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"Vertical and Adiabatical Ionization Energies and Electron Affinities
of New Si_nC and Si_nO ($n=1-3$) Molecules"

by

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**VERTICAL AND ADIABATIC IONIZATION ENERGIES AND
ELECTRON AFFINITIES OF NEW Si_nC and Si_nO ($n=1-3$)
MOLECULES.**

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Abstract

Vertical and adiabatic ionization potentials as well as electron affinities have been calculated for SiC , Si_2C , Si_3C , SiO , Si_2O and Si_3O 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 (± 0.3 eV). The calculated vertical first IPs of SiC , Si_2C , Si_3C and SiO molecules agree within 0.2 eV with experimental appearance potentials for these species.

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I. INTRODUCTION

Recently, silicon-carbon Si_nC and silicon-oxygen Si_nO ($n=2,3$) molecular clusters have been studied theoretically.^{1,2} Geometrical structures and vibrational frequencies for the ground electronic states have been obtained for Si_2C and Si_3C 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_nC and Si_nO (for $n=1-3$). 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 (MP_n), quadratic configuration interaction (QCISD(T)), conventional configuration interaction (CISD) and Green function methods (the OVGf and ADC(3) approaches discussed below)) and different types of atomic basis sets in performing the calculations whose results are reported here.

II. COMPUTATIONAL DETAILS

The bond lengths of the neutral, cationic and anionic SiC , Si_2C , Si_3C , SiO , Si_2O and Si_3O species were optimized by employing analytical gradients³ using the Gaussian 92 program⁴ with polarized split-valence basis sets ($6-311+\text{G}^*$)⁵⁻⁷ at $\text{MP2}(\text{full})$ levels ($\text{UMP2}(\text{full})$ for open shell systems). Our optimal geometric parameters are presented in Fig. 1 and our simulated IR-spectra based on the $\text{MP2}(\text{full})/6-311+\text{G}^*$ calculated frequencies are drawn in Fig. 2.

The MP2(full)/6-311+G* equilibrium geometries were used to evaluate electron correlation corrections in the frozen-core approximation by full fourth order⁸ Møller-Plesset perturbation theory and by the (U)QCISD(T) method⁹ 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 PMP4.¹⁰

The vertical ionization energies and electron affinities were also calculated by two approximations to the many-body one-particle Green function,¹¹⁻¹⁶ namely the Outer Valence 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.¹¹⁻¹³ The renormalization procedure includes three cases described in details 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, 2 hole + 1 particle, and 2 particle + 1 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.

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When complete break-down of the one-particle description occurs, the pole strengths are much smaller than unity, and instead of one photo electron line, there appear a number of additional lines known as shake-up (or shake-off) satellites.

The SCF calculations preceding the OVGF and ADC(3) calculations employed the MOLCAS-2 suite of programs¹⁷. For these calculations, we used the very large ANO basis set of Widmark et.al.¹⁸. For the Si atom, this consists of (17s12p5d4f) elementary functions and [6s5p2d1f] contracted functions, and for the C and O atoms of (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 loss¹⁹. (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 (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 $\pm$ values are assigned to the range of energies predicted by the various methods.

II" RESULTS AND DISCUSSION

SiC, SiC⁺ and SiC⁻. The neutral SiC molecule is known to have a triplet $^3\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$) ground electronic state.^{21,22} Our calculated bond length $R_e(\text{Si-C})=1.702 \text{ \AA}$ and harmonic frequency $\nu_e=896 \text{ cm}^{-1}$ agree reasonably with experimental data: $R_e(\text{Si-C})=1.722 \text{ \AA}$ ²¹ and 964.6 cm^{-1} .²¹ An experimental appearance potentials has been determined for SiC: $9.2\pm 0.4 \text{ eV}$ 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: $^4\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$) and $^2\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3$) for SiC⁺, when an electron is removed from the highest σ - or π -MO. We examined these two states as well as the $^2\Sigma^+$ ($1\sigma^2 2\sigma^1 1\pi^4$) state. A simple MO picture of the valence MOs suggests the following: 1σ -MO is bonding (s_C+s_{Si}) ; 2σ -MO is antibonding (s_C-s_{Si}) ; 1π -MO is bonding ($p_{x,y,C}+p_{x,y,Si}$) and 3σ -MO is bonding ($p_{z,C}-p_{z,Si}$). From this simple picture we expect that the detachment of an electron either from the bonding 1π -MO (to give the $^4\Sigma^-$ final state) or from the bonding 3σ -MO (yielding the $^2\Pi_i$ 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).

The energy order of the ionic states is not easy to predict from the simple MO picture. The $^4\Sigma^-$ state is found to be the lowest cationic state. The $^2\Pi_i$ and $^2\Sigma^+$ states are 2.5 eV 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 $^4\Sigma^-$; 1.675 Å and 952 cm⁻¹ for $^2\Pi_i$; 1.504 Å and 1443 cm⁻¹ for $^2\Sigma^+$. We estimate the first vertical $IP_v=8.9\pm0.2$ eV for producing $^4\Sigma^-$ SiC⁺ to be in the range 8.8 eV (PMP4), 9.0 eV (QCISD(T)) and 9.0 eV (CISD(4)), which agrees well with the experimental appearance potentials 9.2 ± 0.4 eV²³ and 9.0 eV.²⁴ Our first adiabatic IP_a is 8.7 ± 0.2 eV.

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 $^2\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$) and $^2\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$) 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 $^2\Sigma^+$ state is found to be the lowest of SiC⁻, however, the $^2\Pi_i$ state lies only 0.4 eV (QCISD(T)/6-311+G(2df)) above the $^2\Sigma^+$ ground state. The optimized bond lengths and vibrational frequencies are: 1.759 Å and 1127 cm⁻¹ for $^2\Sigma^+$ and 1.710 Å and 951 cm⁻¹ for $^2\Pi_i$. 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 $EA_v=2.32$ eV. Although $EA(\text{SiC})$ is very high, it is lower than $EA(\text{C}_2)=3.269\pm0.006$,^{25a} $EA(\text{C}_2)=3.273\pm0.008$ ^{25b} and close to $EA(\text{Si}_2)=2.176\pm0.002$ eV,^{26a} $EA(\text{Si}_2)=2.199\pm0.012$.^{26b} The SiC⁻ ion also has an excited bound $^2\Pi_i$ state which lies below the ground $^3\Pi$ state of SiC by 1.83 eV and thus may be found in the gas phase experiments. The next $^2\Pi_r$ state of SiC⁻ with $1\sigma^2 2\sigma^2 1\pi^4 2\pi^1$ orbital occupancy is not electronically bound and corresponds to a resonance 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.²³ In the first infrared work, Weltner and Mcleod²⁷ 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 ²⁸ 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 $\nu_3(b_2)$ antisymmetric Si-C stretching and $\nu_1(a_1)$ 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 Presilla-Márquez and Gráham.²⁹ This confirmed a previously observed vibration at 1188.4 cm⁻¹ as the $\nu_3(b_2)$, antisymmetric Si-C stretching mode, and resulted in the identification of a new vibration at 839.5 cm⁻¹ as the $\nu_1(a_1)$ symmetric Si-Si stretching fundamental. No bending mode has been observed. Ab initio calculations performed by Grev and Schaefer^{1a}, Bolton et al^{1b} and Rittby^{1c} predicted a singlet angular C_{2v} (¹A₁) 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^{1c} or 2.1^{1a} kcal/mol. Experimental appearance potentials are known for Si₂C 9.2±0.3 eV²³ and 9.1 eV,²⁴ 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_e(Si-C)=1.707 Å, valence angle Si-C-Si=114.7° and harmonic frequencies $\nu_1(a_1)$ =844 cm⁻¹, $\nu_2(a_1)$ =129 cm⁻¹ and $\nu_3(b_2)$ =1208 cm⁻¹. Our bond length and valence angle reasonably agree with other CCSD(T)/TZ+2P (1.708 Å and

