

Structure and bonding in mixed silicon–carbon clusters and their anions

S. Hunsicker and R. O. Jones

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

Received 28 May 1996; accepted 21 June 1996)

Density functional calculations with simulated annealing have been performed for singly charged mixed silicon-carbon cluster anions Si_nC_m^- and for neutral Si_nC_m clusters with up to eight atoms. The calculations predict the existence of a number of previously unknown isomers and identify two classes of anion structure: carbon-rich (chainlike) and silicon-rich (three-dimensional), with pronounced differences in the vertical detachment energies (VDE, transitions to states of the neutral clusters). The results provide insight into recent photoelectron detachment measurements on the anions. © 1996 American Institute of Physics. [S0021-9606(96)02436-1]

I. INTRODUCTION

Elements belonging to the same group of the periodic table have properties in common, and carbon and silicon (group 14) are no exceptions. Nevertheless, their differences are very pronounced. The immense variety of organic chemistry, reflecting the ability of carbon to form single, double, and triple bonds, is not shared by silicon, which favors multidirectional single bonds. It is perhaps not surprising that the structures of the elemental clusters show striking differences.

For C_n clusters with $n=3-10$, *ab initio* calculations¹ predict linear structures for odd n and cyclic structures for even n , and there is experimental evidence for both linear and ring geometries.^{2,3} Larger clusters form monocyclic or bicyclic rings,⁴ and many with $n \geq 28$ give rise to fullerene structures.⁵ Important structural information on clusters has been provided in recent years by photoelectron (PE) spectroscopy. For C_n^- anions,^{3,6} the spectra consist of sharp features for $n=3-9$ and of relatively broad features for $n \geq 10$. For $n < 10$, the energy required to detach an electron from an anion (vertical detachment energy, VDE) is much lower for n odd than for n even, and the pattern inverts for larger n . Both observations are consistent with a transition from linear to ring structures at $n=10$.⁷

By contrast, Si_n clusters are predicted to be cage-like for $5 \leq n \leq 11$,⁸ and the peaks in the abundance spectra corresponding to fullerene structures in C_n are absent in Si_n ,⁹ although density functional (DF) calculations with molecular dynamics (MD) predict that silicon clusters with $n \geq 25$ have a compact inner shell surrounded by a cage-like structure.¹⁰ The PE spectra of Si_n^- for $n \leq 12$ (Ref. 11) and Raman spectra of Si_n^- for $n=4,6,7$ (Ref. 12) have been interpreted using cage-like structures.¹³⁻¹⁵ Furthermore, these investigations have shown that the geometries of C_n and Si_n cluster anions can differ substantially from those of their neutral counterparts.

While the combination of theoretical and experimental studies has led to a rather detailed picture of the elemental clusters, this is not so for mixed clusters Si_nC_m . It is natural to expect that such clusters exhibit structural features of C_n and Si_n , and this has been confirmed by a number of studies in the past years. The experimental work includes absorption spectra in matrices^{16,17} and in the gas phase,^{18,19} and the recent PE studies²⁰ of Si_nC_m^- anions. These data provide a challenge to theoreticians, as does the large number of topo-

logically distinct isomers that can occur in mixed clusters. While there have been numerous calculations on individual clusters, the *anionic* structures, which are essential for interpreting PE data, have not yet been studied systematically. This is one of our main aims. We note that the *bulk* phases of SiC also have remarkable properties. There are more than 100 crystalline forms (“polytypes”),²¹ characterized by different stacking sequences of close-packed layers that can have long periods. The amorphous phase (*a*-SiC) is a high-temperature semiconductor whose structure has been the subject of some debate. A recent study using a combination of MD and DF calculations²² showed that the structure has many (40-45%) homonuclear bonds, with the C atoms tending to form chainlike structures.

We describe here the results of an extended series of DF calculations on Si_nC_m^- anions ($n+m \leq 8$) and their neutral counterparts. The method has been applied previously to analyze the PE spectra of S_n^- and P_n^- clusters,^{23,24} and we focus here on the PE spectra of the mixed group 14 clusters.²⁰ G. Ganteför and G. Schulze Icking-Konert of our institute have provided preliminary PE data of higher resolution²⁵ that is generally consistent with our analysis. The present calculations use the local spin density (LSD) approximation for the exchange-correlation energy. A study of the effects of non-local (gradient-corrected) modifications, with particular emphasis on the elemental clusters C_n and Si_n , is in progress.

II. COMPUTATIONAL DETAILS

We have used a combination of DF calculations with molecular dynamics (MD) for all clusters. The use of MD is advantageous, since there are numerous possible isomers and the nature of the most stable is not generally known. Details of the method are provided in previous applications.^{23,24} The calculations adopt periodic boundary conditions (PBC) with a (simple cubic) unit cell with lattice constant 20 a.u., a plane wave basis set with a single point ($k=0$) in the Brillouin zone, and the LSD approximation to the exchange-correlation energy. Energetically favorable regions of the energy surface were located using a plane wave expansion with a cutoff energy of 7.5 a.u., and structure refinement was carried out with a cutoff of 15 a.u. The electron-ion interaction is described by the non-local pseudopotential of Troullier and Martins,²⁶ using the *d*-component of the potential as

TABLE I. Si_nC_m^- clusters: Vertical detachment energies (VDE, eV, with uncertainties in brackets) derived from photoelectron spectra (“N,” Ref. 20) and present calculations (“Calc.”). Values in square brackets belong to isomers that are not the most stable.

| Total atoms | Composition | | Figure | VDE | |
|-------------|-------------|-----|--------|------------|--------|
| | n | m | | N | Calc. |
| 3 atoms | 1 | 2 | 1(b) | 1.54(0.06) | 1.69 |
| | 2 | 1 | 1(c) | ... | 1.18 |
| 4 atoms | 1 | 3 | 1(e) | 2.76(0.04) | 2.86 |
| | 1 | 3 | 2(a) | 1.93(0.10) | 2.08 |
| | 2 | 2 | 2(b) | 1.93(0.08) | 2.07 |
| 5 atoms | 3 | 1 | 2(e) | 1.54(0.08) | 1.69 |
| | 1 | 4 | 3(a) | 2.34(0.04) | 2.27 |
| | 2 | 3 | 3(d) | 1.71(0.10) | 1.82 |
| | 3 | 2 | 4(a) | ... | 1.88 |
| 6 atoms | 4 | 1 | 4(d) | 3.12(0.10) | 3.21 |
| | 1 | 5 | 4(f) | 3.14(0.03) | 3.22 |
| | 2 | 4 | 5(c) | 2.49(0.08) | 2.59 |
| | 3 | 3 | 6(a) | 2.16(0.08) | 2.51 |
| | 4 | 2 | 6(e) | 2.10(0.08) | 2.18 |
| 7 atoms | 5 | 1 | 7(b) | 1.74(0.08) | 1.81 |
| | 2 | 5 | 7(e) | 2.16(0.06) | 2.18 |
| | 6 | 1 | 8(c) | 1.74(0.08) | [1.79] |
| 8 atoms | 7 | 1 | 8(e) | 2.92(0.08) | [3.32] |

the reference local part (“ sp –nonlocality”). The choice of unit cell size was tested by calculating the three most stable isomers of Si_6C^- [see Sec. III.F.2.]. Using a cell with lattice constant 30 a.u. and the same energy cutoff (yielding ~ 37000 and ~ 230000 plane waves in the expansion of the wave functions and the density, respectively), the energy ordering and the relative stabilities of the isomers differed by less than 0.03 eV, and the bond lengths and bond angles by less than 2%. Additional tests are described in Sec. IV.

We focus on cluster geometries and the energy differences between states of the charged and neutral systems [vertical detachment energies (VDE) and relative energies of the isomers of the neutral and charged clusters]. The methods used to correct the calculation of the Coulomb energy in a system with PBC, and for describing the multiplet structures of the clusters, are described in Ref. 23. To check further the approximations inherent in MD/DF calculations, particularly the pseudopotential description of the electron-ion interaction and the use of a supercell with PBC, we have performed all-electron DF calculations for many of these clusters.²⁷ The agreement is generally good and will be discussed in specific cases in Sec. IV. The vibration frequencies were determined by all-electron calculations.

III. RESULTS OF CALCULATIONS, COMPARISON WITH OTHER WORK

In this section we present our results for structures, vibration frequencies, and vertical excitation energies (Table I). In Tables II–V we include C-C bonds shorter than 3.82 a.u. and Si-Si bonds shorter than 5.3 a.u., corresponding to the first minima of the pair correlation functions of liquid C (Ref. 28) and Si (Ref. 29), respectively. The cutoff distance for Si-C bonds is the mean value (4.57 a.u.). In Figs. 1–8,

TABLE II. Structure parameters for isomers of Si_nC_m^- , $n+m=2-4$, with energies ΔE relative to the ground state (eV). Bond lengths d_{ij} in a.u. and bond angles α_{ijk} in degrees. Additional labels refer to the figures, where the atom numberings are also defined.

| Molecule | Symmetry | State | ΔE |
|--|----------------|--------------|------------|
| SiC^- | $C_{\infty v}$ | $^2\Sigma^+$ | 0.00 |
| $d_{12}=3.17$ | | | |
| SiC_2^- 1(a) | C_{2v} | 2B_2 | 0.00 |
| $d_{12}=2.49$; $d_{13,23}=3.56$; $\alpha_{123,213}=70^\circ$; $\alpha_{132}=41^\circ$ | | | |
| SiC_2^- 1(b) | $C_{\infty v}$ | $^2\Pi$ | 0.03 |
| $d_{12}=2.43$; $d_{23}=3.32$ | | | |
| Si_2C^- 1(c) | $D_{\infty h}$ | $^2\Pi_g$ | 0.00 |
| $d_{12,13}=3.25$ | | | |
| SiC_3^- 1(e) | $C_{\infty v}$ | $^2\Pi$ | 0.00 |
| $d_{12}=2.45$; $d_{23}=2.52$; $d_{34}=3.22$ | | | |
| SiC_3^- 1(f) | C_{2v} | 2A_2 | 0.49 |
| $d_{12,23}=2.58$; $d_{14,34}=3.78$; $d_{24}=3.45$; $\alpha_{123}=152^\circ$; $\alpha_{214,234}=62^\circ$ | | | |
| SiC_3^- 2(a) | C_{2v} | 2B_1 | 0.67 |
| $d_{12,23}=2.70$; $d_{13}=2.76$; $d_{14,34}=3.54$; $\alpha_{123}=61^\circ$; $\alpha_{214,234}=126^\circ$; $\alpha_{143}=46^\circ$ | | | |
| Si_2C_2^- 2(b) | C_s | $^2A''$ | 0.00 |
| $d_{12}=2.49$; $d_{13}=3.56$; $d_{14}=3.49$; $d_{23}=3.77$; $d_{34}=4.56$; $\alpha_{123}=66^\circ$ | | | |
| $\alpha_{214}=155^\circ$; $\alpha_{143}=50^\circ$; $\alpha_{234}=89^\circ$ | | | |
| Si_2C_2^- 2(c) | $D_{\infty h}$ | $^2\Pi_g$ | 0.10 |
| $d_{12}=2.48$; $d_{14,23}=3.26$ | | | |
| Si_3C^- 2(e) | C_{2v} | 2A_2 | 0.00 |
| $d_{12,14}=3.38$; $d_{13}=3.58$; $d_{23,24}=4.49$; $\alpha_{214}=161^\circ$; $\alpha_{234}=96^\circ$ | | | |

“bonds” are shown for internuclear separations less than 5.3 a.u., irrespective of atomic species, and light and dark spheres denote Si and C atoms, respectively.

