

A combined experimental and theoretical study of the neutral, cationic, and anionic Si_3N cluster molecule

Norman Goldberg, Muhammad Iraqi, and Helmut Schwarz

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17 Juni, D-10623 Berlin, Germany

Alexander Boldyrev and Jack Simons

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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Collision experiments and high-level *ab initio* calculations are used for the first characterization of the neutral, cationic, and anionic Si_3N cluster molecules. The experimentally observed fragmentation processes are well described by calculated reaction energies of all dissociation channels. In addition, the geometries and harmonic frequencies of Si_nN ($n=1-3$) have been calculated for the cationic, anionic, and neutral species.

I. INTRODUCTION

In the last couple of years the search for new materials that possess unique physical properties has been going through a revival phase. The development of novel sophisticated experimental techniques, such as laser desorption (LD) and chemical-vapor deposition (CVD), have led to the generation of hitherto unknown, unusual compounds. Amongst these materials, carbon- and silicon-containing nitrides have received special interest.¹ Thus, the covalently bound polymer carbon(IV) nitride has only recently been synthesized by a combination of LD and CVD techniques.² This structurally, not yet fully characterized, substance seems to exhibit the theoretically predicted physical properties such as an extreme hardness and diatomiclike modules of elasticity. It is believed to possess a structure similar to the binary silicon nitride $\beta\text{-Si}_3\text{N}_4$.

In general, it is known that the *p*-block main-group elements form nitrides with exceptional chemical inertness and mechanical hardness.³ However, binary silicon nitrides are not only of interest to material scientists. Small silicon-containing clusters are believed to be formed in silicon-etching processes and thus, as they can also be viewed upon as prototypes for the interaction of main-group elements with silicon sites in clusters and surfaces, have received much attention by experimentalists⁴ as well as theoreticians.⁵

To our knowledge there exists very little information on small binary silicon-nitrogen clusters. Recently, Brodie *et al.*^{4(d)} have carried out pyrolysis solid-state nuclear magnetic resonance (NMR) studies on silazanes in order to obtain mechanistic insight into the genesis of the siliconnitride solid ($\beta\text{-Si}_3\text{N}_4$), and some of us have been able to characterize the Si_2N and Si_2O cluster molecules^{4(e)} by neutralization-reionization mass spectrometry (NRMS).⁶ This mass spectrometric technique has been applied successfully for the generation of numerous elusive silicon-containing molecules, which due to the facile intermolecular reactions could not be studied in the condensed phase.⁷

In this publication we wish to report the results of combined experimental and *ab initio* investigations on the hitherto unknown Si_3N cluster and its cationic Si_3N^+ and anionic Si_3N^- counterparts. The cationic and neutral species have

been structurally characterized by collisional-activation and neutralization-reionization mass spectrometry.⁸ High-level *ab initio* methods have been employed for the structural and energetic description of the various experimentally observed neutral, cationic, and anionic Si_nN and Si_n ($n=1-3$) molecules. Calculated structural data of the experimentally observed species will be given together with vibrational spectra to facilitate the spectroscopic observation of these novel molecules.

II. EXPERIMENTAL DETAILS

The collision experiments were performed in a substantially modified zero aberration (ZAB) four sector tandem mass spectrometer with *BEBE* modification (*B* stands for magnetic and *E* for electrostatic analyzer). For a detailed description of the mass spectrometer the reader is referred to previous publications.⁹ For the cluster generation, trisilylamine, $\text{N}(\text{SiH}_3)_3$ was used as the precursor molecule. This compound was prepared via standard literature procedures.¹⁰ Care had to be taken to avoid possible leaks in the inlet system because oxygen traces can lead to sudden explosion of the amine. The sample was introduced into the ion source of the mass spectrometer through a chemical ionization gas inlet system. The cationic cluster could easily be obtained upon dissociative electron impact ionization of $\text{N}(\text{SiH}_3)_3$. The source conditions were as follows: electron energy 50 eV; repeller voltage ~ 30 V; ion source temperature, 200 °C; accelerating voltage 8 kV. The ions of interest were mass selected by means of $(B1)(E1)$. Collision experiments were performed with 80% transmittance (*T*) of the ion beam in order to ensure single-collision conditions. In the case of the collisional activation (CA) mass spectrum, helium was introduced as a collision gas into the second part of a differentially pumped tandem collision cell. For the neutralization-reionization experiments xenon was used as the neutralization agent in the first part of the tandem collision cell. The remaining ions were electrostatically deflected from the beam by means of an electrode (charged to 1000 V) situated between the two collision cells. The neutral molecules were reionized by colliding the beam with oxygen. For a particle $m/z=98$ having been accelerated to 8 keV

