Vertical and Adiabatic Ionization Energies and Electron Affinities of New Si$_n$C and Si$_n$O ($n = 1$–$3$) Molecules

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Vertical and adiabatic ionization potentials (IPs) as well as electron affinities have been calculated for SiC, Si$_2$C, Si$_3$C, SiO, Si$_2$O, and Si$_3$O using five different sophisticated ab initio methods with large basis sets. The geometry and harmonic frequencies have been calculated at the second-order Møller–Plesset level. Results of the calculations using all five methods are in a good agreement among themselves ($\pm 0.5$ eV). The calculated vertical first IPs of SiC, Si$_2$C, Si$_3$C, and SiO molecules agree within 0.2 eV with experimental appearance potentials for these species.

Introduction

Recently, silicon–carbon (Si$_n$C) and silicon–oxygen (Si$_n$O) ($n = 2,3$) molecular clusters have been studied theoretically. Geometrical structures and vibrational frequencies for the ground electronic states have been obtained for Si$_2$C and Si$_3$C that agree well with the available experimental data. In this study, we present ab initio calculations at several levels of theory for vertical and adiabatic ionization potentials and vertical and adiabatic electron affinities for Si$_2$C and Si$_3$O ($n = 1$–$3$). These data may be valuable for future mass spectrometric and spectroscopic studies because several of these molecules have not been experimentally observed. Hence, theoretically predicted appearance potentials may be helpful for guiding experimental detection. To achieve as reliable results as possible, we have used several methods (Møller–Plesset perturbation theory and by the (U)QCISD(T) method) and different types of atomic basis sets in performing the calculations whose results are reported here.

Computational Details

The bond lengths of the neutral, cationic, and anionic SiC, Si$_2$C, Si$_3$C, SiO, Si$_2$O, and Si$_3$O species were optimized by employing analytical gradients using the Gaussian 92 program with polarized split-valence basis sets (6-311+G$^*$) at MP2(full) levels (UMP2(full)) open shell systems). Our optimal geometric parameters are presented in Figure 1, and our simulated IR spectra based on the MP2(full)/6-311+G$^*$ calculated frequencies are drawn in Figure 2. The MP2(full)/6-311+G$^*$ equilibrium geometries were used to evaluate electron correlation corrections in the frozen-core approximation by full fourth-order Møller–Plesset perturbation theory and by the (U)QCISD(T) method using 6-311+G(2df) basis sets. The UHF wave functions for open shell systems were projected to pure spectroscopic states for which the corresponding results are denoted PUSCF, PMP2, PMP3, and PMP4.

The vertical ionization energies and electron affinities were also calculated by two approximations to the many-body one-particle Green function (OVGF) and the third-order algebraic diagrammatic construction (ADC(3)). In the OVGF method, all the diagrams up to and including the third-order terms which appear in the expansion of the self-energy are included, and a renormalization procedure is used for the higher order corrections. The renormalization procedure includes three cases described in detail in ref 15 and represents a geometric-type approximation to the self-energy. Usually the approximation denoted case b in ref 15 was chosen. Whenever the OVGF approximation was applicable, all three procedures yielded very similar results.

The ADC(3) method takes all one-hole, one-particle, two-hole + one-particle, and two-particle + one-hole configurations and their interactions into account. Contributions from so-called constant or energy-independent diagrams were evaluated by the iterative procedure of ref 16. The value of the pole strengths (the residues of the Green function at each pole) are also calculated within the Green function method and measure the validity of the one-particle picture of ionization (or electron capture). The electron correlation effects make processes other than the simplest Koopmans’ theorem ionization events available, in which case the pole strengths are no longer equal to unity but remain close to unity when the one-particle picture of ionization (or attachment) remains valid. When complete breakdown of the one-particle description occurs, the pole strengths are much smaller than unity, and instead of one photoelectron line, there appear a number of additional lines known as shake-up (or shake-off) satellites. The SCI calculations preceding the OVGF and ADC(3) calculations employed the MOLCAS-2 suite of programs. For these calculations, we used the very large ANO basis set of Widmark et al. For the Si atom, this consists of (17s12p5d4f) elementary functions and [6s5p2d1f] contracted functions, and for the C and O atoms, (14s9p4d3f) elementary and [4s3p2d1f] contracted functions. The ANO basis set is especially suited for the calculation of properties where an extensive correlation treatment is necessary and an extended basis set including diffuse functions is required. It involves minimal contraction loss. The so-called general contraction scheme is used in these ANO basis sets where all elementary functions enter each contracted function. These basis sets are probably the best for the precise calculation of ionization potentials and electron affinities.