A. SiC^-

Although C_2 and Si_2 are well-known,³⁰ SiC was identified only eight years ago by Bernath *et al.*,³¹ who resolved the 0-0 band of the $d^1\Sigma^+ - b^1\Pi$ transition in the vibration-rotation spectrum and estimated the bond length r_e of the $^3\Pi$ [$\dots \pi^3\sigma^1$] ground state to be 3.248 ± 0.002 a.u. The molecule has subsequently been detected at millimeter wavelengths in the envelope of a carbon star.³² Our calculations also give a $^3\Pi$ ground state, and the bond length (3.24 a.u.) agrees well with the above value. The first excited state ($^3\Sigma^-, \dots \pi^2\sigma^2$) is 0.42 eV less stable, compared with a configuration interaction (CI) value of 0.44 eV.³³ The lowest singlet $^1\Sigma^-$ state [$\dots \pi^4$] was found at 0.76 eV (CI: 0.65 eV).³³

The addition of an electron to these SiC triplet states yields a $^2\Sigma^+$ ground state of SiC^- [$\dots \pi^4\sigma^1$], with a $^2\Pi$ state [$\dots \pi^3\sigma^2$] 0.47 eV higher. As observed previously in Si_2 ,³⁴ the bond in the anion is shorter than in the neutral cluster (see Table II), consistent with the higher occupancy of the bonding π -orbitals. The vertical excitation energies from the ground state of SiC^- to states of SiC are predicted to be: 2.55 eV ($^3\Pi$, VDE), 3.25 eV ($^3\Sigma^-$), 3.27 eV ($^1\Pi$), and 3.30 eV ($^1\Sigma^+$). We know of no measured PE spectra for this molecule.

B. Three-atom clusters

1. SiC_2^-

The present calculations predict a C_{2v} (1A_1) ground state for SiC_2 with $\alpha_{\text{CSiC}}=41^\circ$. A linear Si-C-C structure is

TABLE III. Calculated vibration frequencies ω_e (cm^{-1}) of selected isomers of neutral clusters Si_nC_m , $n+m \leq 5$.

| Molecule | Symmetry | Method | Frequency ω_e |
|-------------------------|------------------------------|----------------------|--|
| SiC_3 | $C_{\infty v}(^3\Sigma^-)$ | here | 168 (π), 442 (π), 588 (σ), 1283 (σ), 1959 (σ) |
| | | HF ^a | 164 (π), 456 (π), 659 (σ) 1275 (σ), 2037 (σ) |
| Si_2C_2 | $C_s(^1A')$ | here | 172 (a''), 269 (a'), 424 (a'), 585 (a'), 673 (a'), 1530 (a') |
| | | HF ^b | 245 (a''), 306 (a'), 537 (a') 668 (a'), 754 (a'), 1560 (a') |
| Si_2C_2 | $D_{\infty h}(^3\Sigma_g^-)$ | here | 123 (π_u), 425 (π_g), 455 (σ_g), 863 (σ_u), 1845 (σ_g) |
| | | HF ^b | 117 (π_u), 278 (π_g), 493 (σ_g), 933 (σ_u), 1801 (σ_g) |
| Si_2C_2 | $D_{2h}(^1A_g)$ | here | 152 (b_{3u}), 288 (b_{2u}), 440 (a_g), 865 (b_{3g}), 907 (b_{1u}), 1011 (a_g) |
| | | HF ^b | 213 (b_{3u}), 397 (b_{2u}), 522 (a_g), 978 (b_{3g}), 1011 (b_{1u}), 1067 (a_g) |
| Si_2C_3 | $D_{\infty h}(^1\Sigma_g^+)$ | here | 97 (π_u), 236 (π_g), 450 (σ_g), 586 (π_u), 875 (σ_u), 1558 (σ_g), 2053 (σ_u) |
| | | MBPT(2) ^c | 85 (π_u), 210 (π_g), 442 (σ_g) 519 (π_u), 869 (σ_u), 1527 (σ_g), 2082 (σ_u) |

^aRef. 44, TZ2P.^bRef. 49, TZ2P.^cRef. 53, DZP.

0.19 eV less stable, and triplet states lie 1.55 and 2.27 eV higher. These results compare satisfactorily with the measured bond angle (40–41°, Ref. 35) and calculated differences between the energies of these isomers, 0.22 eV (Ref. 36) and 0.16 eV,³⁷ respectively. Our calculated bond lengths [$r_{\text{SiC}}=3.48$ a.u., $r_{\text{CC}}=2.41$ a.u.] compare well with measured values [3.42, 2.36].³⁸

The addition of an electron stabilizes the linear isomer [$^2\Pi$, 1(b)] with respect to the C_{2v} form, which is now only 0.02 eV higher than a C_{2v} (2B_2) isomer [1(a)]. A comparison of the C_{2v} isomers shows that the bonds in SiC_2 are longer than those in the anion by about 3%, while the bond angles remain the same. The calculated values of the VDE are 1.50 eV (C_{2v}) and 1.69 eV ($C_{\infty v}$), and vertical excitations to the first excited states are 3.69 eV ($C_{\infty v}$, $^3\Pi$) and 2.99 eV (C_{2v} , 3B_2), respectively.

Available photoelectron spectra are consistent with the above assignment. While the PE spectrum²⁰ shows a rather broad peak at 1.54 ± 0.06 eV that is consistent with either

TABLE IV. Structure parameters for isomers of Si_nC_m^- , $n+m=5$, with energies ΔE relative to the ground state (eV). Bond lengths d_{ij} in a.u. and bond angles α_{ijk} in degrees. Additional labels refer to the figures, where the atom labels are also defined.

| Molecule | Symmetry | State | ΔE |
|--|----------------|-----------|------------|
| SiC_4^- 3(b) | $C_{\infty v}$ | $^2\Pi$ | 0.00 |
| $d_{12}=2.43$; $d_{23}=2.50$; $d_{34}=2.42$; $d_{45}=3.27$ | | | |
| Si_2C_3^- 3(d) | $D_{\infty h}$ | $^2\Pi_u$ | 0.00 |
| $d_{12,23}=2.46$; $d_{15,34}=3.22$ | | | |
| Si_3C_2^- 4(a) | C_{2v} | 2B_1 | 0.00 |
| $d_{12}=2.51$; $d_{14,24}=3.82$; $d_{15,23}=3.33$; $d_{34,45}=4.56$; $\alpha_{123}=150^\circ$; $\alpha_{143}=84^\circ$; $\alpha_{345}=130^\circ$; | | | |
| Si_4C^- 4(d) | C_{2v} | 2A_1 | 0.00 |
| $d_{12,15}=3.47$; $d_{13,14}=3.84$; $d_{23,24,35,45}=4.54$; $d_{34}=4.67$; $\alpha_{215}=146^\circ$; $\alpha_{314}=75^\circ$ | | | |

structure, there is no sign of increased intensity near 3.0 eV that should be observable if the C_{2v} structure were more stable.

2. Si_2C^-

The neutral Si_2C dimer also has C_{2v} and $D_{\infty h}$ structures with comparable energies, the 1A_1 state of the C_{2v} isomer being 0.11 eV more stable than the $^1\Sigma_g^+$ state of the linear isomer. The energy difference is similar to previous calculations [0.08 eV (Ref. 39); 0.09 eV (Ref. 40)], as are the struc-

TABLE V. Structure parameters for isomers of Si_nC_m^- , $n+m=6,7$, with energies ΔE relative to the ground state (eV). Bond lengths d_{ij} are in a.u., bond angles α_{ijk} in degrees. Additional labels refer to the figures, where also the atom labels are defined.

| Molecule | Symmetry | State | ΔE |
|---|----------------|-----------|------------|
| SiC_5^- 4(f) | $C_{\infty v}$ | $^2\Pi$ | 0.00 |
| $d_{12}=2.44$; $d_{23}=2.50$; $d_{34}=2.42$; $d_{45}=2.49$; $d_{56}=3.25$ | | | |
| SiC_5^- 5(a) | C_{2v} | 2A_1 | 0.81 |
| $d_{12,45}=2.56$; $d_{13,35}=3.55$; $d_{16,56}=3.42$; $d_{23,34}=2.55$; $\alpha_{165}=68^\circ$; $\alpha_{123}=88^\circ$; $\alpha_{234}=157^\circ$; $\alpha_{216}=159^\circ$ | | | |
| Si_2C_4^- 5(c) | $D_{\infty h}$ | $^2\Pi_u$ | 0.00 |
| $d_{12,34}=2.47$; $d_{16,45}=3.19$; $d_{23}=2.43$ | | | |
| Si_3C_3^- 6(a) | C_1 | 2A | 0.00 |
| $d_{12}=2.45$; $d_{16}=3.24$; $d_{23}=2.49$; $d_{34,35}=3.55$; $d_{45}=4.24$; $\alpha_{435}=73^\circ$ | | | |
| Si_4C_2^- 6(e) | C_1 | 2A | 0.00 |
| $d_{12}=2.97$; $d_{14,23}=3.46$; $d_{15}=3.89$; $d_{16}=3.53$; $d_{25}=3.90$; $d_{26}=3.52$; $d_{34}=4.69$; $d_{35}=4.62$; $d_{45}=4.63$; $d_{56}=4.64$ | | | |
| Si_5C^- 7(b) | C_s | $^2A'$ | 0.00 |
| $d_{12}=3.42$; $d_{13}=3.83$; $d_{14}=3.59$ $d_{15}=3.83$; $d_{23}=4.78$; $d_{25}=4.79$; $d_{26}=4.65$; $d_{34,45}=4.43$; $d_{35}=4.59$; $d_{36}=4.46$; $d_{56}=4.45$ | | | |
| Si_5C^- 7(c) | C_{2v} | 2B_2 | 0.00 |
| $d_{12,13,14,15}=3.61$; $d_{16}=4.08$; $d_{23,45}=4.50$; $d_{25,34}=5.24$; $d_{26,36,46,56}=4.60$ | | | |
| Si_2C_5^- 7(e) | $D_{\infty h}$ | $^2\Pi_g$ | 0.00 |
| $d_{12,45}=2.45$; $d_{17,56}=3.22$; $d_{23,34}=2.43$ | | | |