energy it takes approximately 6 μ s to travel from the first to the second collision cell, thus providing a lower limit for the minimal lifetime of the neutral molecule. The ionic dissociation products were recorded by scanning the second magnetic analyzer (B2). To improve the signal-to-noise ratio of the spectra the data of 20–50 accumulated scans were on-line processed with an AMD-Intectra data system.

III. COMPUTATIONAL DETAILS

The bond lengths and angles of neutral, cationic and anionic SiN, Si₂N, and Si₃N, as well as Si₂ and Si₃ were optimized by employing analytical gradients¹¹ using the GAUSSIAN 92 program¹² with polarized split-valence basis sets (6-311+G*) (Refs. 13 and 14) at the self-consistent field (SCF) and the MP2(full) level [USCF and UMP2(full) for open shell systems of theory]. Our optimal geometric parameters are presented in Fig. 1 and our simulated IR-spectra based on the MP2(full)/6-311+G* calculated frequencies and their intensities 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 order¹⁵ Møller-Plesset perturbation theory and by the (U)QCISD(T) method¹⁶ using 6-311+G(2df) basis sets. The USCF wave functions for open shell systems were projected to pure spectroscopic states for which the corresponding results are denoted PUSCF, PMP2, PMP3, and PMP4.¹⁷ Calculated reaction energies and available experimental data are presented in Table I.

IV. THEORETICAL RESULTS

A. SiN, SiN⁺, and SiN⁻

The neutral SiN molecule is known to have a doublet $^2\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$) ground electronic state.^{18,19} The lowest excited state $^2\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$) is only 0.25 eV higher in energy.¹⁹ At our highest level [QCISD(T)+ZPE] (where ZPE is the zero-point energy) the $^2\Sigma^+$ state is indeed found to be the ground state and the first excited $^2\Pi_i$ state is 0.35 eV higher in energy. Our calculated bond length $R_e(\text{Si-N})=1.53$ Å for the ground $^2\Sigma^+$ state at the MP2(full)/6-311+G* level is somewhat shorter than the experimental value 1.57 Å.^{18,19} To the best of our knowledge, experimental structural data on SiN⁺ and SiN⁻ are not known.

From the $^2\Sigma^+$ and $^2\Pi_i$ electronic states of the SiN molecule, the two cationic triplet $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$) and $^3\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$) states are expected to be the most stable. Bruna, Peyerimhoff, and Buenker²⁰ (BPB) studied five low-lying $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$), $^3\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$), $^1\Pi$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$), $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4$), and $^1\Delta$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$) electronic states of SiN⁺ using large-scale configuration interaction (CI) calculations and found that the $^3\Sigma^-$ is the most stable and the first $^3\Pi$ state is 0.21 eV higher in energy.²⁰ We repeated the calculations of the both the $^3\Sigma^-$ and $^3\Pi$ states at the MP2(full)/6-311+G* level and our bond lengths $R_e(\text{Si-N})=1.78$ Å ($^3\Sigma^-$) and $R_e(\text{Si-N})=1.65$ Å ($^3\Pi$) reasonably agree with the $R_e(\text{Si-N})=1.81$ Å ($^3\Sigma^-$) and $R_e(\text{Si-N})=1.71$ Å ($^3\Pi$) BPB data.¹³ Our ($^3\Sigma^+ \rightarrow ^3\Pi$) excita-

tion energy (0.13 eV) is also close to the 0.21 eV BPB value. Our first adiabatic ionization energy (IE) for SiN is 10.0 eV at the QCISD(T) level.