116.9°),^{1b} and MBPT2/6-311G(2d) (1.703 Å and 119.5°)^{1c} ab initio data if we take into account the flexible structure of this species. Our harmonic symmetric and antisymmetric stretching frequencies $\nu_1(a_1)=844\text{ cm}^{-1}$ and $\nu_3(b_2)=1208\text{ cm}^{-1}$ also reasonably agree with experimental data $\nu_1(a_1)=839.5\text{ cm}^{-1}$,²⁹ and $\nu_3(b_2)=1188.9\text{ cm}^{-1}$.²⁸

From the $1a_1^2 1b_2^2 2a_1^2 2b_2^2 1b_1^2 3a_1^2 1a_2^0 4a_1^0$ ground electronic SCF configuration, we found in OVGf and ADC(3) calculations that the lowest energy cationic states are: 2A_1 ($1a_1^2 1b_2^2 2a_1^2 2b_2^2 1b_1^2 3a_1^1$), 2B_1 ($1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 1b_1^1$) and 2B_2 ($1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2 2b_2^1$) and the lowest anionic states are: 2A_2 ($1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2 1a_2^1$) and 2A_1 ($1a_1^2 1b_2^2 2a_1^2 2b_2^2 1b_1^2 3a_1^2 4a_1^1$).

In Koopmans' approximation, the energy order of the cationic states is given as $^2A_1 < ^2B_1 < ^2B_2$. However, as shown in Table I, at all correlated levels and even at the Δ SCF level, the order of the cationic states is different: $^2B_2 < ^2A_1 < ^2B_1$. Results of the calculations of the vertical IPs obtained at correlated levels agree within 0.25 eV for all five methods: Δ MP4, Δ QCISD(T), Δ CISD(4), OVGf and ADC(3). On the basis of these data, we estimate the vertical ionization potentials to be: $IP(^2B_2)=9.1\pm0.2\text{ eV}$, $IP(^2A_1)=9.3\pm0.2\text{ eV}$ and $IP(^2B_1)=9.4\pm0.2\text{ eV}$. The first vertical IP agrees well with the experimental appearance potential for Si_2C $9.2\pm0.3\text{ eV}$ ²³ and 9.1 eV .²⁴

All of these 2A_1 , 2B_1 and 2B_2 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 ionization energy larger than 12 eV are not well represented as the ionization from a single MO (see Table I). For example, ionization from the next $2a_1$ -MO of Si_2C 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 I) while the configuration of the $2a_1^{-1}$ 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 I).

Geometry optimization of the 2A_1 , 2B_1 and 2B_2 states of Si_2C^+ leads to a linear SiCSi structure. The 2A_1 and 2B_1 states collapse into the degenerate $^2\Pi_u$ ($1\sigma_g^2 1\sigma_u^2 2s_g^2 2\sigma_u^2 1\pi_u^3$) state, and the 2B_2 state collapses into the $^2\Sigma_u^+$ ($1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^1$). For both of these linear states, the optimal geometries are presented in Fig. 1, and the corresponding adiabatic ionization potentials, $IP_a(^2\Pi_u)$ and $IP_a(^2\Sigma_u^+)$, are equal to 9.0 ± 0.2 eV and 9.2 ± 0.2 eV, respectively. Harmonic frequencies have been calculated only for $^2\Sigma_u^+$ state, because for the Hartree-Fock based MP2 method, the bending vibrations are not degenerate. As a result, even though $\nu_1(\sigma_g)=584$ cm^{-1} and $\nu_2(\pi_u)=92$ cm^{-1} appear reasonable, the antisymmetric stretching frequency $\nu_3(\sigma_u)=2405$ cm^{-1} is too high probably due to symmetry breaking.

The lowest unoccupied $1a_2^-$ and $4a_1^-$ -MOs in Si_2C have positive energies at the optimal geometry of the neutral Si_2C molecule; therefore, at the 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_v of Si_2C calculated for the 2A_2 and 2A_1 states are 0.6 ± 0.2 eV and 0.1 ± 0.2 eV, respectively. Geometry optimization of the 2A_2 state leads to a linear structure and a $^2\Pi_g$ final electronic state, while the final geometric structure of the 2A_1 state is bent. Moreover, in the $Si_2C^- (^2A_1)$ 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 $Si_2C^- (^2A_1)$ has significant Si-Si bonding. The

calculated IR-spectrum of Si_2C^- ($^2\text{A}_1$) is presented in Fig. 2. The adiabatic electron affinities for producing the two anion states, $\text{EA}_a(^2\Pi_g)$ and $\text{EA}_a(^2\text{A}_1)$, are 0.9 ± 0.2 eV and 0.7 ± 0.2 eV, respectively.

Si_3C , Si_3C^+ and Si_3C^- . This molecule has been detected in mass spectroscopic experiments and an appearance potential of 8.2 ± 0.3 eV has been reported.²³ The experimental spectrum of Si_3C has been observed³⁰ in a Fourier transform infrared study of the products of the vaporization of carbon/silicon mixtures trapped in Ar. An ab initio structure of the Si_3C has been determined by Rittby^{1d} at the MBPT2/DZP level, where a rhomboid singlet structure of C_{2v} symmetry with carbon-silicon transannular bonding between the two equivalent Si_b 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.³⁰ No experimental or theoretical geometries or vibrational spectra are known for cationic or anionic states of Si_3C thus far.

