermans, X. Wang, N. Veldeman, E. Janssens, R.E. Silverans, P. Lievens, Int. J. of Mass Spect. **252**, 145, 2006.
- ❖ J. B. Jaeger, T. D. Jaeger, and M. A. Duncan, J. Phys. Chem. A **110**, 9310 (2006).
- ❖ N. Uchida, L. Bolotov, T. Miyazaki, and T. Kanayama, J. Phys. D: Appl. Phys. **36**, L43 (2003).
- ❖ M. Ohara, K. Koyasu, A. Nakajima, and K. Kaya, Chem. Phys. Lett. **371**, 490 (2003).
- ❖ H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).

Méthode

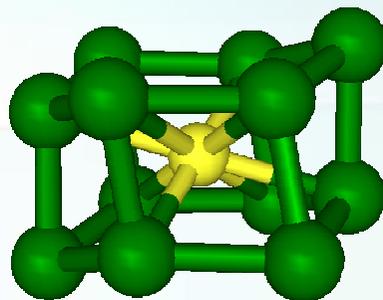
- B3LYP/6-31+G(d) avec Gaussian 98 et Q-Chem
- Optimisation de la géométrie à partir des structures issues de la littérature

Structures de type cage

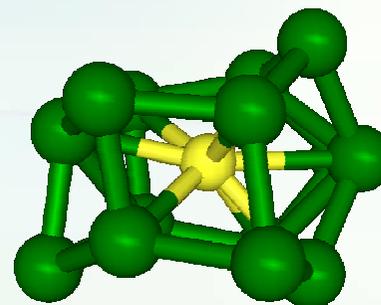
$Li@Si_n$ ($n=10-20$)



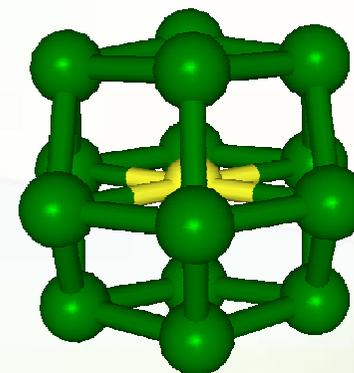
$Si_{10}Li$ (D_{4d})



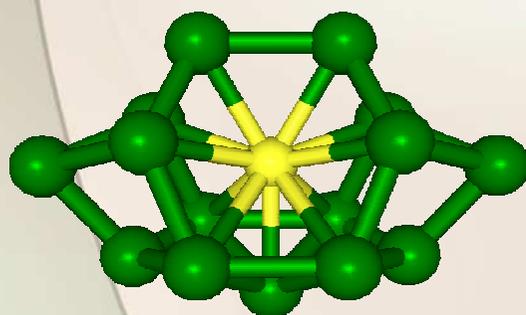
$Si_{12}Li$ (C_1)



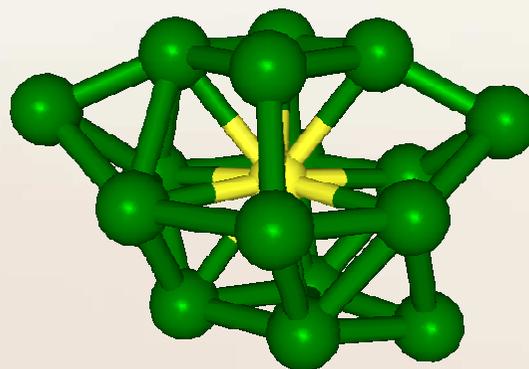
$Si_{14}Li$ (C_1)



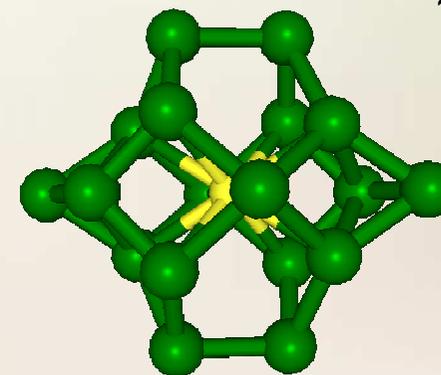
$Si_{14}Li$ (D_{4h} ;
0.55eV)



$Si_{15}Li$ (C_{2v})