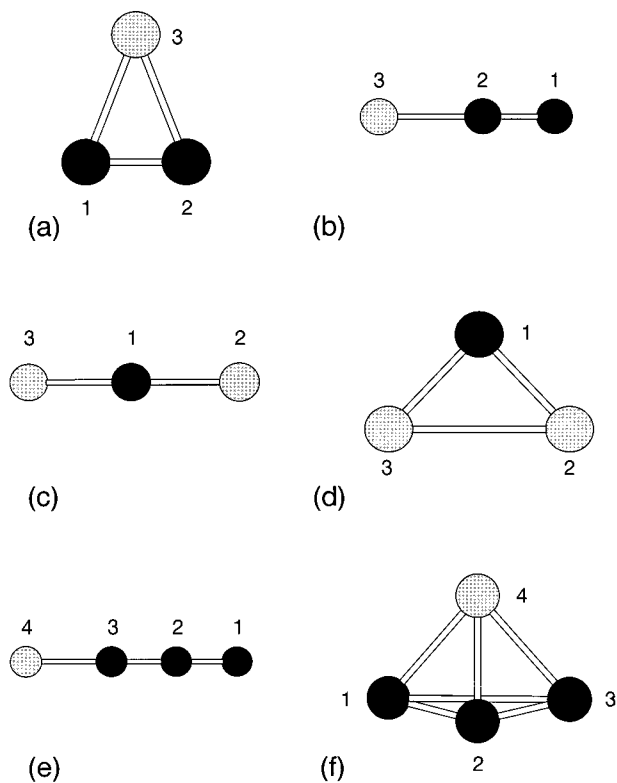


FIG. 1. Structures of (a),(b) SiC_2^- (c),(d) Si_2C^- and (e),(f) SiC_3^- . Light spheres are Si atoms, dark spheres are C atoms.

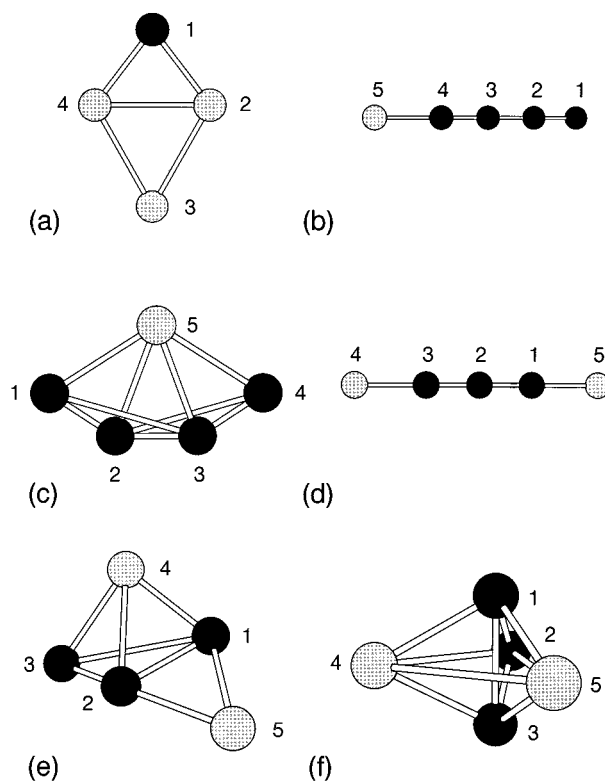


FIG. 3. Structures of (a) Si_3C^- , (b),(c) SiC_4^- and (d)–(f) Si_2C_3^- .

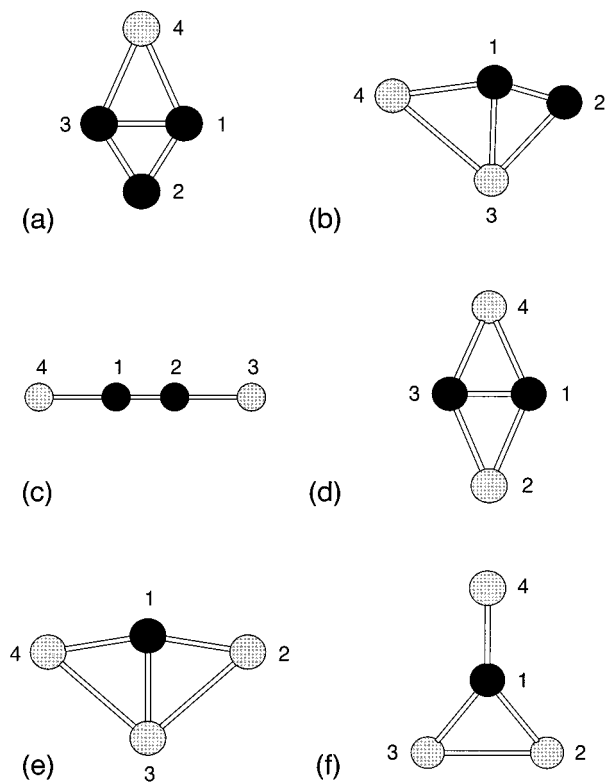


FIG. 2. Structures of (a) SiC_3^- , (b)–(d) Si_2C_2^- and (e),(f) Si_3C^- .

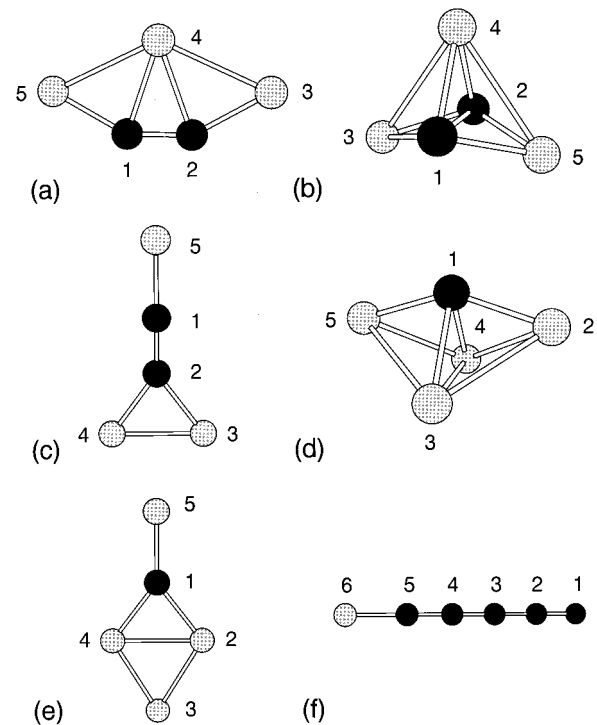
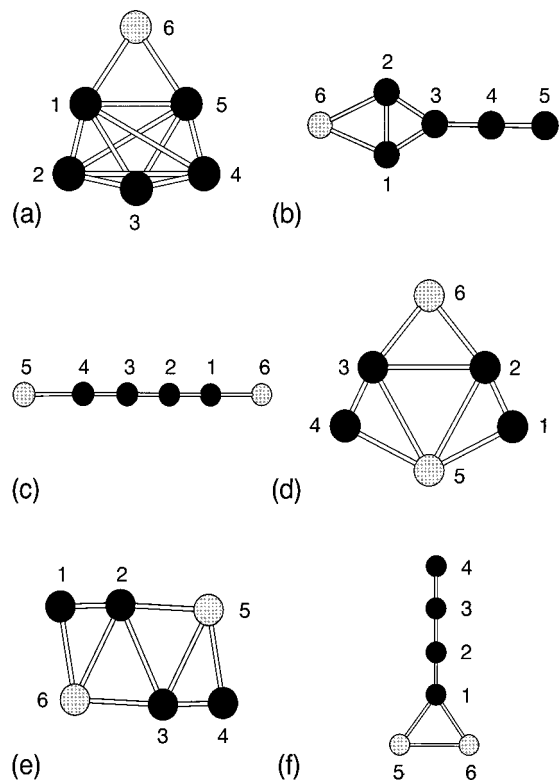
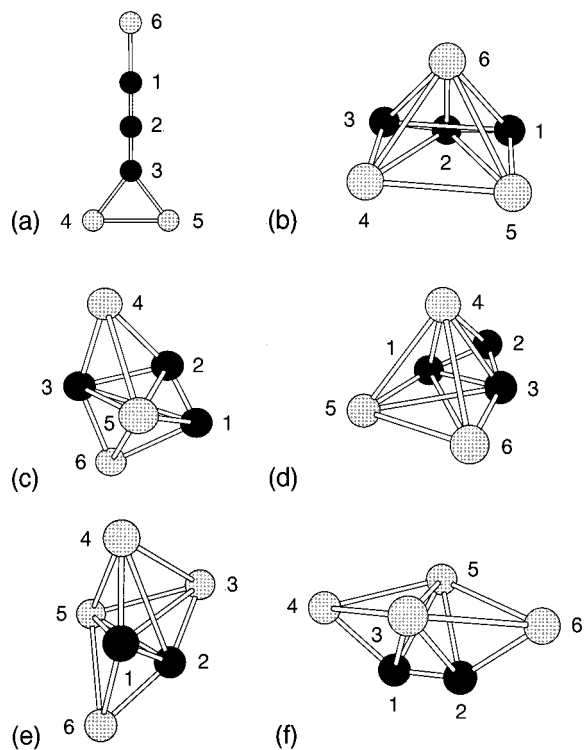
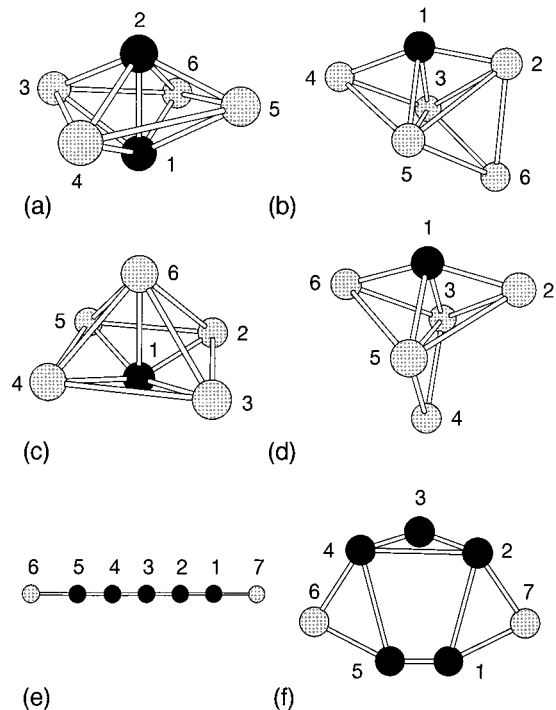
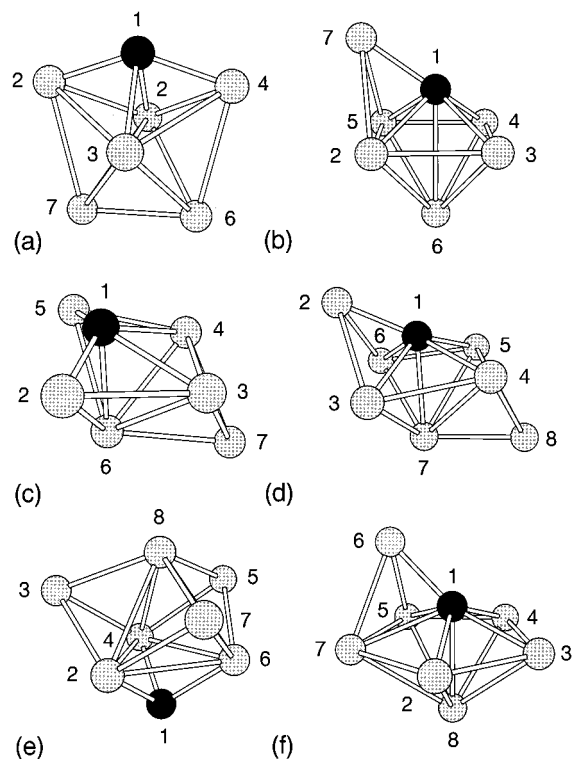