We optimized the geometry and calculated harmonic frequencies for singlet ($1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^2 1a_2^0 2b_1^0$) rhomboid neutral Si_3C (this geometry is shown in Fig. 1). Our geometry and vibrational spectrum (Fig. 2) for this structure agree well with the MBPT2/DZP optimized geometry and corresponding vibrational spectrum by Rittby.^{1d}

We studied one cationic state $^2\text{B}_2$ ($1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^1$), which should be the lowest positive ion according to the vertical IPs calculated at the OVGF and ADC(3) levels. The $3b_2$ -MO does not contain contributions from carbon AOs, and has antibonding overlap between AOs from the bridged silicon atoms, however it has a strong bonding interaction between the terminal and bridged silicons. Therefore, detachment of an electron from the $3b_2$ -MO should lead to a distortion in which an increase of the $\text{Si}_t\text{-Si}_b$ bonds

might be expected. Indeed, geometry optimization for the 2B_2 state of Si_3C^+ leads to a structure where the Si_b-Si_t distance increases and the valence angle Si_tCSi_b increases from 81° to 96° (the geometries are shown in Fig. 1 and the simulated IR-spectra are presented in Fig. 2).

We achieved agreement for both vertical IPs (2B_2 and 2A_1) within 0.3 eV for the four different theoretical approaches used: PMP4, CISD(4), OVGf and ADC(3). From these four methods our best estimates of the two vertical IPs are: 8.2 ± 0.2 eV (2B_2) and 9.1 ± 0.2 eV (2A_1). The first IP agrees well with the experimental appearance potential of 8.2 ± 0.3 eV.²³ The geometry of the 2B_2 state differs significantly from the neutral molecule, therefore the Franck-Condon factor for this ionization process should be rather small although the adiabatic correction (0.4 eV) to the IP is not large (the corresponding adiabatic IP(2B_2) is 7.8 ± 0.2 eV (from PMP4 and CISD(4))).

Based on the MO energy ordering and results of our OVGf and ADC(3) calculations, we found two low energy anionic states: 2A_2 ($1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^2 1a_2^1$) and 2B_1 ($1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^2 2b_1^1$). The orbital energy is negative for the $1a_2$ -LUMO and positive for the $2b_1$ -MO. Both $1a_2$ - and $2b_1$ -MOs are pure π -type orbitals. The $1a_2$ -MO is antibonding with respect to Si_b-Si_b interaction, but because these two atoms are situated far from each other, occupation of this MO should not lead to any essential geometrical changes. The $2b_1$ -MO is antibonding with respect to C- Si_t interaction, so elongation of the C- Si_t bond might be expected in the corresponding anion. As shown in Fig. 1, these types of distortions have been found upon geometry optimization. The vertical electron affinities of these two states, EA_v , are estimated to be 1.3 ± 0.2 eV and 0.3 ± 0.2 eV for the 2A_2 and 2B_1 states, respectively. Geometry optimization does not significantly change the geometry of the Si_3C^- (2A_2) state as expected; so the adiabatic $EA_a = 1.4 \pm 0.2$ eV

is very close to the vertical electron affinity. The optimal geometry of Si_3C^- ($^2\text{B}_1$) is very different from the optimal neutral geometry (mainly because the C-Si_l bond elongates by 0.26 Å), so after geometry relaxation within C_{2v} symmetry the $\text{EA}(^2\text{B}_1)=0.7$ eV is higher than the vertical EA. However frequency calculations for Si_3C^- (C_{2v} , $^2\text{B}_1$) have shown that this structure is not a minimum but a saddle point (with one imaginary frequency). The vector belonging to this imaginary frequency leads to an inplane distortion. Beginning with a geometry slightly distorted from C_{2v} ($^2\text{B}_1$) symmetry, we refined the geometry optimization within C_s symmetry. This optimization leads to a C_{2v} ($^2\text{A}_2$) structure. With our current computational tools we are not able to find excited states for the negative Si_3C^- ion, but we expect the existence of an excited state on the basis of our calculations in the framework of C_{2v} symmetry.

SiO, SiO⁺ and SiO⁻. The SiO molecule is experimentally known to exist in a singlet $^1\Sigma^+$ ground state with a bond length of 1.5097 Å and 1241.56 cm⁻¹ vibrational frequency.³¹ For SiO⁺, Huber and Herzberg³¹ suggest 1.519 Å as the bond length of the ground $^2\Sigma^+$ electronic state for which the experimental ionization potential is 11.6 ± 0.2 eV³² or 11.43 eV.³³ We optimized the geometry of SiO at the MP2(full)/6-311+G* level and found an equilibrium bond length of 1.536 Å and a harmonic frequency of 1183 cm⁻¹.

The ionization energy of the 3σ -MO is smaller than that of the 1π -MO at the Koopmans' approximation and in the OVGf and ADC(3) methods. The vertical ionization energies $\text{IP}(^2\Sigma^+)=11.7\pm 0.2$ eV and $\text{IP}(^2\Pi_1)=12.1\pm 0.3$ eV can be considered as the recommended values derived from the results of the present PMP4, QCISD(T), CISD(4), OVGf and ADC(3) calculations (see Table I). The former $\text{IP}(^2\Sigma^+)$ is in reasonable agreement with experimental data.

Geometry relaxation does not change the lowest IP significantly

$IP_a(^2\Sigma^+)=11.6\pm0.2$ eV; the adiabatic correction to the second IP is also small $IP_a(^2\Pi_i)=11.7\pm0.2$ eV. The optimized bond lengths and vibrational frequencies for these two cationic states are: 1.534 Å and 1051 cm^{-1} for $\text{SiO}^+ (^2\Sigma^+)$, and 1.651 Å and 938 cm^{-1} for $\text{SiO}^+ (^2\Pi_i)$.

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

Si_2O , Si_2O^+ and Si_2O^- . Van Zee et al³⁴ reported detection of SiSiO ($X^3\Sigma$) on the basis of their ESR spectra. However, DeKock et al^{2a} have shown that the triplet SiOSi linear structure is more stable than the triplet SiSiO by ca. 10 kcal/mol using CISD/TZ+2P and CASSCF/TZ+2P methods. Recently Boldyrev and Simons^{2b} showed, at the QCISD(T)/6-311+G(2df) level, that indeed the ground state of this molecule has an angular singlet $C_{2v}(^1A_1)$ structure (see Fig. 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 Si_2O molecule should be considered.

The assignment of the ionization spectrum of Si_2O is unambiguous due to the significant gap (about 3.6 eV) between the lowest-energy 2A_1 (involving detachment of an electron from $4a_1$ -HOMO) and the next 2B_2 state. The $4a_1$ -MO is σ -bonding and π -bonding with respect to Si-Si and its contributions from the oxygen atomic orbitals are modest. Therefore, after ionization, one expects elongation of the Si-Si bond length and a relatively small change in the Si-O bond lengths. The vibrational $\nu_1(a_1)$ and $\nu_2(a_1)$ frequencies in $\text{Si}_2\text{O}^+ (^2A_1)$ which can be attributed to the Si-O stretch and Si-Si stretch are expected to be approximately the same and lower, respectively, than the corresponding values

in the neutral Si_2O molecule. Results of our calculations agree with this qualitative picture (see Fig 1 and Fig 2).