The experimental electron affinity is not known for SiN. The lowest singlet anion electronic state $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$) may be derived from either the ground or the first excited electronic state of neutral SiN when an electron is added to the lowest energy available molecular orbital (MO). The isoelectronic SiO molecule has a singlet $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$) ground state with its first excited state lying more than 4 eV higher in energy.¹⁸ Therefore we studied only the $^1\Sigma^+$ state for SiN⁻.

The optimized bond lengths and vibrational frequencies at the MP2(full)/6-311+G* level are 1.63 Å and 1005 cm⁻¹, which agree well with results of Peterson and Woods²¹ $R_e(\text{Si-N})=1.605$ Å and $\omega_e=1092$ cm⁻¹ for SiN⁻ ($^1\Sigma^+$) at the MP4 level. The first adiabatic electron affinity of SiN is found to be 3.36 eV at the PMP4 level and 2.91 eV at the QCISD(T) level, both of which are lower than the experimental electron affinity (EA) (3.821 eV) (Ref. 22) of the valence isoelectronic CN molecule. The electron affinity of SiN, calculated indirectly by Peterson and Woods is 3.32 eV.²¹ Dissociation energies [at the QCISD(T) level] for SiN⁺ into Si⁺+N, SiN into Si+N, and SiN⁻ into Si⁻+N are 52, 96, and 135 kcal/mol, respectively.

B. Si₂N, Si₂N⁺, and Si₂N⁻

The neutral Si₂N molecule and Si₂N⁺ cation were recently observed in mass spectrometric studies,^{4(d)} but to our knowledge, there exist no analogous experimental data on Si₂N⁻, and theoretical data are not available for any of these species.

We optimized the geometry for the cation Si₂N⁺ using the MP2(full)/6-311+G* method starting from an angular C_{2v}(¹A₁) structure with an initial SiNSi angle equal to 140°. We converged to $R_e(\text{Si-N})=1.631$ Å, and a valence angle of Si-N-Si=180°. That is, the optimal structure I (geometry shown in Fig. 1 and simulated IR spectrum in Fig. 2) of SiNSi⁺ is linear D_{∞h} ($^1\Sigma_g^+$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2 1\pi_g^0$), which is different from the isoelectronic SiCSi molecule,^{23,24} which has a singlet bent C_{2v}(¹A₁) structure. Our most favorable dissociation energies [at the QCISD(T) level, see Table I] for Si₂N⁺ is into Si⁺+SiN (+167 kcal/mol).

We optimized the geometry for both linear D_{∞h} ($^2\Pi_g$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2 1\pi_g^1$) and bent C_{2v} (2A_1 : $1a_1^2 1b_2^2 2a_1^2 1b_2^2 3a_1^2 2b_1^2 4a_1^1$) structures of Si₂N. At the MP2(full)/6-311+G* level, the C_{2v} is a minimum (see the structure II in Fig. 1 and the simulated IR spectrum in Fig. 2), but the D_{∞h} ($^2\Pi_g$) structure III has one imaginary frequency whose eigenvector leads to a linear C_{∞v} ($^2\Pi$: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 2\pi^1$) structure IV which is only 0.36 kcal/mol lower in energy at this level of theory. Optimization of the C_{∞v}($^2\Pi$) structure within the MP2(full)/6-311+G* framework gives a minimum with two nonequivalent bond lengths $R_e(\text{Si}_1\text{-N})=1.573$ Å and $R_e(\text{Si}_2\text{-N})=1.694$ Å. The distortion of Si₂N from D_{∞h} into C_{∞v} symmetry at MP2(full) level is due to an artifactual symmetry breaking. For our large 6-311+G(2df) basis sets, the energy of the linear D_{∞h}

