Pseudopotential Calculations on Alkali Silicide Clusters with Si₂ and Tetrahedral Si₄ Backbones

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Abstract: The binary clusters Li_2Si_2, Na_2Si_2 and Li_4Si_4, Na_4Si_4 built of linear and tetrahedral silicon backbones, respectively, have been investigated by SCF pseudopotential calculations. Special interest was focused on the relationships to the corresponding carbon clusters which though not yet experimentally proved found considerable theoretical attention recently. The existence of the silicon clusters, however, has been observed for numerous solid crystalline compounds and supported by mass spectra. The equilibrium structures are the butterfly geometry for the M_2Si_2 clusters and the heterocubane arrangement for the M_4Si_4 clusters. The dimerization of $2M_2Si_2$ to M_4Si_4 clusters is energetically favored in any case. Binding and correlation energies are given for different models. Population analysis indicates multicenter M–Si bonding for the most stable clusters investigated in this work.

Our interest in mixed clusters has been stimulated by inspection of solid semiconducting and intermetallic phases that belong to the so-called Zintl compounds.[1] A number of recent reviews and publications focus on the idea that many of such solids are composed of clusters that can well be stable or stabilized in the form of isolated units.[2-5] There are still numerous clusters in solid phases that are not known in isolated form and that seem somewhat unusual moieties for the eyes of the molecular and complex chemists.[5-8] It has been shown in a few cases that clusters which exist in solid phases can be isolated in stable form by different techniques. We concentrate in this work on M_2Si_2 and M_4Si_4 clusters that are part of the structures of binary alkali silicides.[9-12] Recent molecular beam experiments show that related M_2X_2 and M_4X_4 units (M = alkali metal; X = group IVA element) are as well relatively stable in isolated form.[13]

Related calculations exist for Li_2C_2, Li_4C_4 (see, e.g., ref 14–16), and Si_2H_2 (see, e.g., ref 17–20).

Computational Details

In this work we use ab initio pseudopotentials, and thus treat explicitly only valence electrons. This point is essential, as we intend to pursue this work also for heavier elements. The pseudopotentials are taken from ref 21–23.

The basis sets employed were (31/31/1) for Si, (32/2) for Li, and (311/1) for Na (for notation see, e.g., ref 24). The d function for Si was taken from ref 25, and the p function for Na has the exponent 0.06. The other basis functions are from ref 23. These basis sets were also used for self-interaction corrected local spin-density (LSD) functional correlation energy calculations.[26] In the case of Li_2Si_2, perturbation and configuration interaction calculations (with single and double excitations) were performed. For this case the basis sets were improved: (211/211/11) for Si and (311/11/1) for Li, respectively. The d functions were taken from ref 22 and 27 (for Li and Si, respectively). The pseudopotentials and basis sets were tested in atomic and molecular X_2 calculations. More details are given in ref 28. All calculations were done with the MELD program of E. R. Davidson and co-workers.

Results and Discussion

We have investigated clusters of the type M_2Si_2 and M_4Si_4 (M:Li,Na) with structures containing linear and tetrahedral silicon backbones, respectively (Figure 1). The corresponding geometrical parameters and energies are collected in Tables I and II.

In the case of the M_2Si_2 clusters we have considered three principal arrangements (Figure 1): a bent doubly bridged one (**1**), a planar doubly bridged one (**2**), and a linear one (**3**). The latter, which is a quite intuitive structure with respect to acetylene, C_2H_2, turns out to be energetically unfavorable (Table II). The former

The relative stability of structures **1** and **2** is more difficult to assert: in SCF they are separated only by 11 kJ/mol. The situation is intermediate between Li_2C_2 and Si_2H_2. The former

Table I. SCF Optimized Geometries of M_2Si_2 and M_4Si_4 Singlet State Clusters[a]

	M = Li	M = Na
structure 1		
R(Si–Si)	4.05	4.06
R(M–Si)	5.00	5.53
∠M–X–M[b]	105	110
structure 2		
R(Si–Si)	4.04	4.04
R(M–Si)	4.91	5.44
structure 3		
R(Si–Si)	3.90	3.91
R(M–Si)	4.60	5.12
structure 4		
R(Si–Si)	4.68	4.70
R(M–Si)	4.93	5.49
structure 5		
R(Si–Si)	4.53	4.52
R(M–Si)	4.57	5.08

[a] Bond distances are given in atomic units (1 bohr = 5.29 10⁻¹¹ m) and bond angles in degrees. [b] X is the midpoint of the Si–Si bond.