FIG. 4. Structures of (a)–(c) Si_3C_2^- , (d),(e) Si_3C^- , and (f) SiC_5^- .

FIG. 5. Structures of (a),(b) Si_5C^- and (c)–(f) Si_2C_4^- .FIG. 6. Structures of (a)–(d) Si_3C_3^- and (e),(f) Si_4C_2^- .FIG. 7. Structures of (a) Si_4C_2^- , (b)–(d) Si_5C^- , and (e)–(f) Si_2C_5^- .FIG. 8. Structures of (a)–(c) Si_6C^- and (d)–(f) Si_7C^- .

tures. The C_{2v} isomer has $r_{\text{SiC}}=3.21$ a.u., $\alpha_{\text{SiCSi}}=116^\circ$, in reasonable agreement with other calculations [(3.22, 119.5, Ref. 39); (3.18, 117.6, Ref. 41)]. Two triplet states were found ~ 2.5 eV above the C_{2v} ground state.

Addition of an electron to the C_{2v} isomer results in an increase in α_{SiCSi} , and one obtains the linear (${}^2\Pi$) isomer of the anion [1(c)] by starting from either neutral structure. A local minimum with C_{2v} geometry [2A_1 , 1(d)] is only 0.01 eV less stable and arises from an equilateral starting structure. The marked differences between the calculated vertical excitation energies for these two anion structures [1.18, 3.49, 3.94 eV for isomer 1(c); 1.56, 2.90, 3.37 eV for 1(d)], however, should enable them to be distinguished in PE measurements. The initial data of Ganteför and Schulze Icking-Konert²⁵ are compatible only with the former.

C. Four-atom clusters

The above results for the neutral triatomic clusters show the competition between cyclic and linear isomers, with Si_2C and SiC_2 having weakly bent and cyclic C_{2v} structures, respectively. Ring and open structures are also nearly degenerate in Si_3 ,⁴² and C_3 is linear both here and in HF-based calculations.¹ Although Si_3^- is cyclic,¹³ our calculations and others indicate that the corresponding *anions* generally favor linear geometries. Si_2C^- and SiC_2^- are linear, and PE spectra of C_3^- indicate a linear structure.⁶ Noting that Si_4^- and possibly C_4 (Ref. 43) are rhombic, we now examine the mixed tetratomic clusters.

1. SiC_3^-

Neutral SiC_3 has a rhombic ground state (C_{2v} , 1A_1) with a transannular C-C bond with $r_{\text{CC}}=2.72$ a.u. (2.78 a.u.)⁴⁴. A second rhombus with a transannular Si-C bond with $r_{\text{SiC}}=3.58$ a.u. (3.55 a.u., Ref. 44) is only 0.08 eV (0.19 eV, Ref. 44) higher. A linear isomer (${}^3\Sigma^-$) lies just 0.01 eV above the more stable rhombus (0.18 eV, Ref. 44). Other structures and electronic states lie at least 0.75 eV above the most stable.

This near degeneracy is lifted in the anion. The linear isomer [1(e)] is now 0.49 eV more stable than 1(f), with 2(a) an additional 0.18 eV higher. Similar to the situation that we found in the Si_n^- helical isomers,²³ the added electron in the linear isomer is localized on the terminal bonds, which are $\sim 2\%$ shorter than in the neutral species. The calculated excitation energies of the linear isomer gives a VDE value of 2.86 eV and a first excited state (${}^1\Sigma^+$) of 3.27 eV, the VDE for 1(f) and 2(a) are 2.08 eV and 2.35 eV, respectively.

The main peak in the PE spectrum (VDE: 2.76 ± 0.4 eV, Ref. 20) is consistent with the calculated value for the linear isomer, but there is a weak signal at 1.93 ± 0.1 eV that may be assigned to a second isomer 2(a). The calculated VDE for structure 1(f) [2.08 eV] agrees satisfactorily with this value, and first results of Ganteför and Schulze Icking-Konert indicate that additional features are consistent with the 1(f) structure. While the linear ground state of SiC_3^- dominates the PE spectra, there are indications of the presence of the other

two isomers. The vibration frequencies are given in Table III and compared with the results of Hartree-Fock calculations.⁴⁴

2. Si_2C_2^-

Rhombic and linear forms of Si_2C_2 have been studied by Trucks and Bartlett,⁴⁵ who calculated energies up to fourth order in perturbation theory. Lammertsma and Güner⁴⁶ predicted a low-lying isomer of C_s symmetry, and Sudharkar *et al.*⁴⁷ compared two rhombic D_{2h} structures in terms of a bond stretch isomerism. Finally, several isomers have been discussed by Fitzgerald and Bartlett.⁴⁸ We consider here both singlet and triplet states of six isomers, the most stable being: (a) the ground state, a D_{2h} (1A_g) rhombus; (b) a distorted trapezoidal C_s structure (${}^1A'$ state) 0.18 eV higher, (c) a linear isomer ($D_{\infty h}$, ${}^3\Sigma_g^-$) a further 0.18 eV higher in energy. This ordering was also found in Ref. 46, where the corresponding energy differences were 0.36 eV and 0.13 eV.

As might be expected from the previous results, the linear isomer [2(c)] is stabilized in the anion, but is 0.1 eV less stable than the distorted trapezoid [2(b)] (C_s , ${}^2A''$ state). The energy of the D_{2h} rhombus [2(d)] in the anion is 0.25 eV higher than in the C_s structure. Several isomers of the neutral species – including a trapezoidal C_{2v} structure (3B_1 state) 0.81 eV and a C_2 isomer (1A_1 state) 1.04 eV above the rhombic isomer – transformed into the C_s isomer, indicating that it has a large “catchment region.” The other structures did not change significantly upon charging. The calculated excitation spectrum for the C_s isomer gives a VDE of 2.07 eV and transition energies into the ${}^3A''$ and the ${}^1A''$ excited states of the neutral species at 2.83 eV and 3.21 eV BE, respectively. For the linear isomer we obtain excitation energies of 2.14 eV (${}^3\Sigma_g^-$, VDE) and 2.49 eV (${}^1\Sigma_g^+$), and a VDE of 1.56 eV for the rhombus.

The PE spectrum²⁰ gives a VDE of 1.93 ± 0.08 eV, in satisfactory agreement with the calculated value for the C_s isomer. A linear isomer cannot be excluded, as the calculated peak positions fall near peaks of the most stable isomer and/or in regions of comparatively high intensity. However, the rhombus is incompatible with the measured spectrum, as its calculated VDE falls in an interval of very low intensity. The availability of PE spectra of higher resolution would be particularly valuable if vibrational fine structure could be measured for comparison with the calculated vibration frequencies (Table III, we show also the HF values of Ref. 49). We note, in particular, the pronounced differences between the highest frequencies calculated for the C_s , $D_{\infty h}$, and D_{2h} isomers (1530, 1845, 1011 cm^{-1} , respectively).

3. Si_3C^-

The neutral cluster and its fundamental vibrations have been identified in the products of vaporization of C/Si mixtures trapped in Ar at 13 K.¹⁶ Rittby⁵⁰ has investigated six different isomeric structures of Si_3C using Hartree-Fock (HF) calculations, and we have calculated both the singlet and triplet states of these structures. We concur that the most stable isomer is a rhomboidal C_{2v} structure (1A_1 state) with two equivalent silicon atoms and a transannular Si-C bond. Another C_{2v} structure (3B_1), similar to the anionic structure

2(f), lies 1.44 eV higher in energy, and a rhomboidal C_{2v} structure with transannular Si-Si bond is an additional 0.40 eV less stable.

The energy ordering of the structures is preserved in the anion, the isomer 2(e) now being only 0.80 eV more stable than 2(f) and 1.20 eV below 3(a). The calculated excitation spectrum for 2(e) gives transitions at 1.69 eV (VDE), 3.16 eV, and 3.51 eV. A fourth at 3.88 eV is for a transition to a state that is not the lowest of symmetry 3B_1 and outside a rigorous treatment by DF theory. The calculated VDE of structures 2(f) and 3(a) are 2.06 eV and 2.47 eV, respectively. As might be expected from the relative stability of 2(e), the measured VDE agrees best with the calculated value for this isomer.

D. Five-atom clusters

1. SiC_4^-

Linear SiC_4 has been studied by HF-based calculations,⁵¹ and a fundamental vibration has been measured.⁵² The linear structure is the most stable in our calculations, with a C_{2v} ring (1A_1) 0.62 eV higher, and there are several others – planar and non-planar – at least 1.0 eV above the energy of the chain.