The vertical and adiabatic ionization energies and electron affinities were also calculated for the lowest cationic and anionic states using single-reference single- and double-excitation CI
Figure 1. Molecular structures and geometrical parameters (distances in angstroms and angles in degrees) at the MP2(full)/6-311+G* level for SiC, SiC+, SiC-, SiO, SiO+, SiO-, SiC+, SiC+, and SiO-.

(CISD). The CISD energies were corrected by the Davidson method20 (CISD(4)) to account for the quadruple and higher order excited configurations. These calculations were also performed using the MOLCAS-2 program, where only the core orbitals were kept frozen in all the Green function and CISD calculations. The final estimates for the vertical and adiabatic ionization potentials and electron affinities are made by averaging the data at the PMP4, QCISD, CISD, OVGF, and ADC(3) levels, and ± values are assigned to the range of energies predicted by the various methods.

Results and Discussion

SiC, SiC+, and SiC-. The neutral SiC molecule is known to have a triplet 3Π (1σ^22σ^21π^3σ^1) ground electronic state.21,22 Our calculated bond length \( R_0(\text{Si-C}) = 1.702 \text{ Å} \) and harmonic frequency \( \nu_3 = 896 \text{ cm}^{-1} \) agree reasonably with experimental data: \( R_0(\text{Si-C}) = 1.722 \text{ Å} \) and \( \nu_3 = 964.6 \text{ cm}^{-1} \). An experimental appearance potential has been determined for SiC: 9.2 ± 0.4 eV in ref 23 and 9.0 eV in ref 24. We were not able to find in the literature any data on the electronic state, bond lengths, or vibrational frequencies of the positive and negative ions of SiC.

From the ground electronic state we can expect two low-energy cationic states: \( ^2\Sigma^+ (1\sigma^22\sigma^11\pi^3\sigma^1) \) and \( ^2\Pi (1\sigma^22\sigma^11\pi^1) \) for SiC+. When an electron is removed from the highest σ- or π-MO. We examined these two states as well as the \( ^2\Sigma^+ (1\sigma^22\sigma^11\pi^1) \) state. A simple MO picture of the valence MOs suggests the following: I σ-MO is bonding (σ_C + σ_Si), 2σ-MO is antibonding (σ_C − σ_Si), 1π-MO is bonding (p_xC + p_ySi), and 3σ-MO is bonding (p_zC − p_zSi). From this simple picture we expect that the detachment of an electron either from the bonding 1π-MO (to give the \( ^2\Sigma^+ \) final state) or from the bonding 3σ-MO (yielding the \( ^2\Pi \) final state) should increase the Si-C bond length and decrease the vibrational frequency. In contrast, detachment of an electron from the antibonding 2σ-MO accompanied by promotion of an electron from 3σ-MO into the 1π-MO (to give the \( ^2\Sigma^+ \) final state) should sharply decrease the Si-C bond length and increase the vibrational frequency. This trend is found in our calculations (see below results for SiC and SiO), but not in all cases.