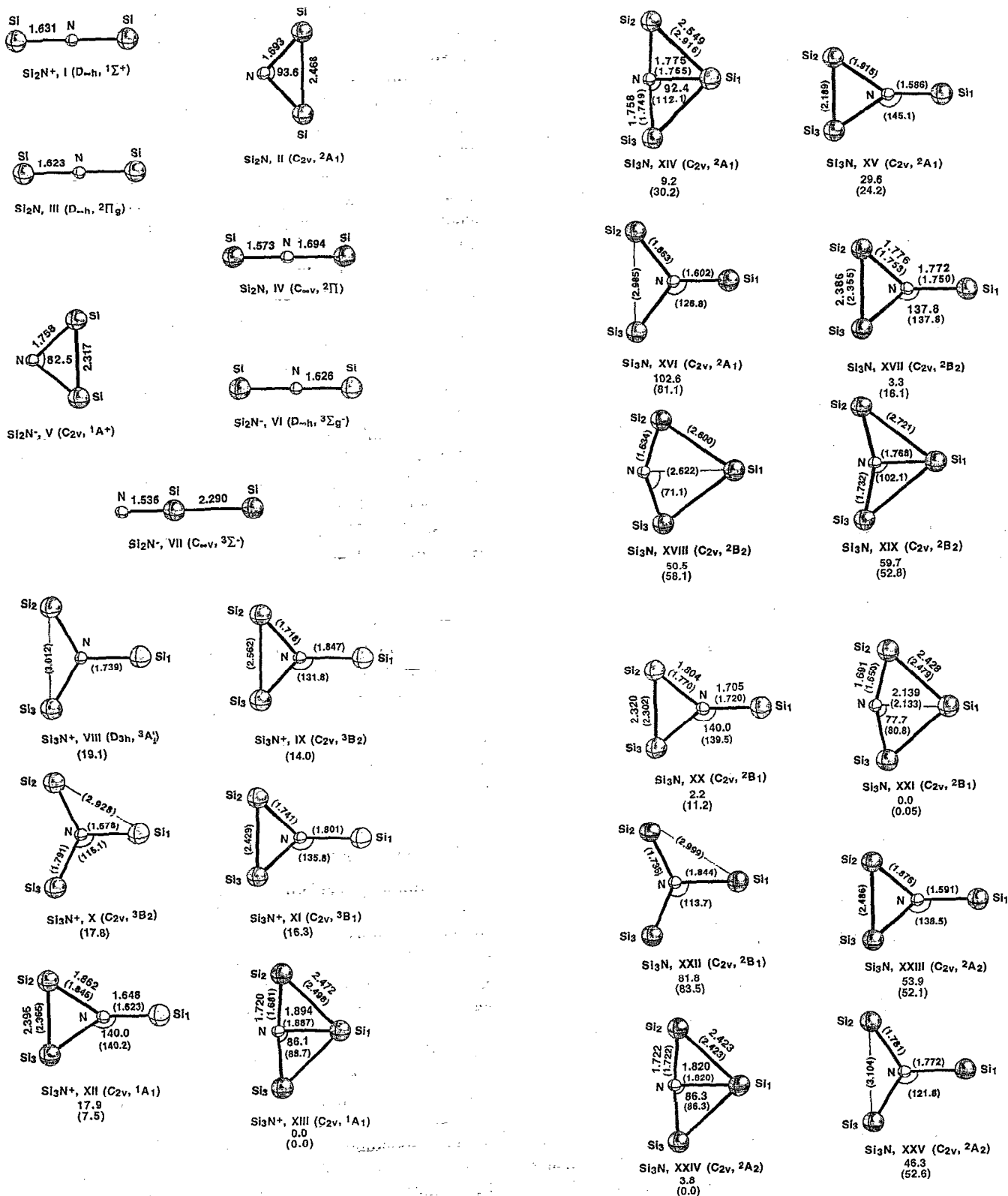


FIG. 1. Computationally optimized geometries at MP2(full)/6-311+G* level of the neutral, cationic and anionic Si_nN and Si_n (n=2,3) species. Geometries at SCF/6-311+G* are given in parentheses. Bond lengths are in Å and bond angles in degrees. Relative energies (in kcal/mol) of Si₃N, Si₃N[±] at the SCF/6-311+G* (in parentheses) and MP2(full)/6-311+G* levels are given under the structures.