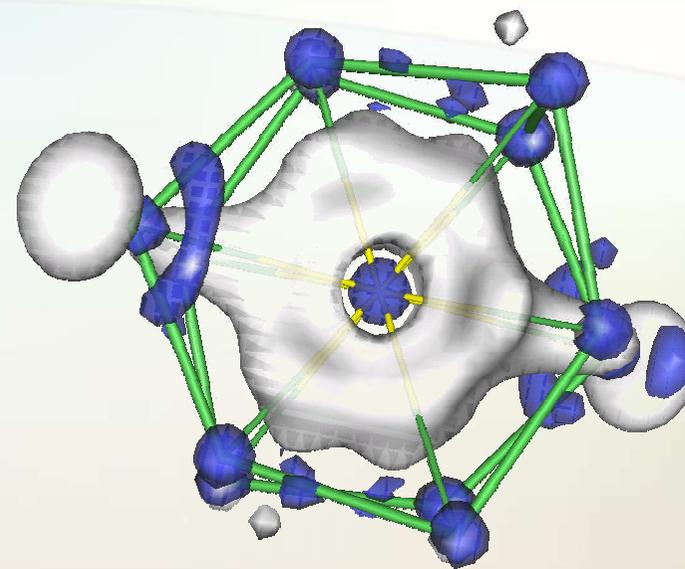
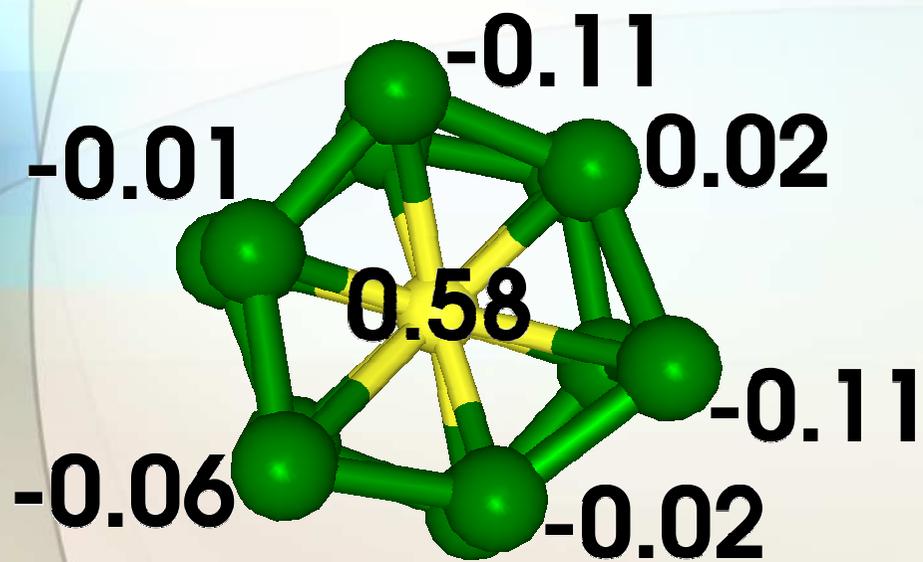


$Si_{16}Li$ (C_1)



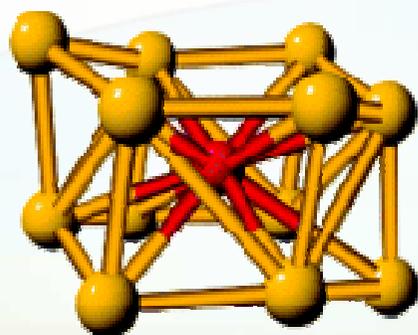
$Si_{18}Li$ (C_i)