The energy order of the ionic states is not easy to predict from the simple MO picture. The \( ^2\Sigma^+ \) state is found to be the lowest cationic state. The \( ^2\Pi \) and \( ^2\Sigma^+ \) states are 2.5 and 5.3 eV higher at the PMP4/6-311+G(2df) level. The optimized bond lengths and frequencies are 1.804 Å and 890 cm\(^{-1}\) for \( ^2\Sigma^+ \), 1.675 Å and 952 cm\(^{-1}\) for \( ^2\Pi \), and 1.504 Å and 1443 cm\(^{-1}\) for \( ^2\Sigma^+ \). We estimate...
The two lowest anion electronic states therefore, our data may help in the identification of Sic- anions. Of Sic- with 1 u22u217r42n1 orbital occupancy is not electronically carbon-13 has been made by Presilla-MBrquez and Graham.29 Transform infrared study of the vibrational spectrum of Si2C and appeared to grow in with the same relative intensity, to the available MOs. Again, from the MO picture, one expects that Sic molecule, so this molecule has two bound negative ion states. The experimental electron affinity is not known for Sic; therefore, our data may help in the identification of Sic- anions. The two lowest anion electronic states 2II(1u22u217r42n1) and 2E*(1s22r1u1u3e) may be derived from the ground electronic state of neutral Sic when an electron is added to the lowest energy available MOs. Again, from the MO picture, one expects that bond lengths and vibration frequencies should decrease and increase, respectively, for both anionic states. The 2E* is found to be the lowest of Sic-; however, the 2II state lies only 0.4 eV (QCISD(T)/6-311+G(2df)) above the 2E* ground state. The optimized bond lengths and vibrational frequencies are 1.759 Å and 1127 cm-1 for 2E* and 1.710 Å and 951 cm-1 for 2II. Both of these states are lower than the neutral Sic molecule, so this molecule has two bound negative ion states. The first adiabatic electron affinity of Sic is 2.25 eV, which differs slightly from the vertical EA, 2.32 eV (EA = electron affinity). Although EA(Sic) is very high, it is lower than EA-(C2) = 3.269 0.006 eV25a and EA(C2) = 3.273 0.008 eV25b and close to EA(Si1) = 2.176 0.002 eV26a and EA(Si2) = 2.199 0.012 eV.26b The Sic-ion also has an excited bound 2II state which lies below the ground 2II state of Sic by 1.83 eV and thus may be found in the gas-phase experiments. The next 2II state of Sic- with 1u22u217r42n1 orbital occupancy is not electronically bound and corresponds to a reasonance lying above the energy of the neutral Sic by 1.8 eV.

Si2C, Si2C+, and Si2C-. The neutral Si2C molecule is one of the major molecular species (8%) observed in mass spectrometric studies of the vaporization of silicon carbide. In the first infrared work, Wettner and Meleod proposed the tentative assignment to Si2C of a vibration observed at 1187 and 1205 cm-1 in spectra of the products of silicon carbide evaporation trapped in Ar and Ne matrices, respectively. Later, Kafafi et al.20 obtained 13C data which led them to assign two absorptions at 1188.9 and 658.2 cm-1, which shifted to 1153.7 and 643.3 cm-1, respectively, and appeared to grow in with the same relative intensity, to the \( \nu_2(\text{Si}) \) antisymmetric Si–C stretching and \( \nu_1(\text{Si}) \) symmetric Si–Si stretching modes, respectively, of Si2C. Finally, a Fourier transform infrared study of the vibrational spectrum of Si2C produced by vaporizing a mixture of silicon and carbon-12 or carbon-13 has been made by Pressilla–Márquez and Graham.29

This confirmed a previously observed vibration at 1188.4 cm-1 as the \( \nu_2(\text{Si}) \) antisymmetric Si–C stretching mode, and resulted in the identification of a new vibration at 839.5 cm-1 as the \( \nu_1(\text{Si}) \) symmetric Si–Si stretching fundamental. No bonding mode has been observed. Ab initio calculations performed by Grev and Scharer,14 Bolton et al.,15 and Ritter16 predicted a singlet angular \( \text{C}_2 \) (A1) structure for Si2C. However, the predicted equilibrium angle Si–C–Si is very sensitive to the basis set1 because this molecule is very floppy with a barrier for linearity of only 1.9 eV or 2.1 kcal/mol. Experimental appearance potentials are known for Si2C, 9.2 ± 0.3 eV23 and 9.1 ± 0.2 eV24 but no electronic, geometric, or vibrational data are available for the cationic or anionic states of Si2C.