As in SiC_2^- and SiC_3^- , the relative stability of the chain [3(b)] is greater (1.08 eV) in the anion, and the other structures are even less stable. As in our earlier calculations for sulfur cluster anions, we find significant differences in the VDE for chain and ring isomers. The calculated VDE for the former (2.27 eV, the next transition is > 4 eV) agrees better with the measured value (2.34 eV, Ref. 20) than the VDE of the latter [3(c), 1.95 eV]. The presence of a single peak in the measured spectrum provides further support for the chain [3(b)].

2. Si_2C_3^-

Si_2C_3 has been investigated in the vapor of Si/C mixtures. Two fundamental vibrations have been identified by Fourier transform infrared spectroscopy,¹⁷ and one of these was also observed using infrared laser spectroscopy.¹⁹ Calculations on the singlet and triplet states of nine different isomers of Si_2C_3 were performed by Rittby.⁵³ The present calculations also predict a linear ($D_{\infty h}$, ${}^1\Sigma_g^+$) ground state, and the energy ordering of the states is very similar to that in Ref. 53. The next energy minimum is 0.68 eV higher and corresponds to a structure that had not been found previously, a planar C_s ring with a C_3 sub-molecule. However, it transforms into the chain on annealing at temperatures up to 600 K. Nine other isomers lie at least 1 eV above the chain, including a C_1 structure similar to the anion structure 3(e) [1.38 eV] and a distorted C_{2v} bipyramid [3(f) is the corresponding anion] 1.55 eV above the minimum.

Adding an electron increases slightly the relative stability of the linear chain [3(d)], but the C_1 isomer [3(e)] 1.45 eV higher becomes more stable than a C_{2v} structure containing a triangular C_3 sub-molecule in a more equilateral form. The bipyramid [3(f)] distorts to C_s symmetry and has an energy 1.46 eV above the most stable isomer. The vertical

excitation energies of the chain [1.82 eV (${}^3\Sigma_u$, VDE), 3.66 eV] are consistent with the measured VDE (1.71 ± 0.1 eV).²⁰ The vibration frequencies are given in Table III, together with the HF values of Ref. 53.

3. Si_3C_2^-

Five different isomers of neutral Si_3C_2 were investigated recently by Froudakis *et al.*⁵⁴ We have considered these and other structures and concur that the most stable structure is a planar C_{2v} pentagon with a C_2 submolecule. The energy is 0.52 eV below the most stable three-dimensional structure, a distorted D_{3h} bipyramid. Other structures (three-dimensional, planar and linear) with higher energies include an Si_3 unit bridged by a C dimer (C_1) lying 0.76 eV above the planar pentagon.

The additional electron has little effect on the relative stability of the isomers 4(a,b), which are also the most stable in the anion. Several isomers that were stable in the neutral cluster transform readily into the pentagon after charging and annealing at 300 – 600 K. The third most stable neutral isomer had not been considered previously, and transforms on charging from a planar pentagonal ring (C_s) with transannular C-C bond into structure 4(c). The latter is nearly degenerate with the bipyramid (0.04 eV less stable).

Our calculations predict the following transition energies into the three lowest excited states of the neutral species for the most stable anion: 1.88 eV (1A_1 state, VDE), 2.59 eV (3B_2 state) and 2.94 eV (1B_2 state). The VDE for the isomers 4(b) and (c) are 2.32 eV (1A_1 state) and 2.73 eV (1A_1 state), respectively. No photoelectron measurements have yet been performed for this cluster, but the pronounced differences between the VDE should facilitate the analysis of future data.

The recent work of Presilla-Márquez *et al.*⁵⁵ was brought to our attention after the present work was submitted. These authors have provided the first observation of Si_3C_2 , using Fourier transform infrared measurements of Si/C vapor trapped in argon, and have performed density functional and HF-based calculations on several isomers. These authors also find the C_{2v} isomer to be the most stable, and assign the measured 956.7 cm^{-1} absorption to a b_2 vibration of this isomer. The new structure [1(B) in Ref. 55], which is related to the C_1 structure described above, lies 0.80 eV above the most stable isomer in these DF calculations.

4. Si_4C^-

Calculations on the Si_4 cluster²⁰ indicate that the most stable isomer is a distorted trigonal (C_{3v}) bipyramid with the C atom at the apex. The present calculations lead to the same conclusion, but a distorted pentagonal ring (C_{2v}) lies only 0.1 eV higher. Another distorted trigonal pyramid (C_{2v}) [anionic structure 4(d)] is an additional 0.19 eV less stable.

The energy ordering differs significantly in the anion. As in the previous calculations,²⁰ the trigonal (C_{2v}) bipyramid [4(d)] is now the most stable, with the planar structure 4(e)

0.38 eV higher in energy (VDE 2.01 eV). All other anionic structures transformed on annealing into 4(d), with VDE 3.21 eV.

The PE spectrum shows a single peak at 3.12 ± 0.10 eV, in good agreement with the calculated value for the most stable form of the anion. The VDE is the highest of the five-membered clusters considered here and is even higher than the experimental value for C_5^- (2.27 eV). This is consistent with the creation of an additional bond between atoms 3 and 4 in 4(d) on adding an electron. The substitution of Si for C causes strain in the underlying D_{3h} trigonal bipyramid of Si_5 , and the bond between atoms (3,4) in neutral Si_4C increases to 5.55 a.u. Furthermore, electrons are attracted to the more compact C atom from Si sites in the cluster, and the extra electron in the anion is repelled by this charge into the Si_4 substructure. The corresponding orbital has a large amplitude between the Si atoms (3,4) and contributes to the formation of a bond (equilibrium distance 4.67 a.u.). The situation is different in Si_5^- , which also has an exceptionally high VDE.^{11,13} Raghavachari and Rohlfling¹³ found that the additional electron of Si_5^- occupies an orbital that is anti-bonding between the two apex atoms. They argue that the strain introduced in the Si_5 structure is compensated by a contraction of the equatorial Si_3 substructure, resulting in a stronger bond.

E. Six-atom clusters

1. SiC_5^-

Earlier calculations of structures of neutral and anionic SiC_5 were extended to calculations of the adiabatic electron affinities (EA) at the PMP4(SDTQ) level.²⁰ We have investigated several neutral isomers, including a linear chain ($C_{\infty v}$), a planar pentagonal ring (C_{2v}), and a planar (C_{2v}) structure of rhombic $SiC_3 + C_2$ [5(b) is the corresponding anion]. The last of these is very flexible: the transannular C_2 fragment in the ringlike SiC_3 submolecule undergoes hindered internal rotation with a very shallow minimum at C_{2v} symmetry. The chain is the most stable form, the other two isomers lying 0.24 eV and 0.39 eV higher, respectively. We considered several other isomers with even higher energies.

The energy ordering is unchanged in the anion, and isomers 5(a) and 5(b) are 0.81 eV and 1.18 eV, respectively, above the linear chain [4(f)]. The excitation energies for the chain [3.22 eV (VDE) and 3.51 eV, corresponding to a transition to the $^1\Sigma^+$ state of SiC_3] are in reasonable agreement with the experimental VDE [3.14 ± 0.03 eV].²⁰ The next peak predicted is outside the range of the measurements.

The PE spectrum²⁰ shows a feature of low intensity near 1.7 eV, which was interpreted as evidence for the planar structure [5(b)]. Starting with this structure, we found a VDE (3.14 eV) that is much higher than the measured value (1.65 ± 0.1 eV). On the other hand, the structure 5(b) is less stable than the linear chain (by 1.19 eV) and also less stable (by 0.38 eV) than structure 5(a), even in the neutral cluster. However, the VDE of this isomer is also large (2.86 eV), so that the origin of the feature near 1.7 eV remains unclear.

The comparatively high VDE of the linear isomer is consistent with the even-odd alternation of VDE in linear and ringlike C_n clusters, since VDE should be lower in even-membered rings than in odd-membered chains.

2. $Si_2C_4^-$

Five different structures of Si_2C_4 were investigated recently by Froudakis *et al.*⁵⁶ We have investigated these and others, and support their prediction that the linear structure ($D_{\infty h}$, $^3\Sigma_u^-$) with terminal Si atoms is the most stable. This is followed by a hexagonal C_s ring [related to the anion 5(d)] 0.79 eV higher in energy and a distortion of this ring to planar C_{2h} symmetry [similar to the anion 5(e)]. The latter is new and lies only 0.08 eV above the C_s ring. An additional 0.64 eV higher in energy is a planar C_{2v} structure with two Si atoms attached to the same end of a C_4 chain submolecule [anionic structure 5(f)]. Other structures considered previously⁵⁶ were found to be 1.08, 2.69 and 1.93 eV above the linear isomer (using the ordering of Ref. 56).

The chain [5(c)] is again stabilized in the anion, lying 0.48 eV below 5(d), 0.62 eV below the ring 5(e), and 0.71 eV below 5(f). Other isomers are even higher in energy. The measured VDE (2.49 ± 0.08 eV, Ref. 20) agrees well with the value for the linear chain (2.59 eV). The assignment of structure at higher energies is not definite, but it is consistent with the calculated excitation energy to the $^1\Sigma_u^+$ state, 2.85 eV.

There are few signs of other electronic excitations in the remainder of the spectrum, in accordance with the gap to the next calculated transition (4.91 eV, $^3\Pi_u$ state) for this isomer, and no other isomer matches the pattern of the peak positions. Our calculated values are 2.75 and 3.50 eV for 5(d), 2.61, 3.68, and 3.86 eV for 5(e), and 3.15, 3.38, and 3.39 eV for 5(f). The VDE of 5(f) (3.15 eV) is higher than the value for 5(c) because the added electron tends to be localized at the ends of the chain. This is energetically more favorable if the terminal atoms are carbon (see Sec. IV).

3. $Si_3C_3^-$

Mühlhäuser and co-workers^{57,58} investigated up to 17 different isomers of this cluster by reoptimizing the most stable HF geometries at the MP2(TZP) and MP2(TZ2P) levels. We have studied eight of their most stable structures as well as other geometries, and also find a distorted C_s pentagonal pyramid with a C_3 submolecule with apical angle 44° to be the most stable. The energy ordering, however, differed somewhat. We found several low-energy isomers not considered previously, including a distorted C_s hexagonal ring with a weakly (135°) bent C_3 submolecule (not included in the figures) 0.51 eV above the minimum structure, and a planar C_{2v} isomer with a linear C_3 submolecule [anion structure 6(a)] 0.85 eV above the minimum.