Transfert de charge pour Li@Si_{12}

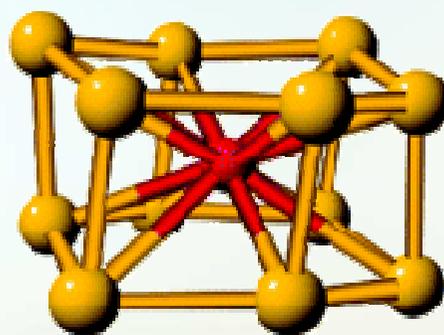


$M@Si_{12}$

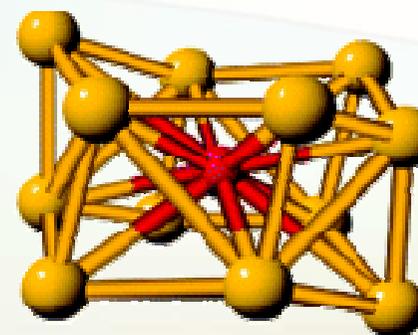
- D. Hossain, F. Hagelberg, C.U. Pittman, S Saebo, J.Phys. Chem C, A paraître, Publié web: 29.08.2007
- Calculs B3LYP/ 6-311+G(d)



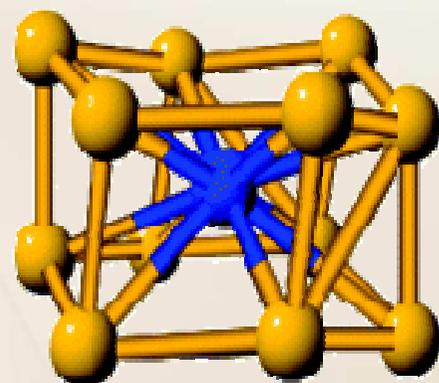
(a) $Li@Si_{12}$



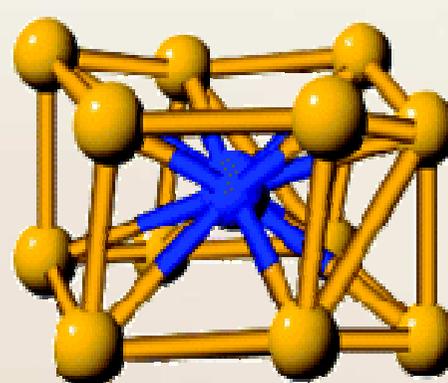
(b) $Li^+@Si_{12}$



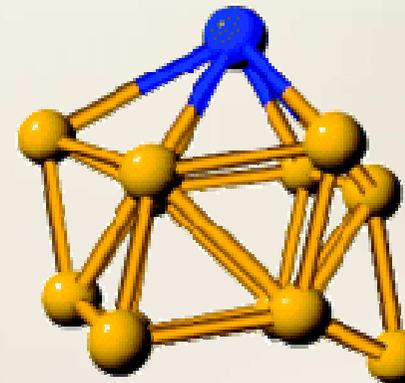
(c) $Li^-@Si_{12}$



(d) $Na@Si_{12}$



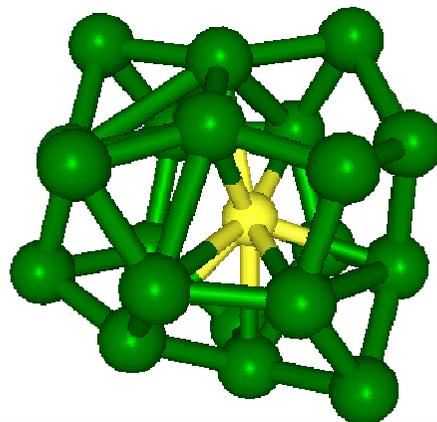
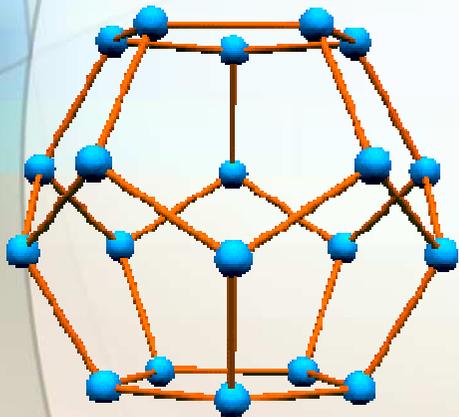
(e) $Na^+@Si_{12}$