The vertical $\text{IP}_v(^2\text{A}_1)$ of Si_2O is predicted to be 7.5 ± 0.2 eV on the basis of the five methods used, which is much lower than the $\text{IP} = 11.7$ eV of SiO . This is because ionization in Si_2O involves detachment of an electron from an orbital residing mainly on the silicon atoms, while in SiO , oxygen AOs also participate in the orbital. The geometric adiabatic correction to the first IP of Si_2O is relatively small (0.3 eV), and so our estimate for the adiabatic $\text{IP}_a(^2\text{A}_1)$ is 7.2 ± 0.2 eV.

The lowest unoccupied $2b_1$ -MO has positive orbital energy, so the anion is predicted to be unstable at the Koopmans' approximation. This $2b_1$ -MO is of π -MO character with bonding interaction both with respect to 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 (Fig. 1) for the Si-Si bond length, but we find the Si-O bond length also increases. The vertical $\text{EA}_v(^2\text{B}_1)$ is found to be 0.9 ± 0.2 eV (see Table I) and its geometrical adiabatic correction is very small (0.1 eV) so our estimate of the adiabatic $\text{EA}_v(^2\text{B}_1)$ is 1.0 ± 0.2 eV. The our harmonic symmetric $\nu_1(a_1) = 741$ cm^{-1} and $\nu_2(a_1) = 445$ cm^{-1} frequencies for $\text{Si}_2\text{O}^- (^2\text{B}_1)$ look reasonable, but the antisymmetric stretching frequency $\nu_3(b_2) = 3917$ cm^{-1} is overestimated again, probably due to symmetry breaking.

Si_3O , Si_3O^+ and Si_3O^- . For the cation, anion, and neutral Si_3O , no experimental data are available. However, ab initio calculations of different geometric structures and electronic states for neutral Si_3O have been previously^{2b} performed, and a rhombus singlet structure $\text{C}_{2v} (^1\text{A}_1)$,

$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 5a_1^2 2b_1^2 3b_2^0 1a_2^0$) found for the ground state (see Fig. 1).

In this work, we optimized geometries of the Si_3O cationic 2B_1 ($1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 5a_1^2 2b_1^1$) and 2A_1 ($1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 2b_1^2 5a_1^1$) states, and the anionic 2B_2 ($1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 5a_1^2 2b_1^2 3b_2^1$) and 2A_2 ($1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 2b_1^2 5a_1^2 1a_2^1$) states, the ion states having been identified on the basis of OVGF and ADC(3) calculations. The resulting geometrical structures and simulated IR-spectra are given in Fig. 1 and Fig. 2, respectively. According to our calculation, the vertical IPs and EAs (based on ΔPMP4 , $\text{CISD}(4)$, OVGF and $\text{ADC}(3)$) are: $\text{IP}_v(^2B_1)=8.1\pm0.2$ eV, $\text{IP}_v(^2A_1)=8.7\pm0.2$ eV, $\text{EA}_v(^2B_2)=1.5\pm0.2$ eV and $\text{EA}_v(^2A_2)=0.6\pm0.2$ eV (see Table I). For all four ionic states, the geometries do not differ significantly from the equilibrium geometry of the neutral Si_3O molecule (see Fig. 1). Therefore, the corresponding adiabatic energy differences are $\text{IP}_a(^2B_1)=7.8\pm0.2$ eV, $\text{IP}_a(^2A_1)=8.6\pm0.2$ eV, $\text{EA}_a(^2B_2)=1.7\pm0.2$ eV, and $\text{EA}_a(^2A_2)=0.7\pm0.2$ eV.

IV. OVERVIEW

In this study we used five sophisticated ab initio methods to calculate ionization potentials and electron affinities: ΔPMP4 , $\Delta\text{QCISD}(T)$, $\Delta\text{CISD}(4)$, OVGF and $\text{ADC}(3)$. In the first three methods, the ionization energy is calculated through separate calculations on the neutral and ionic states, while two latter 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 $\Delta\text{QCISD}(T)$ are based on the unrestricted Hartree-Fock reference wavefunction 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 SiC, 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 results³⁵⁻³⁷ 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 break down of the one-electron picture of ionization for ionization energies larger 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 Si₂O and Si₃O than in the Si₂C and Si₃C because in Si₂O and Si₃O the LUMO and a few other unoccupied MOs are lower in energy than are the corresponding MOs in Si₂C and Si₃C.

Our calculations of the vertical IPs and EAs of SiC, Si₂C, Si₃C, SiO, Si₂O and Si₃O agree among the five methods to within 0.5 eV. Our estimated first vertical IPs agree well with the experimental appearance potentials: 8.9 ± 0.2 eV vs 9.2 ± 0.4 eV²³ and 9.0 eV²⁴ for SiC; 9.1 ± 0.2 eV vs 9.2 ± 0.3 eV²³, 9.0 ²⁴ for Si₂C; 8.1 ± 0.2 eV vs 8.2 ± 0.3 eV²³ for Si₃C; 11.7 ± 0.2 eV vs 11.6 ± 0.2 eV³² and 11.42 ³³ for SiO, respectively. We expect similar accuracy for the unknown Si₂O and Si₃O first IPs.

The IP=11.7 eV of SiO is approximately 3 eV higher than the IP=8.9 eV of SiC. SiO has no positive electron affinity while SiC has a large EA=2.3 eV. In comparison, Si₂ has IP=7.87 eV,⁴⁰ and EA=2.2 eV.²⁶

There are several interesting observations to be made relative to our calculated IPs and EAs of Si_nC and Si_nO and the available experimental data for pure silicon clusters.³⁸⁻⁴¹ The corresponding carbon clusters have linear geometries and therefore are not appropriate species for such comparison.

When another silicon atom is added to these clusters, things change; IP=7.5 eV of Si_2O is lower than IP=9.1 eV of Si_2C , and both of these molecules have electron affinities near 1 eV. The corresponding Si_3 cluster has IP=7.9 eV,⁴¹ 8.14 eV⁴² and EA=2.33 eV.⁴³

Adding yet another Si atom, one finds that both Si_3O and Si_3C have similar IPs (ca. 8 eV) and comparable EAs (ca. 1.5 eV, see Table I), and that the corresponding Si_4 cluster has IP=7.6 eV,⁴¹ 8.11 eV,⁴² 7.3 eV⁴⁴ and EA=2.15 eV.⁴³ The IP and EA values for Si_4 are close to the corresponding values for Si_3O and Si_3C implies that ionization and electron capture in Si_3C and Si_3O involves primarily the silicon part of the cluster.

As the number of silicon atoms increases in Si_nX species, where X is more electronegative atom than silicon, we expect that the ionization potentials and electron affinities will become closer to the corresponding values of pure silicon clusters Si_n . It appears follows from our calculations that this is the case even for rather small ($n \geq 3$) clusters.

CONCLUSIONS

(1) The results of our IP calculations for SiC , Si_2C , Si_3C and SiO agree within 0.3 eV with experimental data and among all five of our methods - PMP4, QCISD(T), CISD(4), OVGF and ADC(3) to within 0.5 eV.