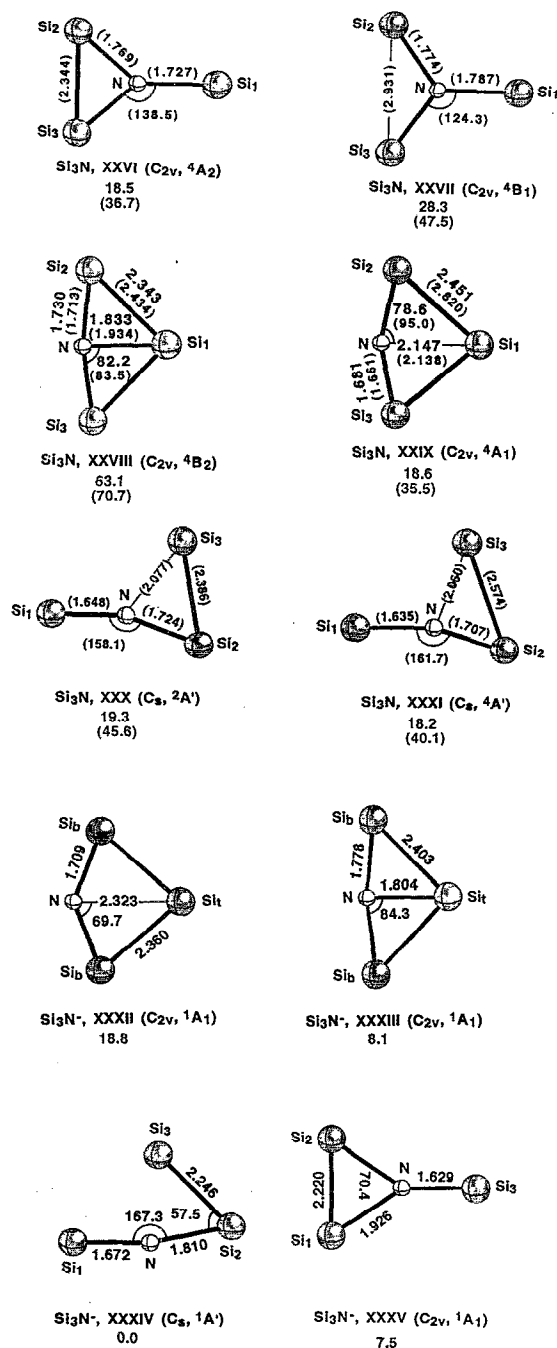


FIG. 1. (Continued.)

structure III is lower at *all* correlated levels [from PMP2 to QCISD(T)] than the $C_{\infty v}$ structure IV using MP2(full)/6-311+G* geometries for both structures. Therefore we optimized the geometry of linear SiNSi at the QCISD(T)/6-311+G* level, where we found no symmetry breaking problem. The linear $D_{\infty h}$ ($^2\Pi_g$) structure is a minimum with $R_e(\text{Si}-\text{N})=1.643$ Å and $\nu_1(\sigma_g)=613$ cm⁻¹, $\nu_2(\pi_u)=221$ cm⁻¹, $\nu'_2(\pi_u)=130$ cm⁻¹, and $\nu_3(\sigma_u)=898$ cm⁻¹ (simulated IR spectrum is shown in Fig. 2). Therefore the global minimum of the Si₂N molecule has a linear $D_{\infty h}$ ($^2\Pi_g$) structure.

Both II and III structures of Si₂N are very close in energy and may coexist in the gas phase. According to our calculations, the energetically favored dissociation path for Si₂N is into SiN+Si (+125 kcal/mol); dissociation into Si₂+N (+152 kcal/mol) is less favorable. Finally, the adiabatic ionization energy of Si₂N is predicted to be 6.2 eV (see Table I).

The Si₂N⁻ anion is isoelectronic with the neutral Si₂O molecule and, according to previous calculations,^{5(b)} the angular C_{2v} (1A_1) structure of Si₂O is the most stable, but two linear SiOSi ($D_{\infty h}$, $^3\Sigma_g^-$) and SiSiO ($C_{\infty v}$, $^3\Sigma_g^-$) structures are 18–27 kcal/mol higher in energy. We optimized the geometry for all of these three structures of Si₂N⁻: V (C_{2v}, 1A_1 : $1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2 2b_2^2 4a_1^2$), VI ($D_{\infty h}$, $^3\Sigma_g^-$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2 1\pi_g^2$) and VII ($C_{\infty v}$, $^3\Sigma_g^-$: $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 2\pi^2$), and found that all three structures are local minima with the singlet V structure being the most stable, as in the case of Si₂O.^{5(b)} However, the linear VI structure is only 5.0 kcal/mol higher in energy at the PMP4/6-311+G(2df) level and 1.7 kcal/mol at the QCISD(T)/6-311+G(2df) level. The VII structure is 39.6 kcal/mol [at the QCISD(T)/6-311+G(2df) level] higher in energy than the most stable V. The geometries of all these structures are presented in Fig. 1 and the simulated IR spectra are shown in Fig. 2.