(f) $Na^-@Si_{12}$

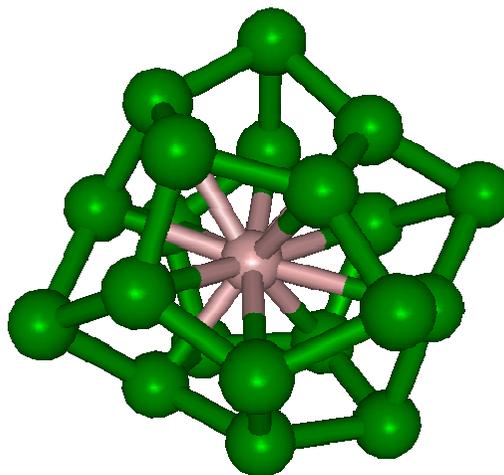
$M@Si_{20}$

$Si_{20}; I_h$



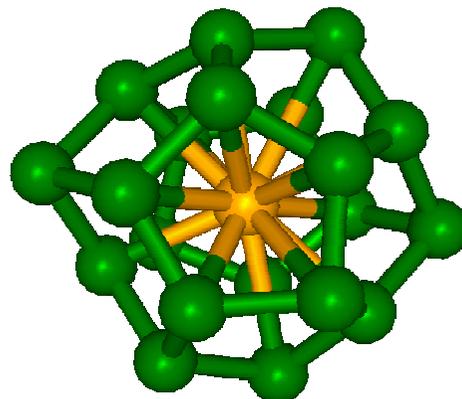
$Li@Si_{20}$

- Symétrie C_1 ; 11 pentagones déformés et un trapèze
- $d_{(Si-Li)} = 2.67-4.33 \text{ \AA}$



$Na@Si_{20}$

- Symétrie C_1 ; 12 pentagones déformés
- $d_{(Si-Na)} = 2.82-4.20 \text{ \AA}$

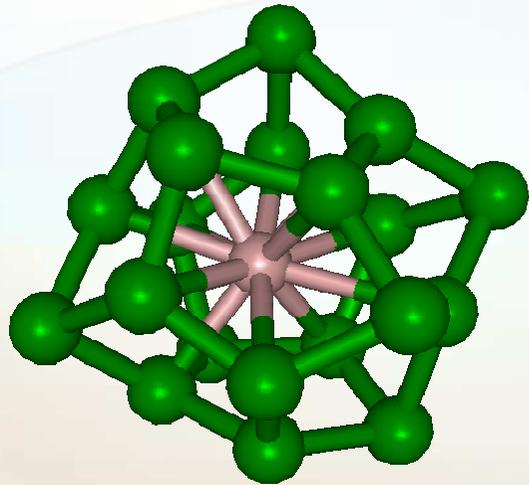


$K@Si_{20}$

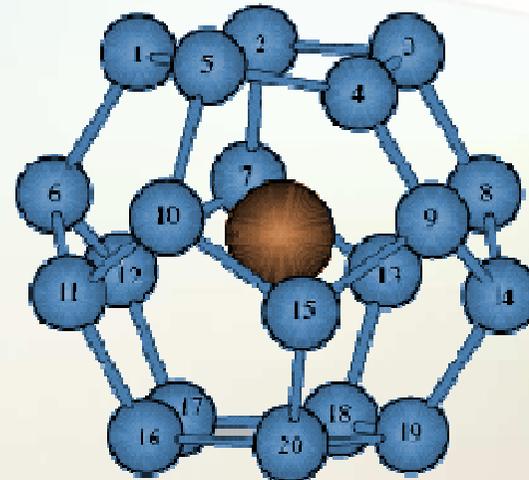
- 12 pentagones peu déformés, une cage plus sphérique
- $d_{(Si-K)} = 3.00-3.84 \text{ \AA}$

Na@Si_{20}

Notre étude B3LYP

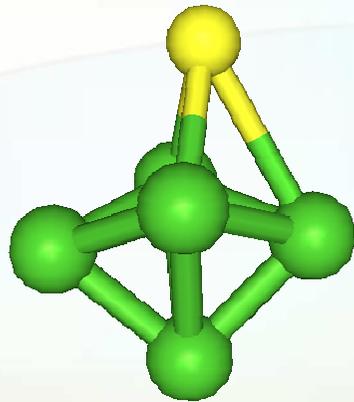


Étude semi empirique

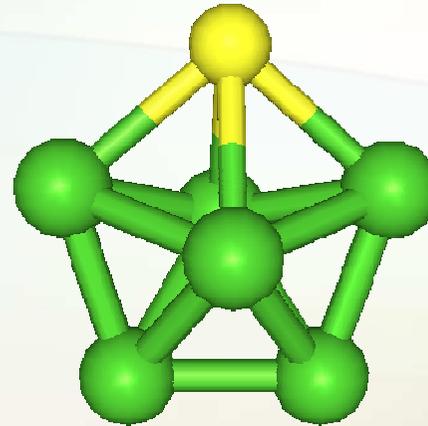


N.A. Borshch, N.S. Pereslavl'tseva,
S.I. Kurganskii, Semiconductors,
40, 1423, 2006