We optimized the geometry for the neutral Si2C and obtained \( R_a(\text{Si–C}) = 1.707 \) Å, valence angle Si–C–Si = 114.7° and harmonic frequencies \( \nu_1(\text{Si}) = 844 \) cm-1, \( \nu_2(\text{Si}) = 129 \) cm-1, and \( \nu_3(\text{Si}) = 1208 \) cm-1. Our bond length and valence angle reasonably agree with other CCSD(T)/TZ2P+ (1.708 Å and 116.9°)10 and MBPT2/6-311G(2d) (1.703 Å and 119.5°)14 ab initio data if we take into account the flexible structure of this species. Our harmonic symmetric and antisymmetric stretching frequencies \( \nu_1(\text{Si}) = 844 \) cm-1 and \( \nu_2(\text{Si}) = 1208 \) cm-1 also reasonably agree with experimental data, \( \nu_1(\text{Si}) = 839.5 \) cm-1 and \( \nu_2(\text{Si}) = 1189.8 \) cm-1.

From the 1a1b12b2a2b21b12b3a12a4a symmetric ground electronic SCF configuration, we found in OVGF and ADC(3) calculations that the lowest energy cationic states are 2A1 (1a1b12b2a2b2 1b2b3a12a4a), 2B1 (1a1b12b2a2b23a12a41b1), and 2B2 (1a1b12b2a2b2 1b23a12b1). The lowest anionic states are 2A2 (1a1b12b2a2b2 2b2b3a12a41a12), and 2A1 (1a1b12b21b2b3a12a4a). In Koopmans’ approximation, the energy order of the cationic states is given as 2A1 < 2B2 < 2B1. However, as shown in Table 1, at all correlated levels and even at the SCF level, the order of the cationic states is different: 2B1 < 2A1 < 2B2. Results of the calculations of the vertical IPs obtained at correlated levels agree within 0.25 eV for all give methods: \( \Delta \text{MP4}, \Delta \text{QCISD(T)}, \Delta \text{CISD(4)}, \text{OVGF}, \) and ADC(3). On the basis of these data, we estimate the vertical ionization potentials to be \( \text{IP}(\text{2B2}) = 9.1 \pm 0.2 \) eV, \( \text{IP}(\text{2A1}) = 9.3 \pm 0.2 \) eV, and \( \text{IP}(\text{2B1}) = 9.4 \pm 0.2 \) eV. The first vertical IP agrees well with the experimental appearance potential for Sic, 9.2 ± 0.3 eV23 and 9.1 ± 0.2 eV24.

All of these 2A1, 2B1, and 2B2 states are well represented by one-configuration wave functions in which the coefficients of the Hartree–Fock determinant in CISD calculations are larger than 0.9 and the pole strengths in the OVGF and ADC(3) calculations are ca. 0.9. However, the higher ionic states with energy larger than 12 eV are not well represented as the ionization from a single MO (see Table 1). For example, ionization from the 2a1- MO of Sic with orbital energy 12.33 eV is accompanied by strong many-body effects. Three peaks may occur in the photoelectron spectrum according to the (ADC(3) calculations (see Table 1) while the configuration of the 2a1 final state remains strong (11.19 eV) and has a relative intensity of 0.67. The remainder of the intensity is shared by satellite lines, among which there is one line at 13.36 eV with a relative intensity of 0.15 (see Table 1).

Geometry optimization of the 2A1, 2B1, and 2B2 states collapse into the degenerate 2II (1u122u121a222u42u1), state, and the 2B2 state collapses into the 2E* (1u122u122a222u42u1), state. For both of these linear states, the optimal geometries are presented in Figure 1, and the corresponding adiabatic ionization potentials, IP(2II) and IP(2E*) are equal to 9.0 ± 0.2 and 9.2 ± 0.2 eV, respectively. Harmonic frequencies have been calculated only for the 2E* state. As a result, even though \( \nu_1(\text{Si}) = 584 \) cm-1 and \( \nu_2(\text{Si}) = 92 \) cm-1 appear reasonable, the antisymmetric stretching frequency \( \nu_1(\text{Si}) = 2405 \) cm-1 is too high, probably due to symmetry breaking.