Table II. Valence Energies of M_xSi_x Clusters (au)[a]

	structure				
	1	2	3	4	5
M = Li	7.888	7.884	7.853	15.880	15.771
M = Na	7.837	7.832	7.801	15.746	15.655

[a] 1 au = 1 hartree = 2.626 MJ/mol. $E(Li, {}^2S)$ = 0.1965 au. $E(Na, {}^2S)$ = 0.1821 au. $E(Si, {}^3P)$ = 3.6684 au. $E(Si_2, {}^3\Sigma_g)$, R = 4.24, equilibrium bond length) = 7.399 au.

Table III. Li_2Si_2 Correlation Energies in Different Approximations

	structure	
method	1	2
second-order perturbation theory	0.293	0.299
third-order perturbation theory	0.228	0.224
fourth-order perturbation theory	0.170	0.167
configuration interaction	0.213	0.214
local spin-density functional	0.217	0.218

is believed to be most stable in the D_{2h} configuration[14,15] and the latter in the C_{2v} form.[17-20] (Inclusion of correlation energy reduces,

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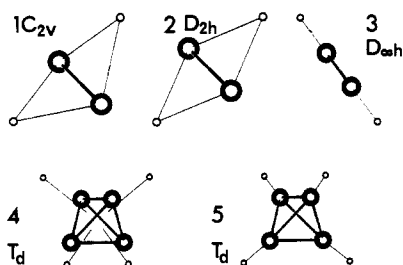
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Figure 1. Structures and point symmetry groups of hypothetical M_2Si_2 (1,2,3) and M_4Si_4 (4,5) clusters: Si large circles, metal atoms small circles.
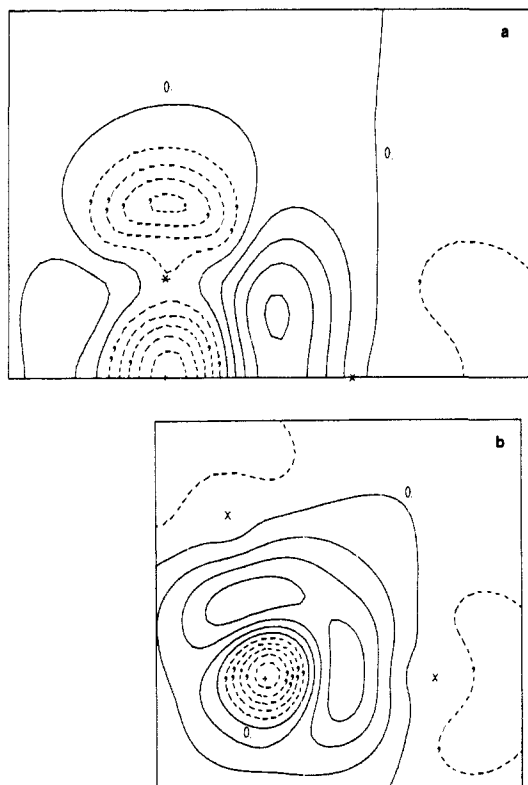

Figure 2. Electronic charge density difference map: Li_2Si_2 (C_{2v}) – Si_2 ($^3\Sigma_g^-$, R = 4.064) – Li – Li'. Full lines represent positive and broken lines negative contours. The difference between two consecutive contours is 0.002 au (1 au = 1.08 T C m^{-3}). *, Si; ×, Li; +, midpoint of Si–Si bond. (a) Plane containing the Si atoms and one of the Li atoms. (b) Plane containing the Li atoms and the midpoint of the Si–Si bond.