Localisation de l'alcalin en surface ?



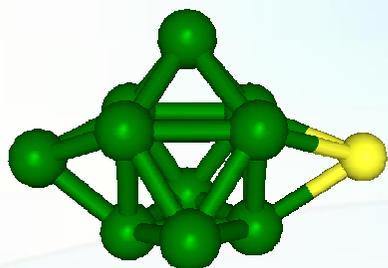
Si_5Li



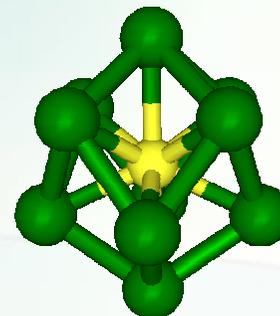
Si_6Li

➔ Recherche d'isomères pour LiSi_n $n > 10$
à partir des structures DFT de Si_n connues

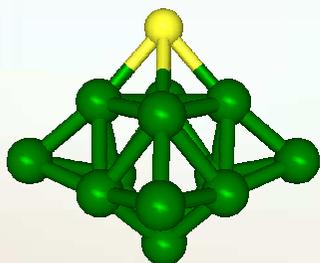
Structures les plus stables de type cages et adsorbé Si_nLi ($n=10,12,14$)



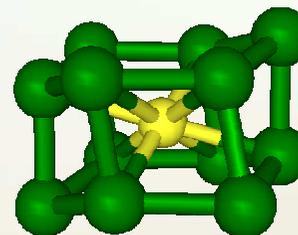