The lowest unoccupied 1a2- and 4a1-MOs in Sic have positive energies at the optimal geometry of the neutral Sic molecule; therefore, at Koopmans’ approximation these states do not have positive vertical electron affinities. However, when correlation and electron relaxation are taken into account, both of these states become bound. The vertical EA, of Sic calculated for the 2A1 and 2A1 states are 0.6 ± 0.2 eV and 0.1 ± 0.2 eV, respectively. Geometry optimization of the 2A1 state leads to a linear structure and a 2II final electronic state, while the final geometric structure of the 2A1 state is bent. Moreover, in the Sic (2A1) structure the silicon–silicon distance is very short (2.46 Å) and only 0.13 Å larger than a normal single Si–Si bond length. We therefore infer that Sic-C (2A1) has significant Si–Si bonding. The calculated IR spectrum of Sic-C (2A1) is presented in Figure 2. The adiabatic electron affinities for producing the two anion states, EAa(2II) and EAa(2A1), are 0.9 ± 0.2 and 0.7 ± 0.2 eV, respectively.

Si2C, Si2C+, and Si2C-. This molecule has been detected in mass spectrometric experiments, and an appearance potential of 8.2 ± 0.3 eV has been reported.21 The experimental spectrum of Sic has been observed26 in a Fourier transform infrared study.
New Si₃C and Si₃O (n = 1-3) Molecules

Figure 2. Calculated infrared absorption spectra for Si₂C, Si₂C⁺, Si₂C⁻, Si₂O, Si₂O⁺, Si₂O⁻, Si₃C, Si₃C⁺, Si₃C⁻, Si₃O, Si₃O⁺, and Si₃O⁻.
TABLE 1: Calculated and Experimental Ionization Potentials and Electron Affinities of Si₂O and Si₂C Molecules

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* In parentheses are given the pole strengths (see text). * Data from ref 32. * Data from ref 33. * Data from ref 34. * Data from ref 35. * Optimization at MP2(full)/6-311+G* converted to DA(π⁺) structure. * Optimization at MP2(full)/6-311+G* converted to DA(π⁺) structure. * The Si₂C⁺(Cₘ⁺ B₁) structure is not a minimum; therefore, the adiabatic presented EA should be considered as an estimate (see text for details).

of the products of the vaporization of carbon/silicon mixtures trapped in Ar. An ab initio structure of the Si₂C has been determined by Rittby at the MBPT2/DZP level, where a rhomboid singlet structure of Cₘ⁺ symmetry with carbon–silicon transannular bonding between the two equivalent Si₃ (Si₈ and Si₉) correspond to nearest and remote silicon atoms, respectively. Atoms has been found. The ab initio vibrational spectrum of this structure by Rittby is in excellent agreement with the experimental data of Presilla-Márquez and Graham. No experimental or theoretical geometries or vibrational spectra are known for cationic or anionic states of Si₂C thus far.

We optimized the geometry and calculated harmonic fre-
New Si$_2$C and Si$_2$O ($n = 1$–$3$) Molecules


The ionization energy of the 3$\sigma$-MO is smaller than that of the 1$\pi$-MO at Koopmans' approximation and in the OVGF and ADC(3) methods. The vertical ionization energies IP($2\Sigma^+$) = 11.7 ± 0.2 eV and IP($\Pi\Pi$) = 12.1 ± 0.3 eV can be considered as the recommended values derived from the results of the present MP4, QCISD(T), CIADC(4), OVGF, and ADC(3) calculations (see Table 1). The former IP($2\Sigma^+$) is in reasonable agreement with experimental data. Geometry relaxation does not change the lowest IP significantly, IP$_{\text{ad}}$(2$\Sigma^+$) = 11.6 ± 0.2 eV; the adiabatic correction to the second IP is also small, IP$_{\text{ad}}$(2$\Pi\Pi$) = 11.7 ± 0.2 eV. The optimized bond lengths and vibrational frequencies for these two cationic states are 1.534 Å and 1051 cm$^{-1}$ for SiO$^+$ (2$\Sigma^+$) and 1.651 Å and 938 cm$^{-1}$ for SiO$^+$ (2$\Pi\Pi$).

According to our calculations (Table 1), SiO has neither a positive vertical nor adiabatic electron affinity.

SiO, SiO$^+$, and SiO$^2$. Van Zee et al. reported detection of SiO$^+(X^\Pi)$ on the basis of their ESR spectra. However, DeKock et al. have shown that the triplet SiO$^+$ linear structure is more stable than the triplet SiO by ca. 10 kcal/mol using CIUSD/TZ+2P and CASCF/TZ+2P methods. Recently Boldyrev and Simons showed, at the QCISD(T)/6-311+G(2df) level, that, indeed, the ground state of this molecule has an angular singlet C$_2$($^1A_1$) structure (see Figure 1) while the triplet structures are local minima and lie 18–27 kcal/mol higher. The latter calculations are sophisticated enough that new experimental studies on the structure of the SiO molecule should be considered.