These energy data indicate that the Si₂N⁻ anion may coexist in two molecular forms in the gas phase. Electron photodetachment experiments of Si₂N⁻ may allow experimental verification of these predictions. Our calculated adiabatic electron affinity is $EA_a(\text{Si}_2\text{N})=1.1$ eV for Si₂N. Our most favorable dissociation energies [at the QCISD(T) level, see Table I] for Si₂N⁺ into Si⁺+SiN, Si₂N into Si+SiN and Si₂N⁻ into SiN⁻+Si are 167, 125, and 80 kcal/mol, respectively.

C. Si₃N, Si₃N⁺, and Si₃N⁻

We initially performed calculations on Si₃N⁺ at the SCF/6-311+G* level and found the high symmetry D_{3h} structure (with $1a_1'^2 1e'^4 2a_1'^2 1a_2'^2 2e'^4 3e'^2$ electronic configuration) to not be a local minimum either in its triplet, or singlet states. The triplet D_{3h} ($^3A'$) structure VIII (Fig. 1) has two imaginary frequencies with two eigenvectors leading to the Y-type structure IX and to the T-type structure X (both have the same electronic configuration: C_{2v} , 3B_2 , $(1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 3b_2^2 5a_1^2)$). The structures IX and X (Fig. 1) are local minimum and saddle point, respectively. The barrier for intramolecular pseudorotation (top of the barrier corresponding to the structure X) is 3.4 kcal/mol at the SCF/6-311+G*+ZPE level. The other triplet (C_{2v} , 3B_1 , $1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 3b_2^2 5a_1^2$) state is a local minimum at the Y-type structure XI. This structure, relative to the IX structure, is 2.4 kcal/mol (at SCF/6-311+G*) higher in energy. However, both of the triplet minima are higher in energy than the singlet surface of the Si₃N⁺ cation.

The high symmetry singlet D_{3h} (1A_1 with $1a_1'^2 1e'^4 2a_1'^2 1a_2'^2 2e'^4 3e'^2$ electronic configuration) structure is not expected to be a minimum because of Jahn–Teller distortion which leads to the Y-type (XII) and the T-type