(2) We have made new predictions of the vertical and adiabatic IPs and EAs of SiC , Si_2C , Si_3C , SiO , Si_2O and Si_3O . 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.

(3) We infer that electron removal or electron attachment in Si_3C and Si_3O involves the silicon part of the clusters because the corresponding ionization energies are close to the corresponding values for Si_4 . In contrast, for Si_2C , Si_2O , SiC and SiO , the IPs and EAs are very different from the corresponding numbers for Si_3 and Si_2 .

(4) Our ADC(3) calculations reveal break-down 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_2O and Si_3O than in Si_2C and Si_3C .

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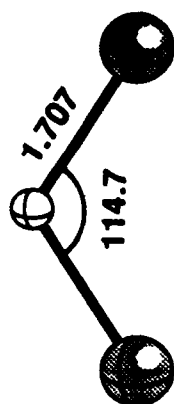
Figure Captions

- Fig. 1** **Molecular Structures and Geometrical Parameters (distances in Å and angles in degrees) at the MP2(full)/6-311+G* level for Si₂C, Si₂C⁺, Si₂C⁻, Si₂O, Si₂O⁺, Si₂O⁻, Si₃C, Si₃C⁺, Si₃C⁻, Si₃O, Si₃O⁺ and Si₃O⁻.**
- Fig. 2** **Calculated Infrared Absorbance Spectra for Si₂C, Si₂C⁺, Si₂C⁻, Si₂O, Si₂O⁺, Si₂O⁻, Si₃C, Si₃C⁺, Si₃C⁻, Si₃O, Si₃O⁺ and Si₃O⁻.**

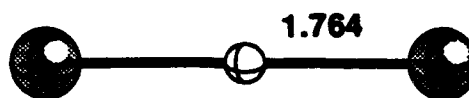
Table I. Calculated and experimental ionization potentials and electron affinity of Si_nO and Si_nC molecules.

Ionic species	State	IP/ EA	Koopmans	ΔPUSCF	ΔPMP2	ΔPMP3	ΔPMP4	ΔQCI SD(T)	CISD+ Davidson correction	OVGFa	ADC(3)a	EXPT
SiO^+	$2\Sigma^+$	IP_v	16.58							15.57 (0.95)		
SiO^+	$2\Pi_1$	IP_v	12.76	9.70	12.27	11.52	12.19	11.96	11.74	12.26 (0.92)	12.21 (0.88)	
		IP_a		9.57	12.02	11.30	11.92	11.70	11.45			
SiO^+	$2\Sigma^+$	IP_v	11.94	10.15	12.01	11.55	11.91	11.48	11.51	11.92 (0.93)	11.66 (0.90)	11.6 $\pm$ 0.2b 11.43c
		IP_a		10.15	12.01	11.55	11.91	11.48	11.51			
SiO^-	$2\Pi_r$	EA_v	-0.59	-0.34	-0.18	-0.04	-0.20	-0.14		-0.06		
		EA_a		-0.24	-0.15	-0.07	-0.15	-0.12				
Si_2O^+	2A_1	IP_v	12.77									
Si_2O^+	2B_2	IP_v	11.00								11.44 (0.59) 12.07 (0.21)	
Si_2O^+	2A_1	IP_v	7.36	6.93	7.39	7.53	7.56	7.58	7.50	7.57 (0.90)	7.29 (0.89)	
		IP_a		6.00	7.21	7.21	7.37	7.34	7.22			
Si_2O^-	2B_1	EA_v	-0.04	0.48	0.99	0.97	0.98	0.95	0.87	0.88 (0.92)	0.82 (0.85)	
		EA_a		0.51	1.08	1.02	1.07	1.01	0.94			
Si_3O^+	2B_2	IP_v	12.32								10.92 (0.28) 11.54 (0.43) 11.96 (0.03) 13.43 (0.07)	
Si_3O^+	2A_1	IP_v	10.93							10.49 (0.85)	10.12 (0.80)	
Si_3O^+	2A_1	IP_v	8.77	7.64	8.83	8.79	8.88			8.72 (0.88)	8.41 (0.86)	
		IP_a		7.48	8.53	8.47	8.58					
Si_3O^+	2B_1	IP_v	8.06	7.13	8.26	8.17	8.27		8.07	8.14 (0.89)	7.86 (0.88)	
		IP_a		6.55	8.00	7.77	7.97		7.68			
Si_3O^-	2B_2	EA_v	0.77	1.63	1.40	1.54	1.38		1.62	1.55 (0.90)	1.39 (0.85)	
		EA_a		1.76	1.73	1.79	1.70		1.71			

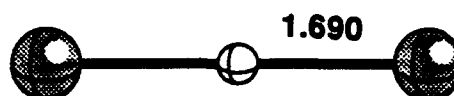
Si ₃ O ⁻	2A ₂	E _A ^v	-0.40	0.74	0.65	0.69	0.73		0.60	0.52 (0.91)	0.43 (0.85)	
		E _A ^a		0.84	0.74	0.79	0.81		0.68			
SiC ⁺	2Σ ⁺	IP _v		13.36	14.37	14.47	14.39		14.17			
		IP _a		14.02	13.91	14.08	13.98	13.92	14.10			
SiC ⁺	2Π _i	IP _v		11.22	10.39	10.47	10.22	10.13	10.15			
		IP _a										
SiC ⁺	4Σ ⁻	IP _v		7.95	8.72	8.73	8.85	8.97				9.2±0.4 ^d 9.0 ^e
		IP _a		7.85	8.57	8.57	8.68	8.78				
SiC ⁻	2Π _i	E _A ^v		0.15	2.14	1.97	2.15	1.82	1.73			
		E _A ^a		0.52	1.94	1.87	2.00	1.83	1.71			
SiC ⁻	2Σ ⁺	E _A ^v		0.07	2.48	2.06	2.22	2.32	2.05			
		E _A ^a		-0.10	2.54	2.01	2.58	2.25	2.00			
Si ₂ C ⁺	2A ₁	IP _v	12.33								11.19 (0.67) 13.36 (0.15) 15.58 (0.02)	
Si ₂ C ⁺	2B ₂	IP _v	9.70	8.32	9.13	9.18	9.16	9.14	9.22	9.33 (0.89)	9.06 (0.86)	9.2±0.3 ^d 9.1 ^e
	2Σ _u ⁺	IP _a		8.61	9.13	9.28	9.17					
Si ₂ C ⁺	2B ₁	IP _v	9.41	7.84	9.68	9.25	9.60		9.30	9.56 (0.88)	9.31 (0.87)	
	2Π _u	IP _a			†				8.94			
Si ₂ C ⁺	2A ₁	IP _v	9.38	7.47	9.55	9.22	9.52	9.37	9.29	9.45 (0.88)	9.19 (0.86)	
	2Π _u	IP _a			†				8.98			
Si ₂ C ⁻	2A ₂	E _A ^v	-0.36	0.94	0.55	0.69	0.67	0.71	0.87	0.55 (0.92)	0.48 (0.87)	
	2Π _g	E _A ^a			g				0.90			
Si ₂ C ⁻	2A ₁	E _A ^v	-0.89	-0.30	0.09	0.07	0.15	0.13	-0.21	-0.13 (0.93)		
		E _A ^a		0.06	0.77	0.73	0.80	0.75	0.65			