Charging appears to favor structures containing an almost linear C_3 submolecule. Examples are the planar C_{2v} isomer [6(a)], which is the most stable in the anion, and the C_s structure 6(b) only 0.31 eV higher (the latter form is 1.43 eV above the minimum in Si_3C_3). Strongly bent C_3 submol-

ecules are not favored in the anion, and the C_s ground state of Si_3C_3 distorts to C_1 symmetry on charging. The final structure [6(c)] is 0.08 eV higher in energy, with a distorted C_s prism 6(d) an additional 0.33 eV less stable. The last structure was derived from the fourth most stable in the neutral cluster (0.71 eV above the minimum), and several other isomers were even higher in energy.

The experimental VDE for this molecule is 2.16 ± 0.08 eV,²⁰ with additional structure between 2.3–2.4 eV and near 2.8 eV. Our value for the most stable isomer is 2.51 eV, and the higher excitation energies are 2.93 eV (3A_1), 3.07 (1A_1) and 3.73 (3A_1), although the last two values belong to states that are not the most stable of a given symmetry. The remaining isomers are less compatible with the features in the spectrum.

4. Si_4C_2^-

Of the four different structures of Si_4C_2 investigated by Froudakis *et al.*,⁵⁶ only one — a C_{2v} isomer similar to the anion structure 6(f) — has been found to be a stable minimum. An octahedron [7(a) for the corresponding anion] is a stationary point only 0.06 eV higher in energy. There were several less stable structures, including a C_1 form [anion structure 6(e)] 0.6 eV above the minimum.

The energy ordering of the anions again differs from that of the neutral species. The most stable [6(e)] is 0.20 eV lower than 6(f) and 0.46 eV more stable than 7(a). The VDE determined from the PE spectrum [2.100 ± 0.08 eV, Ref. 20] agrees well with our result for 6(e) [2.18 eV]. The second peak measured at ≥ 3.30 eV is consistent with the first excitation energy [3.48 eV (3A state)] calculated for this isomer. We shall now show that the significantly lower VDE found in the other low-energy isomers [6(f), 7(a)] can be related to structural differences.

The C atoms of 6(e) are “embedded” into the Si substructure, and the high coordination inhibits the formation of double bonds. The bond is strained considerably in the neutral cluster, resulting in an interatomic distance of 3.12 a.u. Isomer 6(f) of the anion resembles a planar Si_4 cluster loosely bound to a C_2 dimer with a double bond of length 2.49 a.u. This short bond lowers the potential between the atoms and the charge on the C atoms is larger than in 6(e). An attached electron will be repelled into the Si substructure, resulting in a higher amplitude of the excess electron in regions of high potential energy (i.e., beyond atoms 4 and 6) than in 6(e). In 6(e) however, the charge localized at the C atoms is weaker than in 6(f), so that an attached electron can move to the region between them. The stronger C-C bond that results has a typical single bond distance of 2.97 a.u., and the VDE is increased. The neutral D_{2h} octahedron underlying the anion structure 7(a) has maximum coordination and no strained bonds. An attached electron occupies antibonding orbitals near the Si atoms, and the bonds between atoms (3,4) and (5,6) open in the anion (to ~ 4.95 a.u.).

5. Si_5C^-

Nakajima *et al.*²⁰ measured the PE spectrum of Si_5C^- (VDE: 1.74 ± 0.08 eV) and also predicted that the most stable isomer is a C_{2v} structure (2A_1) similar to 7(d). However, we found two isomers with energies ~ 0.28 eV lower — a distorted octahedron [7(c)] and a slightly more stable ($\Delta E = 0.01$ eV) C_s variant [7(b)]. Isomer 7(b) can be viewed as a SiC molecule [atoms 1 and 2 in 7(b)] attached to a Si_4 cluster. The bond lengths in the latter (4.43–4.45 a.u.) indicate a bond order of between one and two and are consistent with this view. Isomer 7(d) is less tightly bound, with double bonds only between atoms (3,4) and (4,5).

The calculated VDE of these isomers are 1.81 eV, 1.54 eV, 2.07 eV, and only the first [7(b)] fits the experimental value. The increase in the measured intensity at higher energies indicates the possible presence of a second peak around ≥ 3.4 eV, consistent with the first excitation energy of our minimum structure [3.38 eV, ($^3A'$) state]. The PE spectrum shows no evidence for the presence of the remaining isomers, although our calculations indicate that the two most stable isomers are almost degenerate. The experimental resolution does not allow the detection of smaller peaks at the corresponding energies (according to our calculations, isomer 7(c) should lead to peaks around 1.54, 3.39 and 3.61 eV).

The higher VDE for 7(d) is a consequence of the different bond strengths of the clusters. The C_s structure has two additional single bonds between atoms (2,6) and (3,5) and twice as many double bonds as the C_{2v} isomer. The stabilization of the structure means that an additional electron moves to the Si substructure, where it has fewer unoccupied bonding orbitals at its disposal.

F. Seven-atom clusters

1. Si_2C_5^-

The PE spectrum²⁰ shows a single peak, with VDE 2.16 ± 0.06 eV. Our calculations indicate the existence of two low-energy isomers of the anion, a $D_{\infty h}$ chain [7(e)] and a C_s pentagonal ring [7(f)] that is 0.72 eV less stable. Similar energy differences and ordering were found for the neutral species. Only the most stable isomer can account for the spectral features, with VDE at 2.18 eV and an excitation energy of 3.73 eV for a transition into the $^3\Sigma_u$ state of the neutral chain. The excitation energies in the ring are well above 3.0 eV, and the high VDE of this isomer is consistent with the observed even-odd alternation of VDE in linear and ringlike C_n clusters.

2. Si_6C^-

The PE spectrum²⁰ shows a distinct peak with VDE 1.74 ± 0.08 eV, and a broader feature with unresolved vibrational fine structure has a maximum around 2.7–3.1 eV. We found a C_{2v} structure [8(a)] to be the most stable both for the anion and the neutral cluster. It can be derived from the minimum structure of Si_5C^- [7(b)] either by capping the face between atoms (3,5,6) with an additional Si atom, or by replacing by a C atom a Si atom of the optimal structure of Si_7 (a pen-

agonal D_{5h} bipyramid).⁸ The distance between the Si atoms (2,7) and (4,6) [5.11 a.u.] is much larger than in Si_n clusters (4.3-4.8 eV),⁵⁹ and our simulations at $T=300$ K lead to low-energy bending vibrations. A C_s structure [8(b)] lies 0.30 eV higher in energy, followed at 0.36 eV by another C_s isomer [8(c)] that can also be derived from the optimal structure of Si_5C^- by capping a face containing a C atom.

Other structures were higher in energy and/or not stable minima on the energy surface, and only the C_s isomer [8(b)] is compatible with the spectral features. The calculated VDE is 1.79 eV, and there are other excitations at 3.17 eV ($^3A''$) and 3.36 eV ($^1A''$). This assignment is not definite, since the energy separation from the most stable isomer and the broad vibrational progression observed around the second feature indicate significantly different geometries in anion and the neutral cluster. This has not yet been observed for this isomer.

Motivated by the similarity between this spectrum and the photoelectron spectrum of pure Si_7 ,²⁰ we replaced Si atoms with C atoms in the lowest-energy isomers of Si_7 . The structure obtained by replacing an axial atom in the D_{5h} pentagonal bipyramid ground state of Si_7 has an energy only 0.07 eV above that of 8(a), but it is unstable during MD runs at ~ 300 K. Replacing Si atoms in several positions in the second most stable Si_7 structure (a C_{3v} tricapped tetrahedron 0.79 eV above the D_{5h} ground state)⁸ leads upon annealing to less stable local minimum geometries or to known structures. Present indications are that structure 8(a) is the most stable isomer, but this assignment must be viewed with caution.

One uncertainty in the present analysis is that the mass of Si_6C^- cannot be distinguished from that of Si_3C_8^- . The clusters are generated by laser vaporization of a SiC rod,²⁰ and the Si:C ratio in the vapor cannot be controlled. Production of Si_3C_8^- in significant amounts would lead to a superposition of the corresponding spectra. The observation of a broad vibrational progression with large vibrational quanta is indeed more consistent with a C_8 submolecule with strong C-C bonds than with a structure containing relatively weak Si-Si or Si-C bonds. However, the same argument also applies to other Si_nC_m^- pairs in clusters discussed above: Si_4C^- and SiC_8^- , Si_4C_2^- and SiC_9^- , Si_5C^- and Si_2C_8^- , and Si_7C^- has the same mass as both Si_4C_8^- and SiC_{15}^- . A possible explanation of the apparent absence of other isomers in the PE spectra of Si_4C^- , Si_4C_2^- and Si_5C^- is that intensities of the clusters in the beam generally decrease with increasing number of atoms. Furthermore, the carbon-rich SiC_8^- , SiC_9^- and Si_2C_8^- should have properties more similar to those of pure carbon clusters. We note that the experimental⁶ VDE of C_8^- and C_9^- (4.42 and 3.70 eV, respectively) are beyond the range of the measurement.

The marked difference between the VDE of isomers 8(a) and 8(c) stems from the fact that the extra electron in 8(a) strengthens the bond between atoms (6,7). If cluster 8(a) is derived from the underlying pentagonal bipyramid of Si_7 by replacing a Si atom by C, considerable strain is introduced into the Si substructure *opposite* to the C site, causing the bond between atoms (6,7) to open (the bond length in the

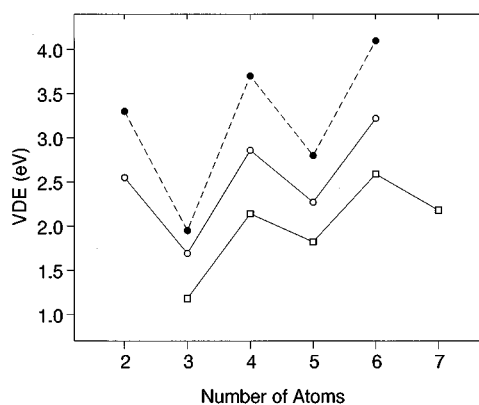


FIG. 9. VDE of linear Si_nC_m^- -clusters, \bullet : $n=0$ (Ref. 6), \circ : $n=1$, \bullet : $n=2$.

neutral isomer is 4.71 a.u.). An attached electron will move away from the negative charge around the C site, resulting in a double bond between atoms (6,7) in the anion (bond length 4.44 a.u.) and stabilization of the state occupied by the excess electron. On the other hand, the replacement of a Si atom by C in the Si_7 cluster [yielding 8(c)] introduces strain *near* the C atom. An attached electron cannot bind strongly to this site, since it will be repelled by the charge on the C site towards the other end of the Si substructure. In this case, the atoms in the Si_7 cluster are highly coordinated, and the excess charge is in regions of high potential energy.