The assignment of the ionization spectrum of SiO is unambiguous due to the significant gap (about 3.6 eV) between the lowest-energy A$_1$(d$\pi$) (involving detachment of an electron from 4a$_1$) and the next B$_1$ state. The 4a$_1$-MO is $\sigma$-bonding with respect to Si–O, and its contributions from the oxygen atomic orbitals are modest. Therefore, after ionization, one expects elongation of the Si–O bond length and a relatively small change in the Si–O bond lengths.

SiO, SiO$^+$, and SiO$^2$. The electronic affinities of these molecules, EA, are estimated to be 1.3 ± 0.2 and 0.3 ± 0.2 eV for the A$_2$ and B$_2$ states, respectively. Geometry relaxation does not significantly change the geometry of the SiO$^+$ (2$\Sigma^+$) state as expected; so the adiabatic EA$_{ad}$ = 1.4 ± 0.2 eV is very close to the vertical electron affinity. The optimal geometry of SiO$^+$ (2$\Sigma^+$) is different from the one calculated by Huber and Herzberg (see Table 1) and its geometrical parameters in the framework of C$_2v$ symmetry, as presented in Figure 2. The simulated IR spectra are presented in Figure 2. According to our calculations (Table 1), SiO$^+$ is predicted to be unstable at Koopmans' approximation.

2b$_2$-MO is of $\pi$-MO character with bonding interaction with respect to both Si–O and Si–Si overlaps. However, Si atoms contribute more to this MO, so a larger change is expected in the Si–Si distance than in the Si–O bond lengths when this orbital is occupied. These qualitative predictions agree with the results of our calculations (Figure 1) for the Si–Si bond length, but we find the Si–O bond length also increases. The vertical EA$_{ad}$(2b$_2$) is found to be 0.9 ± 0.2 eV (see Table 1) and its geometrical parameters in the framework of C$_2v$ symmetry, as presented in Figure 2. The simulated IR spectra are presented in Figure 2.
Experimental appearance potentials: 8.9 eV for Si\(^{+}\), 9.0 eV for Si\(^{2+}\), and 8.1 eV for Si\(^{3+}\) lead to satellite lines in the photoelectron spectra. The satellite ionization energies larger than 1.1-1.2 eV, where many-body effects have a breakdown of the one-electron picture of ionization for Si\(^{+}\), are promising results that have recently appeared in the literature. However, promising results have also been obtained in the calculations of different geometric structures and electronic states for neutral Si\(^{3}\)O and Si\(^{2}\)O have been previously\(^{25}\) performed, and a rhombus singlet structure C\(_{2v}\) (1A\(_{1}\); 1a\(_{1}\); 2a\(_{1}\); 2b\(_{2}\); 4a\(_{1}\); 5a\(_{1}\)) has been found for the ground state (see Figure 1).

In this work, we optimized geometries of the Si\(^{2}\)O cationic B\(_{2}\) (1a\(_{1}\); 2a\(_{1}\); 2b\(_{2}\); 4a\(_{1}\); 5a\(_{1}\)) and anionic B\(_{2}\) (1a\(_{1}\); 2a\(_{1}\); 2b\(_{2}\); 4a\(_{1}\); 5b\(_{1}\); 5a\(_{1}\)) and A\(_{2}\) (1a\(_{1}\); 2a\(_{1}\); 2b\(_{1}\); 4a\(_{1}\); 5b\(_{1}\); 5a\(_{1}\)) states, the ion states having been identified on the basis of OVGF and ADC(3) calculations. The resulting geometrical structures and calculated IR spectra are given in Figures 1 and 2, respectively. According to our calculation, the vertical IPs and EAs (based on ΔMP4, ΔCISD(4), OVGF, and ADC(3)) are IP\(_{\text{v}}\) (B\(_{2}\)) = 8.1 ± 0.2 eV, IP\(_{\text{a}}\) (A\(_{2}\)) = 8.7 ± 0.2 eV, EA\(_{\text{v}}\) (B\(_{2}\)) = 1.5 ± 0.2 eV, and EA\(_{\text{a}}\) (A\(_{2}\)) = 0.6 ± 0.2 eV (see Table 1). For all four ionic species, the geometries do not differ significantly from the equilibrium geometry of the neutral Si\(^{3}\)O molecule (see Figure 1). Therefore, the corresponding adiabatic energy differences are IP\(_{\text{a}}\) (B\(_{2}\)) = 7.8 ± 0.2 eV, IP\(_{\text{a}}\) (A\(_{2}\)) = 8.6 ± 0.2 eV, EA\(_{\text{a}}\) (B\(_{2}\)) = 1.7 ± 0.2 eV, and EA\(_{\text{a}}\) (A\(_{2}\)) = 0.7 ± 0.2 eV.