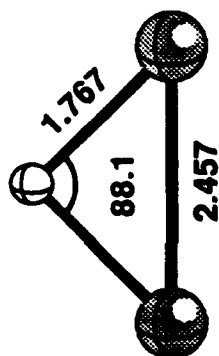
Si_2C (C_{2v} , 1A_1)



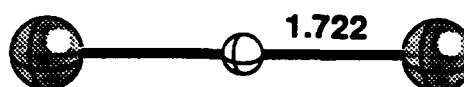
Si_2C^+ ($\text{D}_{\infty h}$, $2\Pi_u$)



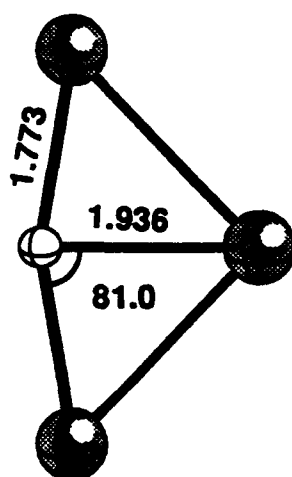
Si_2C^+ ($\text{D}_{\infty h}$, $2\Sigma_u^+$)



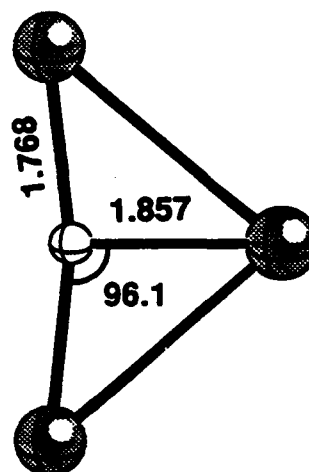
Si_2C^- (C_{2v} , 2A_1)



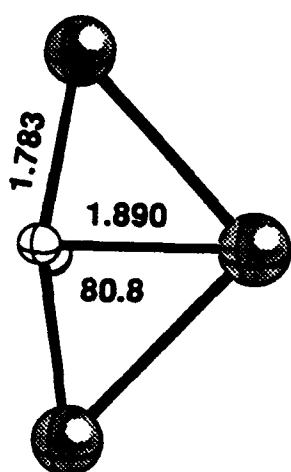
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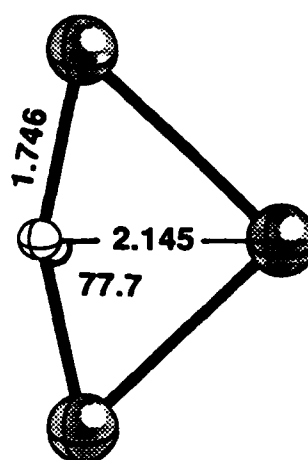
Si_3C (C_{2v} , 1A_1)



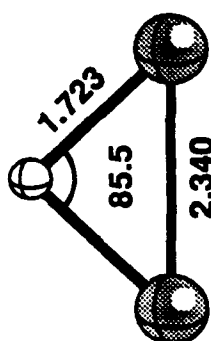
Si_3C^+ (C_{2v} , 2B_2)



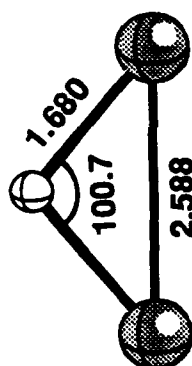
Si_3C^- (C_{2v} , $2A_2$)



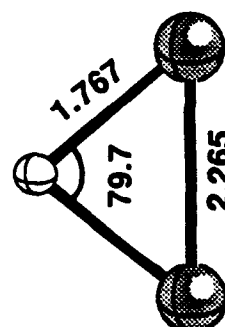
Si_3C^- (C_{2v} , $2B_1$)



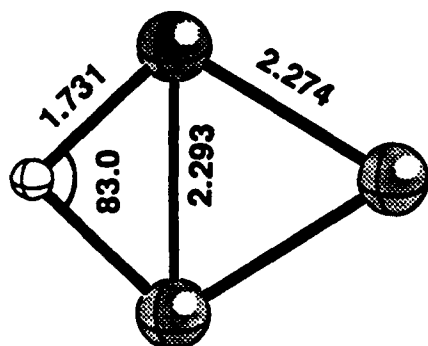
Si_2O (C_{2v} , $1A_1$)



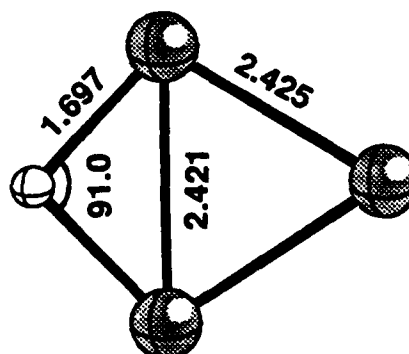
Si_2O^+ (C_{2v} , $2A_1$)



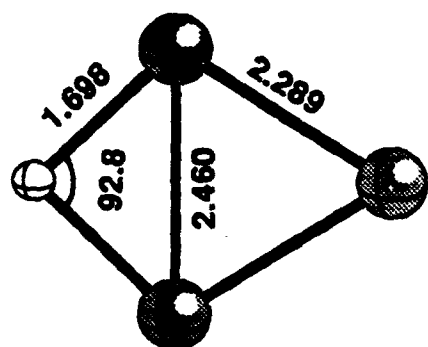
Si_2O^- (C_{2v} , $2B_1$)



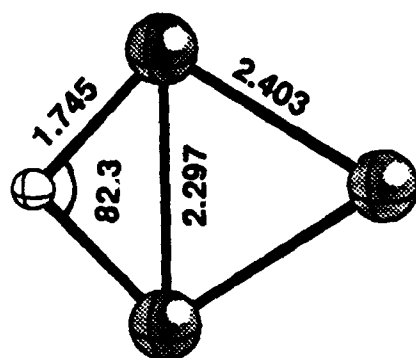
Si_3O (C_{2v} , $1A_1$)



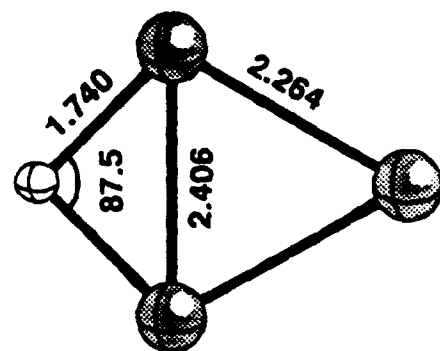
Si_3O^+ (C_{2v} , $2B_1$)