however, the energy difference in the latter case.) In order to decide which structure is more stable in the case of Li_2Si_2, we

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Table IV. Li_2Si_2 Internally Consistent SCF Orbital Energies (hartrees)

valence orbital	structure		
	1	2	3
$1a_1/1a_{1g}/1\sigma_g$	1.049	1.050	1.036
$1b_1/1b_{1u}/1\sigma_u$	0.848	0.848	0.873
$2a_1/2a_{1g}/2\sigma_g$	0.683	0.669	0.722
$1b_2/1b_{3u}/1\pi_u$	0.696	0.712	0.648
$3a_1/1b_{2u}/1\pi_u$	0.668	0.663	0.648

Table V. Li_4Si_4 Internally Consistent SCF Orbital Energies (hartrees)

valence orbital	structure	
	4	5
$1a_1$	1.149	1.143
$1t_2$	0.919	0.905
$2a_1$	0.711	0.757
$2t_2$	0.673	0.676
$1e$	0.653	0.620

Table VI. Na_2Si_2 Internally Consistent SCF Orbital Energies (hartrees)

valence orbital	structure		
	1	2	3
$1a_1/1a_{1g}/1\sigma_g$	1.042	1.042	1.031
$1b_1/1b_{1u}/1\sigma_u$	0.845	0.845	0.863
$2a_1/2a_{1g}/2\sigma_g$	0.677	0.670	0.714
$1b_2/1b_{3u}/1\pi_u$	0.689	0.702	0.646
$3a_1/1b_{2u}/1\pi_u$	0.666	0.658	0.646

Table VII. Na_4Si_4 Internally Consistent SCF Orbital Energies (hartrees)

valence orbital	structure	
	4	5
$1a_1$	1.138	1.138
$1t_2$	0.911	0.898
$2a_1$	0.713	0.746
$2t_2$	0.667	0.671
$1e$	0.644	0.618

performed calculations with larger basis sets and included correlation, without improving on the geometry. The larger basis set lowers the energy of 1 and 2 by 0.010 and 0.009 hartree, respectively (0 and 0.008 hartree for Li and Si_2, $^3\Sigma_g^-$, R = 4.24), and thus it enhances the energy difference between 1 and 2 to 16 kJ/mol. There is no significant change when the correlation energy is included (Table III), both with the local spin-density functional (15 kJ/mol) and in the CI calculation (14 kJ/mol) (although there is a more drastic effect in second order). Thus the SCF result is confirmed: 1 is the most stable conformation for the M_2Si_2 cluster in question.

M_4Si_4 clusters have been investigated for two different geometrical arrangements: M atoms being in the μ_3-bridging position (heterocubane, Figure 1, 4) and M atoms being terminally bonded (Figure 1, 5), respectively. Arrangement 5 is surely unstable with respect to 4 (Table II). The M_4Si_4 cluster with structure 4 is the most stable unit investigated in this work. It has considerably lower energy (~0.1 hartree, Table II) than two of the most stable M_2Si_2 clusters of type 1. For structure 4 (M = Li) the energy gradients vanish. The inspection of the force constants makes us

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believe that it corresponds to a (local) minimum. We made also some test calculations on planar M_4Si_4 structures, without obtaining a stabilization relative to **4**. Solid compounds display exactly this findings: while MC compounds occur only as acetylides M_2C_2, MSi phases contain only heterocubanes M_4Si_4 (M = Na, K, Rb, Cs).[10-12,14] There is, however, no experimental proof up to now for the Li_4Si_4 cluster in the solid state. This may be due to the lacking of favorable 3D structure with the small Li atoms. Very recent results reveal that ternary compounds M_3LiSi_4 do exist, where the Li atoms cover faces of Si_4 tetrahedrons.[29]

The relative stability of **1** and **2** over **3** and of **4** over **5** shows that bridged structures are favored. These have longer Si-Si and M-Si bond lengths.