G. Si_7C^-

The PE spectra of Si_7C^- and Si_8^- are very similar,²⁰ suggesting that the structures may be related by the simple replacement of one Si atom by C. Two low-energy structures for Si_8 have been reported,⁸ and we find a bicapped C_{2h} octahedron to be 0.41 eV more stable than a tetracapped C_{2v} tetrahedron. The stability of six different anionic structures by replacing a Si atom by C have been studied by simulated annealing. Five structures unrelated to those of Si_8 were also studied. The most stable isomer [8(d), C_s] can be derived from the most stable structure of Si_8 or by capping either of the low-energy isomers 8(b) and 8(c) of Si_6C^- . The C_s isomer is only 0.10 eV more stable than a C_{3v} structure 8(e) and 0.44 eV more stable than the C_s isomer 8(f).

The first and the last structure cannot account for the features contained in the spectrum, since their VDE (2.05 eV and 2.45 eV, respectively) are much lower than the experimental value 2.92 ± 0.08 eV.²⁰ This favors the C_{3v} isomer, whose VDE is 3.32 eV. The lowest excitation energies of this structure (at 3.47 and 3.55 eV, although the latter corresponds to a 1A_1 state that is not the lowest) are beyond the range of the measurement. We note that the spectrum might be affected by the presence of isomers of Si_4C_8^- and SiC_{15}^- , whose masses are the same as that of Si_7C^- .

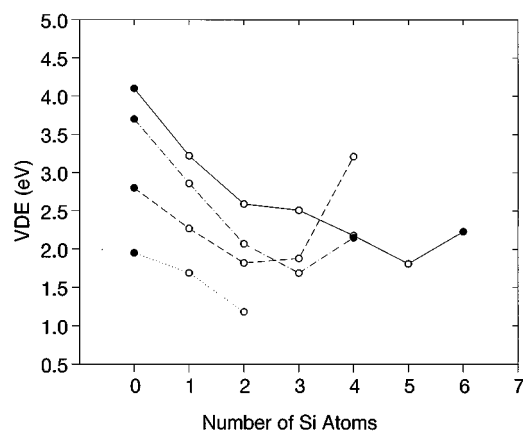


FIG. 10. VDE of Si_nC_m^- -clusters, $n+m=6$ (full line), 5 (dashed), 4 (dash-dotted), 3 (dotted). Experimental values (●) from Refs 6 (C_n^-) and 20 (Si_n^-).

IV. TRENDS AND DISCUSSION

The large number of possible structures in mixed Si_nC_m^- -clusters makes a discussion of the VDE even more complicated than in the homonuclear S_n^- (Ref. 23) and P_n^- clusters.²⁴ Nevertheless, it is possible to discern several trends. In highly symmetric clusters ($C_{\infty v}$, $D_{\infty h}$, ...) such as linear C_n chains, where the even-numbered chains – apart from C_2 – have $^3\Sigma_g^-$ ground states with two unpaired π electrons, it is not possible to occupy all bonding orbitals. An electron attached to an even-numbered chain will therefore enter a HOMO and be more strongly bound (and have a higher VDE) than in odd-numbered chains, where it enters the LUMO. In Fig. 9 we show the experimental VDE of C_n^- clusters (uppermost curve)⁶ and the VDE of linear chain isomers of Si_nC_m^- with one and two C atoms replaced by Si atoms. The even-odd alternation prevails even in the presence of Si, although weaker in amplitude. Since the partially empty π levels are bonding, electron attachment to even-numbered chains generally shortens and strengthens the bonds.

The absence of p -electrons in the core of C means that the s - and p -valence orbitals are compact and of the comparable extent. It follows⁶⁰ that the C-C bond is stronger than other bonds between group 14 atoms and shows a greater ease of σ - π transfer. In the absence of spin, the occupation of π -orbitals is favored in C-C bonds, while σ -occupancy is favored in bonds between Si atoms.⁵⁸ The replacement of C by Si in a cluster gives rise to both considerable strain and polar C-Si bonds. Our calculations show that the electrons bind more strongly to C sites, and that the resulting negative charge (as measured, for example, by the Mulliken charges) tends to repel added electrons into silicon subunits. If all bonds in the latter are saturated, the excess electron becomes localized in regions of high potential energy, favoring a low VDE. On the other hand, it may stabilize Si-Si bonds that had been strained by the presence of C atoms, increasing the VDE. The interplay of these two effects can account for the irregular behavior of VDE of Si-

rich clusters, including the unusually high VDE of Si_4C^- (Fig. 10) and the tendency of the experimental VDE (Ref. 20) of Si_n^- clusters to be larger than those of the Si_nC^- clusters with the same number of atoms (see Fig. 10). If we identify the VDE with the binding energies of the attached electrons, we see that the binding is strongest in C_n chains, and becomes progressively weaker as C atoms are replaced by Si.

The plot of calculated and measured VDE^{6,20} for some of the most stable isomers with $n+m=3,4,5,6$ (Fig. 10) provides further information. The isomers in the first three columns are mostly linear, and the even-odd alternation accounts for the shift in the onset of $n+m=5$ curve to smaller values than in the $n+m=4$ curve. Apart from such shell-closure effects, which are most important in the carbon-rich linear chains and monocyclic rings, the results confirm the expectation from simple electrostatics that the VDE increases with increasing cluster size.

We conclude this section with comparisons of the MD/DF results with those of all-electron calculations²⁷ on these clusters, all with the LSD approximation for the exchange-correlation energy. There are three main aspects: First, the structures of the most stable isomers obtained from minimization of the total energy by either method are in very good agreement, the differences being of the same order of magnitude as found in extending the basis set (see Sec. II). Second, less strongly bound states are often characterized by shallow minima in relatively flat energy surfaces, and the optimized structures are more sensitive to the method used. Furthermore, the all-electron calculations usually determine the closest stationary point in the energy surface, as well as imaginary frequencies if they exist. The ability of MD to overcome small energy barriers and lead to large geometry changes has been observed in several cases. Finally, we discuss the relative energies of the isomers and the VDE, using the six-atom clusters Si_2C_4 , Si_3C_3 , Si_4C_2 as representative examples.

In Si_4C_2^- , the energies of 6(f) and 7(a) relative to the most stable isomer 6(e) are 0.15 eV and 0.63 eV, respectively, compared with MD/DF values of 0.20 eV and 0.46 eV. The all-electron values of the VDE for 6(e) and 6(f) (2.39 eV, 1.24 eV, respectively) are a little higher than the MD/DF values (2.18 eV, 1.02 eV). The VDE reflects a transition from a local minimum in the energy surface of the anion to a part of the energy surface of the neutral cluster that may be varying rapidly. It is particularly sensitive to differences in the calculations, and we view this agreement as satisfactory. While the structures of the most stable isomers of Si_3C_3^- and Si_2C_4^- using the two methods are in very good agreement, the structures and relative energies of the other isomers show differences. The higher-lying isomers in Si_3C_3^- are more than 1 eV less stable than the ground state in the all-electron calculations, while the MD/DF energy differences are ~ 0.5 – 0.7 eV. However, the VDE of the most stable isomer (all-electron: 2.54 eV, MD/DF 2.51 eV) agree well, as do the corresponding values in Si_2C_4^- (2.63 eV, 2.59 eV). In the latter, however, structure 5(e) is not a stationary point in the energy surface in the all-electron calculations,

and the relative energy of 5(d) is higher than in the MD/DF calculations.

In order to study this discrepancy further, we have performed additional MD/DF calculations for Si_2C_4^- using a larger unit cell (lattice constant 30 a.u.) and a larger plane wave basis expansion (cutoff energy 20 a.u.). These improvements in the calculation brought only modest changes in the structures and energy differences: The three higher-lying states now lie 0.7–0.9 eV above isomer 6(e), instead of 0.5–0.7 eV. Changes of this order reflect our experience with other cluster systems.

V. CONCLUDING REMARKS

We have described an extensive series of density functional calculations (using a LSD approximation for the exchange-correlation energy) on mixed clusters of C and Si with up to eight atoms. We have considered neutral clusters and, in order to analyze photoelectron spectra of anion beams, their singly charged anions. Agreement with previous work is generally very good. The number of topologically distinct isomers is very large in these systems, however, and the use of molecular dynamics has enabled us to identify previously unknown structures. “All-electron” DF calculations lead to a consistent picture for the structures and vertical detachment energies for the most stable isomers, although the structures and relative energies of some higher-lying isomers show differences from the MD/DF results.

The results have enabled us to identify two types of Si_nC_m^- clusters with distinct trends in the vertical detachment energies:

- (a) Carbon-rich clusters with linear or near-linear C_n sub-molecules. The VDE show an even-odd alternation due to shell-closure effects. Since there are few Si atoms in the cluster, the effective charges at the C sites are small and insignificant for the VDE.
- (b) Silicon-rich clusters, where the behavior of the VDE is dominated by the charge localized around the C atoms in the neutral clusters. The added electron in the anion is repelled to the Si sites, where it is comparatively weakly bound unless it can stabilize the Si_n substructure.

A reliable description of the geometry, the electron density and spin densities of the anion clusters is crucial for a qualitative understanding and a quantitative description of PE spectra. DF theory satisfies these requirements, and a comparison of theory and experiment has allowed us to identify anionic geometries and assign excited states. Essential to this assignment is the observation that structures with similar energies can have very different VDE, those with similar VDE quite different energies. The spectra can be ascribed unambiguously to isomers that are the most stable within the LSD approximation, with the exceptions of Si_6C^- and Si_7C^- , where the measured VDE agree better with the values calculated for isomers that are less than ~ 0.4 eV higher in energy. Recent studies of the effects of gradient corrections to the exchange-correlation potential report large changes in

the energy ordering of C_n isomers.^{61,62} We are studying these effects in selected C_n , Si_n , and Si_nC_m clusters.

ACKNOWLEDGMENTS

We thank numerous colleagues of our institute for discussions, particularly P. Ballone for much help and advice, and G. Ganteför and G. Schulze Icking-Konert for providing data prior to publication. The German Supercomputer Center (HLRZ) provided a grant of CPU time on the Cray YMP8/8128 in the Forschungszentrum Jülich.