$\text{Si}_3\text{O}^+ (C_{2v}, ^2A_1)$



$\text{Si}_3\text{O}^- (C_{2v}, ^2B_2)$



$\text{Si}_3\text{O}^- (C_{2v}, ^2A_2)$

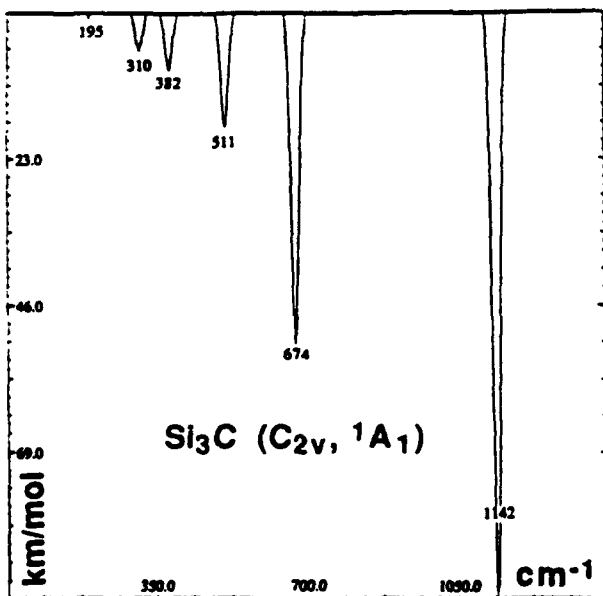
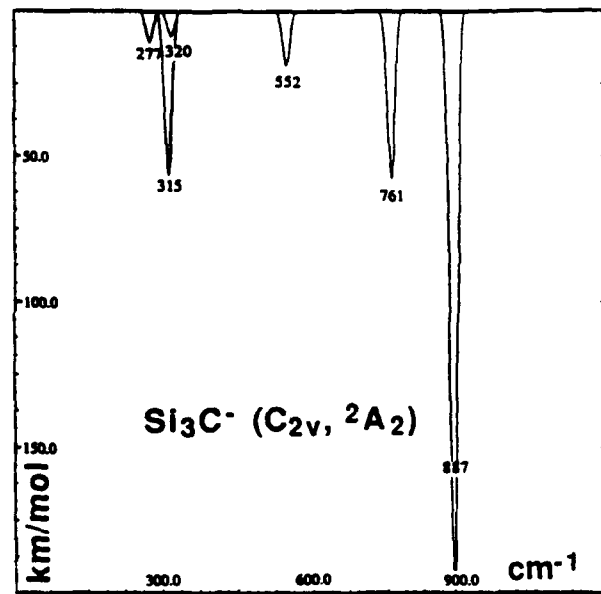
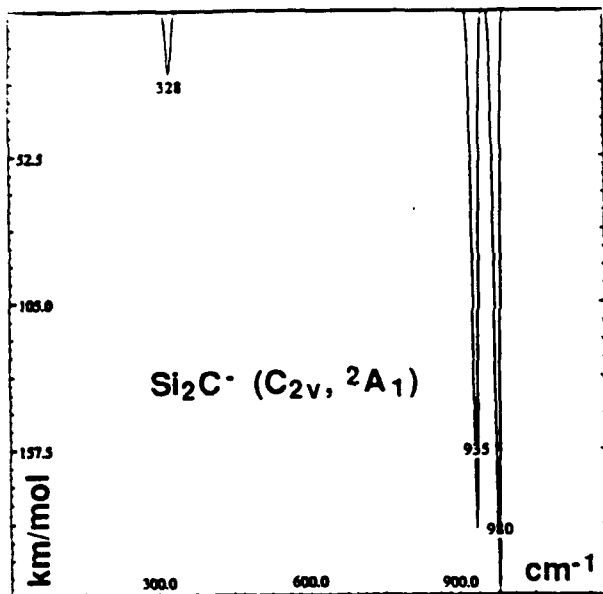
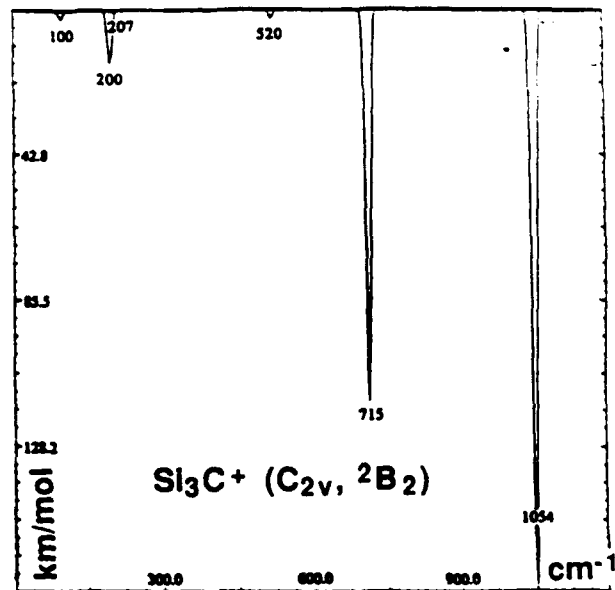
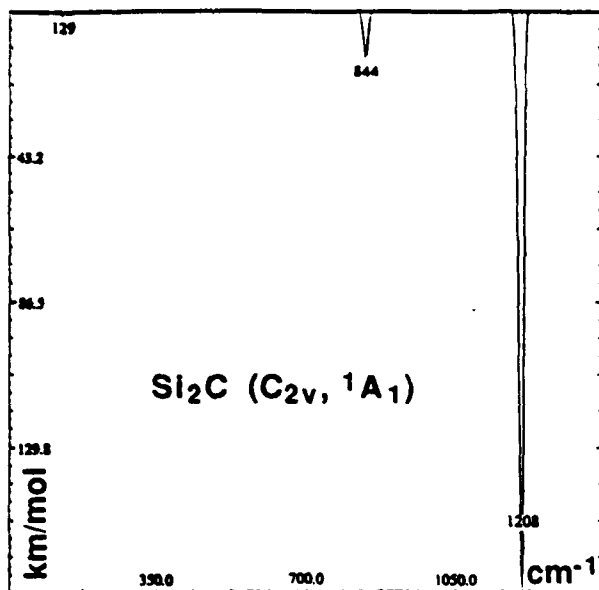