Overview

In this study we used five sophisticated ab initio methods to calculate ionization potentials and electron affinities: ΔMP4, ΔQCSID(T), ΔCISD(4), OVGF, and ADC(3). In the first three methods, the ionization energy is calculated through separate calculations on the neutral and ionic states, while the latter two methods compute the ionization energy directly as a sum of electron relaxation and electron correlation corrections to the corresponding orbital energy. Both approaches have advantages and disadvantages. Indirect methods such as ΔMP4 and ΔQCSID(T) are based on the unrestricted Hartree–Fock reference wave function, and therefore the resulting wave function does not necessarily represent a pure spectroscopic state. Direct methods have no problems with the purity of the spectroscopic states, but current tools may be applied only for closed shell species whose ionization energies are to be computed. Therefore, in cases such as Si\(^{2}\)C, where the neutral and both ionic (positive and negative) states are open shell, direct methods are not applicable. Another disadvantage of the current direct methods is connected with the calculation of adiabatic IPs and EAs. However, promising results\(^{6-9}\) have recently appeared in the literature, where geometry optimization as well as frequency calculations are computed in direct methods. It seems that a combination of the direct and indirect methods is a powerful approach to examining the ionization processes.

Our ADC(3) calculations reveal for all the species studied here a breakdown of the one-electron picture of ionization for ionization energies larger than 1.1–1.2 eV, where many-body effects lead to satellite lines in the photoelectron spectra. The satellite lines should be more pronounced in the case of Si\(^{3}\)O and Si\(^{2}\)O than in the Si\(^{2}\)C and Si\(^{3}\)C because in Si\(^{3}\)O and Si\(^{2}\)O the LUMO and a few other unoccupied MOs are lower in energy than are the corresponding MOs in Si\(^{2}\)C and Si\(^{3}\)C.

Our calculations of the vertical IPs and EAs of Si\(^{2}\)C, Si\(^{3}\)C, Si\(^{2}\)O, Si\(^{3}\)O, and Si\(^{4}\)O agree within 0.3 eV with experimental data and among all five of our methods—ΔMP4, ΔQCSID(T), ΔCISD(4), OVGF, and ADC(3)—to within 0.5 eV.

We have made new predictions of the vertical and adiabatic IPs and EAs of Si\(^{2}\)C, Si\(^{3}\)C, Si\(^{2}\)O, Si\(^{3}\)O, and Si\(^{4}\)O. For the neutral and ionic states of these species, we calculated the infrared spectra to assist in identification of these species in the gas-phase or matrix isolation.

We infer that electron removal or electron attachment in Si\(^{2}\)C and Si\(^{3}\)O involves the silicon part of the clusters because the corresponding ionization energies are close to the corresponding values for Si\(^{2}\)C and Si\(^{3}\)C. In contrast, for Si\(^{3}\)C, Si\(^{3}\)O, Si\(^{2}\)O, and Si\(^{4}\)O, the IPs and EAs are very different from the corresponding numbers for Si\(^{2}\)C and Si\(^{3}\)C.

Our ADC(3) calculations reveal breakdown of the one-electron picture of ionization at ionization energies higher than 11–12 eV where many-body effects lead to satellite lines in the photoelectron spectra. The satellite lines should be more pronounced in the case of Si\(^{3}\)O and Si\(^{2}\)O than in Si\(^{2}\)C and Si\(^{3}\)C.

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