- ¹ See, for example, K. Raghavachari and J.S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987), and references cited therein; J.M.L. Martin, J.P. François, and R. Gijbels, *ibid.* **93**, 8850 (1990).
- ² L.N. Shen and W.R.M. Graham, *J. Chem. Phys.* **91**, 5115 (1989); P.A. Withey, L.N. Shen, and W.R.M. Graham, *ibid.* **95**, 820 (1991); Z. Vager, H. Feldman, D. Kella, E. Malkin, E. Miklazky, J. Zajfman, and R. Naaman, *Z. Phys. D* **19**, 413 (1991).
- ³ D.W. Arnold, S.E. Bradforth, T.N. Kitsopoulos, and D.M. Neumark, *J. Chem. Phys.* **95**, 8753 (1991).
- ⁴ H. Handschuh, G. Ganteför, B. Kessler, P.S. Bechthold, and W. Eberhardt, *Phys. Rev. Lett.* **74**, 1095 (1995).
- ⁵ T. Guo, M.D. Diener, Y. Chai, M.J. Alford, R.E. Haufler, S.M. McClure, T. Ohno, J.H. Weaver, G.E. Scuseria, and R.E. Smalley, *Science* **257**, 1661 (1992).
- ⁶ S. Yang, K.J. Taylor, M.J. Craycraft, J. Conceicao, C.L. Pettiette, O. Cheshnovsky, and R.E. Smalley, *Chem. Phys. Lett.* **144**, 431 (1988).
- ⁷ J.D. Watts and R.J. Bartlett, *J. Chem. Phys.* **97**, 3445 (1992); C. Liang and H.F. Schaefer III, *ibid.* **93**, 8844 (1990); V. Parasuk and J. Almlöf, *Theor. Chim. Acta* **83**, 227 (1992).
- ⁸ K. Raghavachari and C.McM. Rohlfling, *J. Chem. Phys.* **89**, 2219 (1988); C.McM. Rohlfling and K. Raghavachari, *Chem. Phys. Lett.* **167**, 559 (1990); W. Andreoni and G. Pastore, *Phys. Rev. B* **41**, 10 243 (1990); S. Li, R.J. Van Zee, W. Weltner, Jr., and K. Raghavachari, *Chem. Phys. Lett.* **243**, 275 (1995).
- ⁹ L.R. Anderson, S. Maruyama, and R.E. Smalley, *Chem. Phys. Lett.* **176**, 348 (1991).
- ¹⁰ U. Röthlisberger, W. Andreoni, and M. Parrinello, *Phys. Rev. Lett.* **72**, 665 (1994).
- ¹¹ O. Cheshnovsky, S. Yang, C. Pettiette, M. Craycraft, Y. Liu, and R. Smalley, *Chem. Phys. Lett.* **138**, 119 (1987).
- ¹² E.C. Honea, A. Ogura, C.A. Murray, K. Raghavachari, W.O. Sprenger, M.F. Jarrold, and W.L. Brown, *Nature* **366**, 42 (1993).
- ¹³ K. Raghavachari and C.McM. Rohlfling, *J. Chem. Phys.* **94**, 3670 (1991).
- ¹⁴ C.McM. Rohlfling and K. Raghavachari, *Chem. Phys. Lett.* **185**, 244 (1991); J.C. Grossman and L. Mitáš, *Phys. Rev. Lett.* **74**, 1323 (1995).
- ¹⁵ C.McM. Rohlfling and K. Raghavachari, *J. Chem. Phys.* **96**, 2114 (1992).
- ¹⁶ J.D. Presilla-Márquez and W.R.M. Graham, *J. Chem. Phys.* **96**, 6509 (1992).
- ¹⁷ J.D. Presilla-Márquez and W.R.M. Graham, *J. Chem. Phys.* **100**, 181 (1994).
- ¹⁸ S.C. Ross, T.J. Butenhoff, E.A. Rohlfling, and C.McM. Rohlfling, *J. Chem. Phys.* **100**, 4110 (1994).
- ¹⁹ A. Van Orden, T.F. Giesen, R.A. Provencal, H.J. Hwang, and R.J. Saykally, *J. Chem. Phys.* **101**, 10 237 (1994).
- ²⁰ A. Nakajima, T. Taguwa, K. Nakao, M. Gomei, R. Kishi, S. Iwata, and K. Koya, *J. Chem. Phys.* **103**, 2050 (1995). The calculations described were MP2/6-31G*.
- ²¹ See, for example, J. Yeomans, *Solid State Phys.* **41**, 151 (1988), and references cited therein.
- ²² F. Finocchi, G. Galli, M. Parrinello, and C.M. Bertoni, *Physica B* **185**, 379 (1993).
- ²³ S. Hunsicker, R. O. Jones, and G. Ganteför, *J. Chem. Phys.* **102**, 5917 (1995).
- ²⁴ R. O. Jones, G. Ganteför, S. Hunsicker, and P. Pieperhoff, *J. Chem. Phys.* **103**, 9549 (1995).
- ²⁵ G. Ganteför and G. Schulze Icking-Konert (unpublished).
- ²⁶ N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ²⁷ DGAUSS program from the UniChem package of Cray Research, Inc. The

- calculations used a triple zeta Gaussian orbital basis with polarization functions (TZ94+p) and the TZ94 auxiliary basis.
- ²⁸G. Galli, R.M. Martin, R. Car, and M. Parrinello, *Phys. Rev. B* **42**, 7470 (1990).
- ²⁹I. Stich, R. Car, and M. Parrinello, *Phys. Rev. B* **44**, 4262 (1991).
- ³⁰K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ³¹P.F. Bernath, S.A. Rogers, L.C. O'Brien, C.R. Brazier, and A.D. McLean, *Phys. Rev. Lett.* **60**, 197 (1988), MR-CI calculations.
- ³²J. Cernicharo, C.A. Gottlieb, M. Guélin, P. Thaddeus, and J.M. Vrtilik, *Astrophys. J.* **341**, L25 (1989).
- ³³T.J. Butenhoff and E.A. Rohlfing, *J. Chem. Phys.* **97**, 1595 (1992), MR-SOCI calculations.
- ³⁴M.R. Nimlos, L.B. Harding, and G.B. Ellison, *J. Chem. Phys.* **87**, 5116 (1987).
- ³⁵R.A. Shepherd and W.R.M. Graham, *J. Chem. Phys.* **82**, 4788 (1985).
- ³⁶R.S. Grev and H.F. Schaefer III, *J. Chem. Phys.* **80**, 3552 (1984), TCSCF calculations.
- ³⁷P.W. Deutsch and L.A. Curtiss, *Chem. Phys. Lett.* **226**, 387 (1994), QCISD(T) calculations with 6-311+G(3df,2p) basis.
- ³⁸D.L. Michalopoulos, M.E. Geusic, P.R.R. Langridge-Smith, and R.E. Smalley, *J. Chem. Phys.* **80**, 3556 (1984).
- ³⁹C.M.L. Rittby, *J. Chem. Phys.* **95**, 5609 (1991), MBPT2/6-311G(2d) calculations.
- ⁴⁰R.S. Grev and H.F. Schaefer III, *J. Chem. Phys.* **82**, 4126 (1985), CISD calculations.
- ⁴¹E.E. Bolton, B.J. DeLeeuw, J.E. Fowler, R.S. Grev, and H.F. Schaefer, III, *J. Chem. Phys.* **97**, 5586 (1992), TZ+2P+f calculations.
- ⁴²Our calculations favor a ${}^3A'_2 D_{3h}$ isomer by 0.08 eV over a ${}^1A_1 (C_{2v})$ isomer, while Hartree-Fock based calculations (CCD+ST(4)) favor the C_{2v} isomer by 0.02 eV. See K. Raghavachari, *J. Chem. Phys.* **83**, 3520 (1985).
- ⁴³W. Andreoni, D. Scharf, and P. Giannozzi, *Chem. Phys. Lett.* **173**, 449 (1990).
- ⁴⁴I.L. Alberts, R.S. Grev, and H.F. Schaefer, III, *J. Chem. Phys.* **93**, 5046 (1990).
- ⁴⁵G.W. Trucks and R.J. Bartlett, *J. Mol. Struct. (Theochem.)* **135**, 423 (1986).
- ⁴⁶K. Lammertsma and O.F. Güner, *J. Am. Chem. Soc.* **110**, 5239 (1988), MBPT(4)/6-31G* calculations.
- ⁴⁷P.V. Sudhakar, O.F. Güner, and K. Lammertsma, *J. Phys. Chem.* **93**, 7289 (1989).
- ⁴⁸G.B. Fitzgerald and R.J. Bartlett, *Int. J. Quantum Chem.* **38**, 121 (1990).
- ⁴⁹J.D. Presilla-Márquez, S. Gay, C.M.L. Rittby, and W.R.M. Graham, *J. Chem. Phys.* **102**, 6354 (1995).
- ⁵⁰C.M.L. Rittby, *J. Chem. Phys.* **96**, 6768 (1992).
- ⁵¹N. Moazzen-Ahmadi and F. Zerbetto, *Chem. Phys. Lett.* **164**, 517 (1989), MBPT(2)/6-311G(d) calculations.
- ⁵²P.A. Withey and W.R.M. Graham, *J. Chem. Phys.* **96**, 4068 (1992).
- ⁵³C.M.L. Rittby, *J. Chem. Phys.* **100**, 175 (1994), MBPT(2) calculations.
- ⁵⁴G. Froudakis, M. Mühlhäuser, and A. Zdetsis, *Chem. Phys. Lett.* **233**, 619 (1995).
- ⁵⁵J.D. Presilla-Márquez, C.M.L. Rittby, and W.R.M. Graham, *J. Chem. Phys.* **104**, 2818 (1996).
- ⁵⁶G. Froudakis, A. Zdetsis, M. Mühlhäuser, B. Engels, N. Flytzanis, and S.D. Peyerimhoff, *J. Chem. Phys.* **101**, 6790 (1994), HF, MP2 and CASTP2 calculations.
- ⁵⁷M. Mühlhäuser, G. Froudakis, A. Zdetsis, and S.D. Peyerimhoff, *Chem. Phys. Lett.* **204**, 617 (1993).
- ⁵⁸M. Mühlhäuser, G. Froudakis, A. Zdetsis, B. Engels, N. Flytzanis, and S.D. Peyerimhoff, *Z. Phys. D* **32**, 113 (1994).
- ⁵⁹B.T. Luke, J.A. Pople, M. Krogh-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar, and P. von R. Schleyer, *J. Am. Chem. Soc.* **214**, 357 (1993).
- ⁶⁰For a discussion in the context of DF theory, see J. Harris and R.O. Jones, *Phys. Rev. A* **19**, 1813 (1979).
- ⁶¹K. Raghavachari, D.L. Strout, G.K. Odom, G.E. Scuseria, J.A. Pople, B.G. Johnson, and P.M.W. Gill, *Chem. Phys. Lett.* **214**, 357 (1993).
- ⁶²K. Raghavachari, B. Zhang, J.A. Pople, B.G. Johnson, and P.M.W. Gill, *Chem. Phys. Lett.* **220**, 385 (1994).