Fig. 2

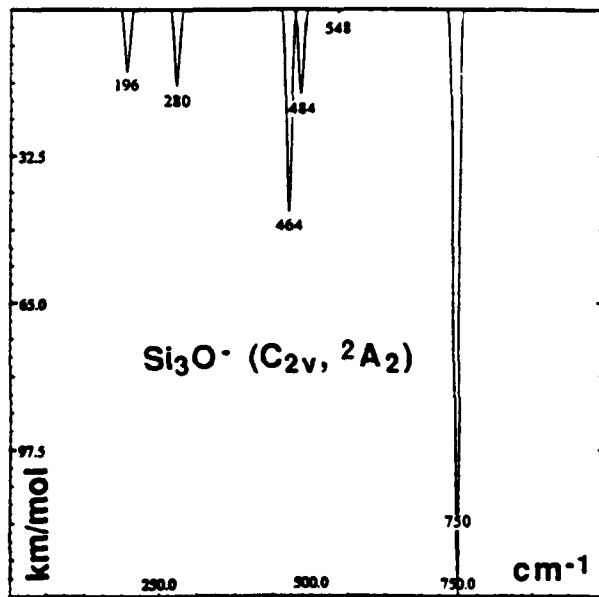
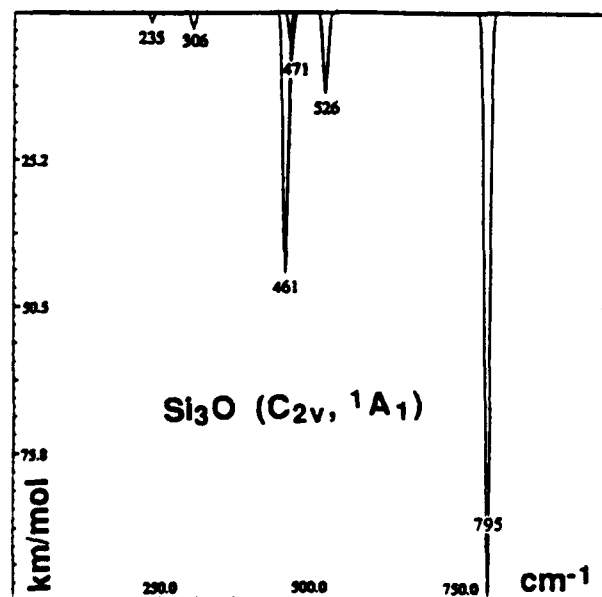
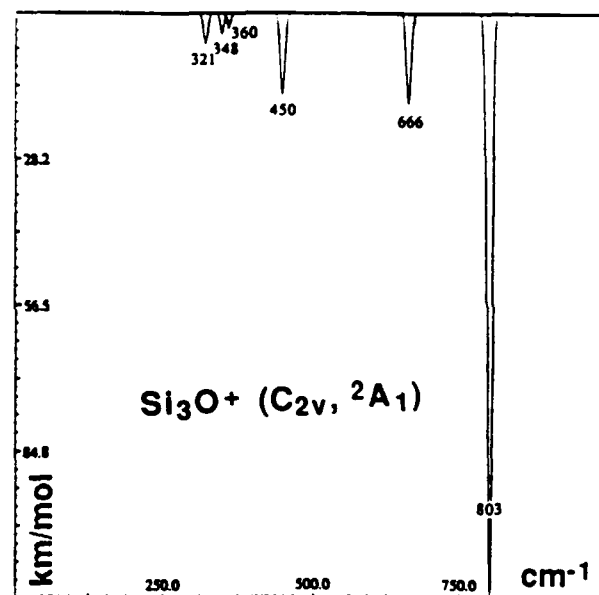
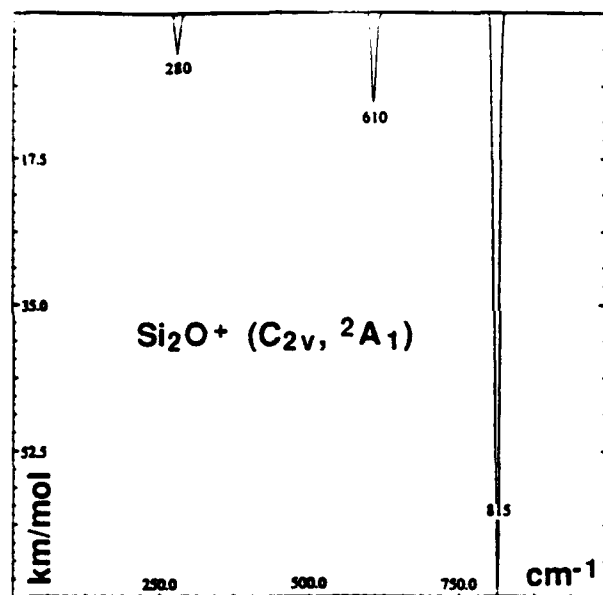
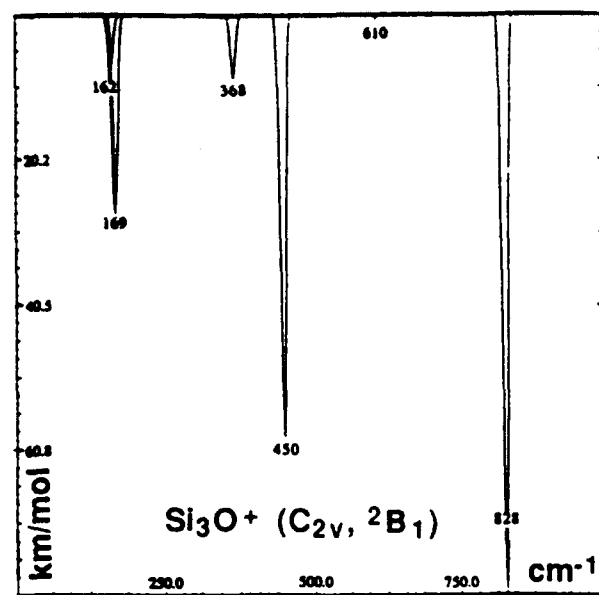
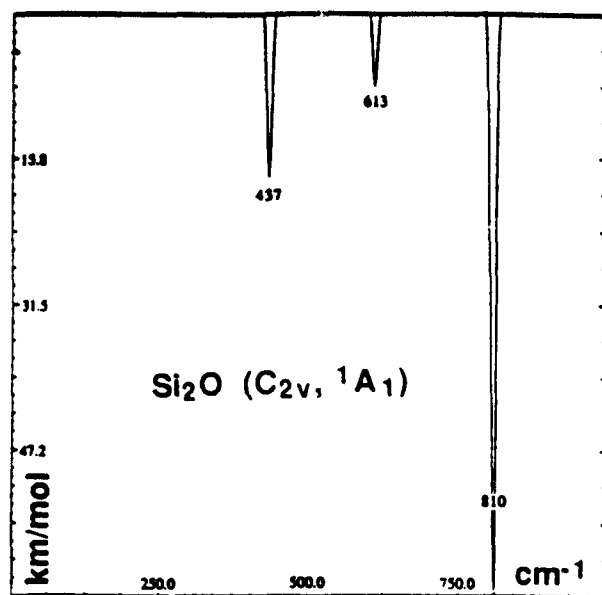


Fig. 2