Si_{10}Li (0.0) C_{3v}



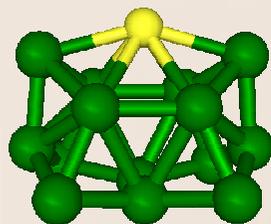
Si_{10}Li (+1.39eV) D_{4h}



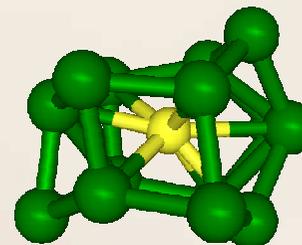
Si_{12}Li (0.00) C_s



Si_{12}Li (+0.65eV) C_i

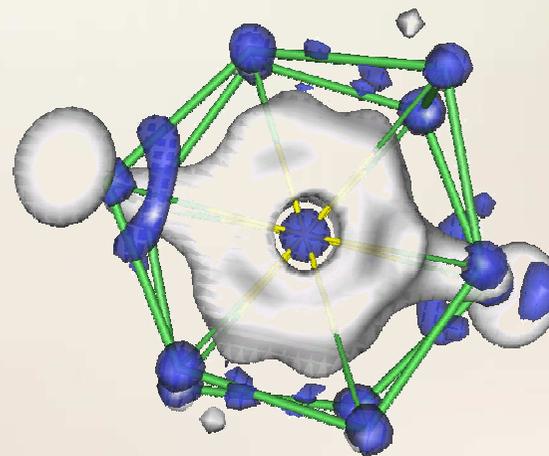
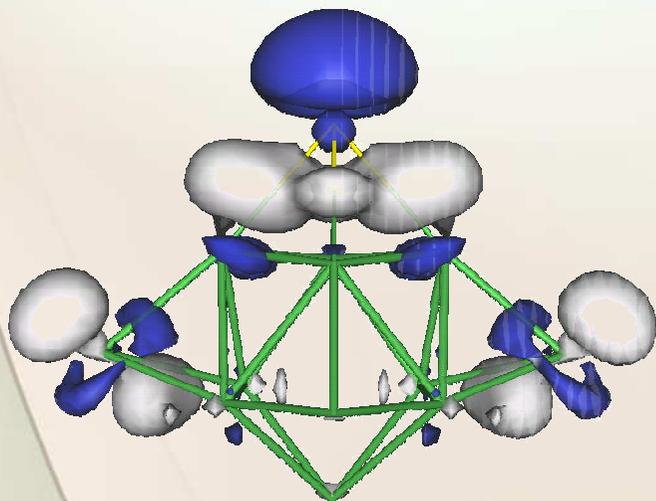
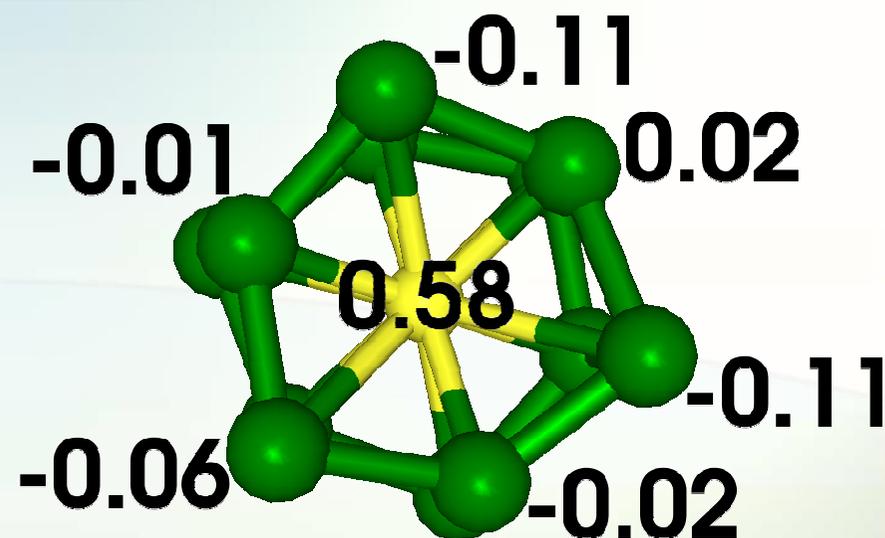
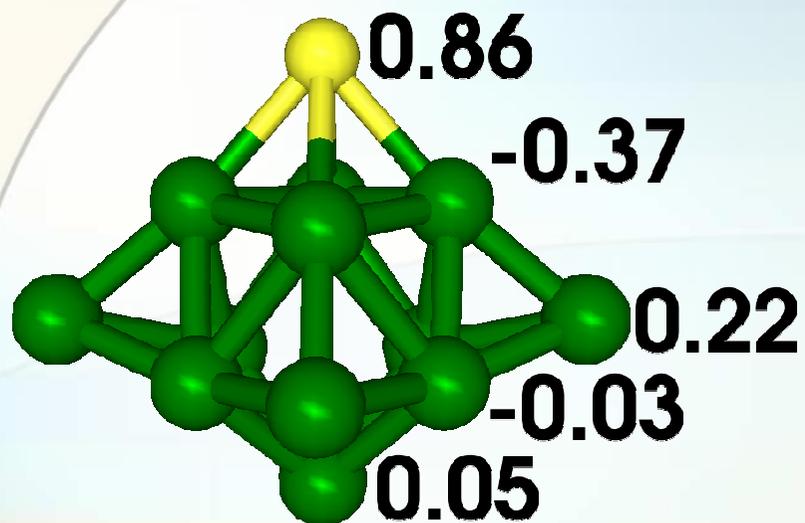