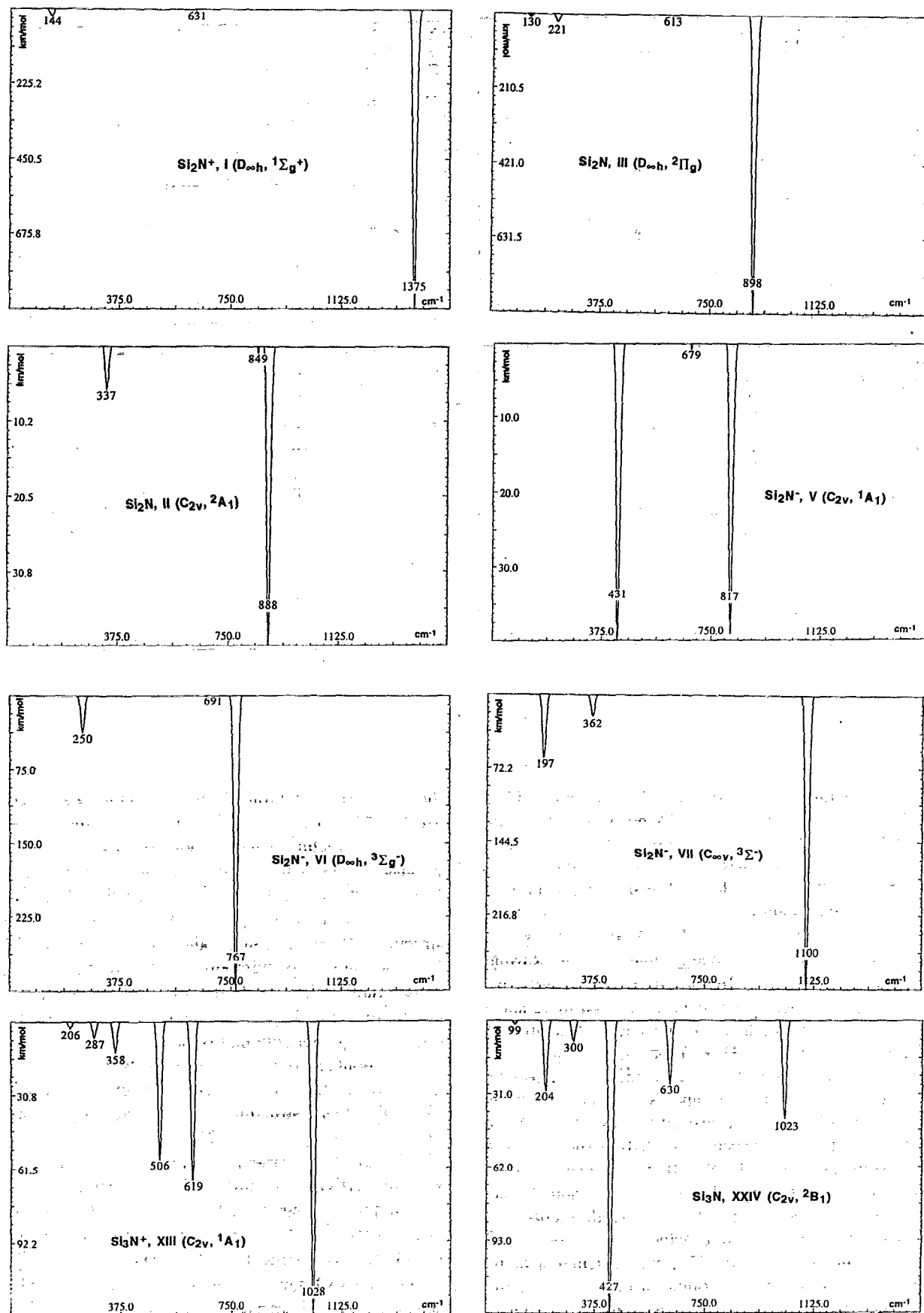


FIG. 2: Simulated calculationally obtained IR spectra of the neutral, cationic, and anionic Si_nN and Si_n ($n=2,3$) species at MP2(full)/level, except structure III of the Si₂N molecule, where calculations were made at QCISD/6-311+G* level (see text).