Figure 2 shows pseudopotential electronic charge density difference maps obtained by subtracting the electronic charge densities of Si_2 and the two Li atoms (positioned as in Li_2Si_2) from that of Li_2Si_2 (structure **1**). Clearly, charge density is accumulated along the lines connecting Li with Si. In structures **1**, **2**, and **4** the densities make us believe that multicenter bonding is a prominent feature of the more stable arrangements M_xSi_x.

In order to enforce this statement we calculated the shared electron numbers,[30] which give indications about the bond strength. The values for three-center-bonding Si_2M in structures **1**, **2**, and **4** are 0.2-0.3 (for comparison: $M_2Si \sim 0$; B-H-B in diborane = 0.7). In structure **3** the value is negligible. The four-center shared electron number for Si_3M is around 0.1. Another significant multicenter character is to be seen for the Si_4 tetrahedron (0.3 for the three-center part, 0.2 for the four-center part).

A qualitative explanation for the relative stability of the different configurations needs, however, some more investigations. An orbital picture might be of some help. This can be obtained by using the internally consistent SCF orbital energies, which sum

up to give the total energy of the molecule under consideration[31] (see Tables IV-VII). For the M_2Si_2 molecules the stabilization of π orbitals (and destabilization of the σ orbitals) when going from **3** to **2** and from **3** to **1** is evident from symmetry considerations with a minimal basis set. The most pronounced effects can be observed on the highest σ and lowest π orbital. The destabilization of the σ is exceeded by the stabilization of the π orbital. Curiously, the change in the orbital energy of the highest occupied molecular orbital (HOMO) reproduces quite well the energy differences between the conformers (e.g., 0.031 mhartree between structures **2** and **3** of Li_2Si_2). This holds also for the M_4Si_4 structures. As the HOMO makes no contribution to the M-Si bonding (with a minimal basis set) in conformations **2** and **3** (or **4** and **5**), it seems necessary to include some indirect effects to explain the relative stability of the bridged structures, such as the avoiding of spatial crowding with longer bonds.[19]

Conclusions

In accordance with experimental data our calculations confirm that a bent μ_2-M_2Si_2 arrangement and a μ_3-M_4Si_4 heterocube structure are the most stable species of the arrangements investigated here. Bridging positions for the M atoms are favored in any case. The bent μ_2-M_2Si_2 cluster can be regarded as a pre-structure of the μ_3-M_4Si_4 unit which itself is a distorted part of a NaCl-like arrangement.

M_2Si_2 can dimerize with a considerable gain in energy to M_4Si_4. This is consistent with mass spectrometric and solid-state investigations that favor the latter.

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Characterization of the Temporary Anion States of Metal Carbonyl Complexes: An MS-Xα and ETS Study of Cr(CO)₆ and Fe(CO)₅

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Abstract: The electron affinities in the 0-5 eV energy range have been determined for chromium hexacarbonyl and iron pentacarbonyl by means of multiple scattering Xα calculations. The total electron scattering cross sections have been estimated with the continuum MS-Xα method. The computational results are compared with the electron transmission spectra and used for the assignment of the experimental features. The ET spectrum of Fe(CO)₅ is presented and assigned for the first time and that of Cr(CO)₆ is reassigned. For both complexes, all the anion states associated with electron capture into the orbitals deriving from the ligand 2π* MOs and into the metal empty d orbitals are assigned to resonances occurring in the 0.4-2.6 eV energy region of the ET spectra. A charge density analysis reveals that a net electronic charge transfer occurs from the ligands to the metal, owing to the acceptor capability of the metal 4s and 4p orbitals. This is consistent with the experimentally observed average stabilization of the anion states localized at the CO ligands with respect to the Π anion state of free CO.

The determination of ionization energies (IEs), electron affinities (EAs), and spatial distributions of frontier molecular orbitals

(MOs) is important for a better understanding of the bonding and of the catalytic properties of transition-metal complexes. Ultraviolet photoelectron spectroscopy together with theoretical calculations have provided a wealth of information on the occupied MOs, whereas the corresponding information on the unoccupied levels is often quite scarce.

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