Si_{14}Li (0.00) C_{2v}

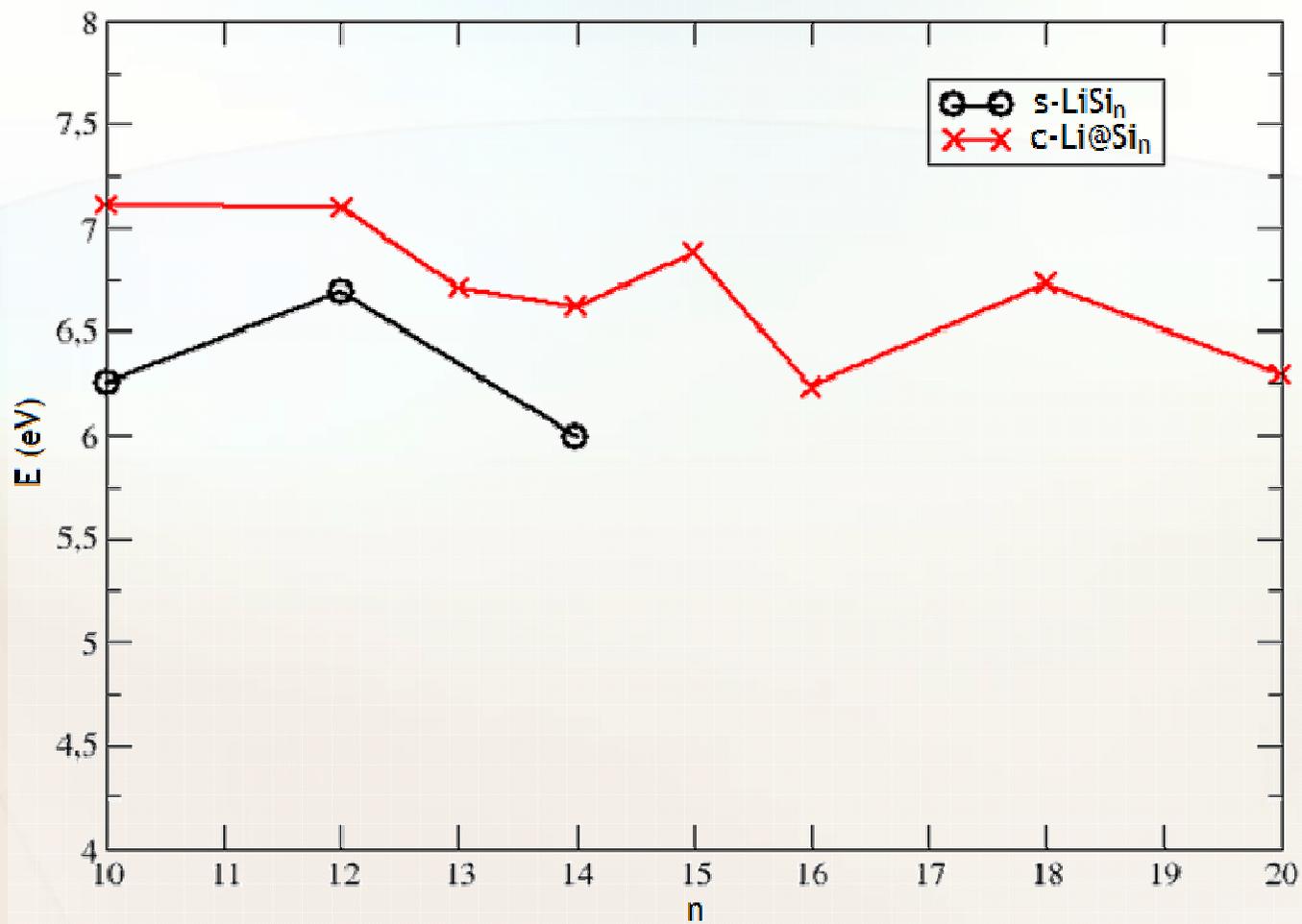


Si_{14}Li (+1.13eV) C_s

Transfert de charge Si_{12}Li



Potentiel de ionisation $s\text{-Si}_n\text{Li}$ et $c\text{-Li@Si}_n$



Cages

Conclusion

- Cages de silicium stabilisées avec un alcalin à l'intérieur
- Difficulté de les produire expérimentalement
- Expt pour Si_nAg , Si_nCu , $n < 12$ le métal est en surface

- M. A. Duncan et al., J. Phys. Chem. A **110**, 9310 (2006).
- S. Neukermans, X. Wang, N. Veldeman, E. Janssens, R.E. Silverans, P. Lievens, Int. J. of Mass Spect. **252**, 145, 2006.

Perspectives

- ❖ Envisager des études similaires avec Rb, Cs...
- ❖ Augmenter le nombre d'atomes d'alcalin sur la surface et dans une cage