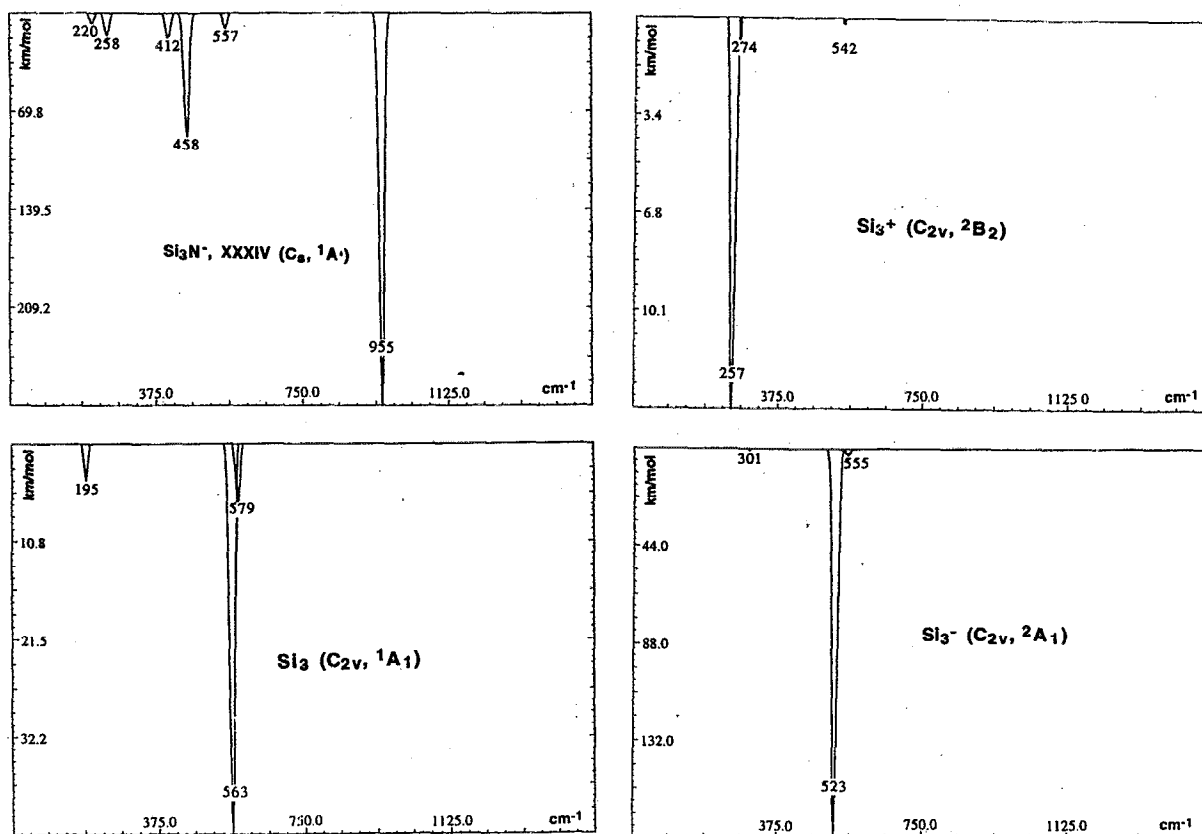


FIG. 2. (Continued.)

(XIII) of structures. The singlet XII structure (C_{2v} , $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_2^2 4a_1^2 2b_2^2 5a_1^2$) is found to be a saddle point, whereas the singlet XIII structure (C_{2v} , $1a_1^2 1b_2^2 2a_1^2 1b_2^2 3a_1^2 2b_2^2 4a_1^2 3b_2^2$) is a global minimum for Si₃N⁺ at the SCF/6-311+G* level. The barrier for intramolecular pseudorotation is 7.0 kcal/mol (SCF/6-311+G*+ZPE). At the SCF level, the singlet potential energy surface is lower in energy than the lowest triplet 3B_2 potential energy surface by more than 10 kcal/mol. Because the singlet surface is expected to be even more stable at correlated levels, we studied only the singlet structures XII and XIII at the MP2(full)/6-311+G* level.

We optimized the geometry and calculated the harmonic frequencies for the singlet XII and XIII structures at the MP2(full)/6-311+G* level. These structures are shown in Fig. 1 and the vibrational spectrum of XIII is shown in Fig. 2. At MP2(full)/6-311+G* level, XIII is a global minimum (similar to the isoelectronic Si₃C molecule^{25,26}) and XII is a saddle point. However, at this level the pseudorotation barrier is substantial [17.3 kcal/mol including ZPE correction]. The global minimum structure XIII was calculated at the QCISD(T) and PMP4 levels to obtain a more accurate dissociation energy. According to our calculations, among all possible dissociational channels Si₃N⁺ into Si+Si₂N⁺ [66 kcal/mol at QCISD(T) see Table I] has the lowest energy.

From the order of the orbitals in Si₃N⁺ (D_{3h}), we pre-

dict that the neutral Si₃N molecule has occupation $1a_1'^2 1e'^4 2a_1'^2 1a_2'^2 2e'^4 3e'^3$ in the high symmetry D_{3h} ($^2E'$) structure, which is not expected to be a minimum because of the Jahn-Teller distortion, which leads to the Y-type (2B_2 , $1a_1'^2 2a_1'^2 1b_2'^2 3a_1'^2 1b_2'^2 4a_1'^2 2b_2'^2 5a_1'^2 3b_2'^2 1a_2'^2$) and T-type (2A_1 , $1a_1'^2 2a_1'^2 1b_2'^2 3a_1'^2 1b_2'^2 4a_1'^2 2b_2'^2 5a_1'^2 3b_2'^2 2b_1'^2 1a_2'^2$) structures. Because orbitals other than the $5a_1$ and $3b_2$ low-lying orbital may play important roles, we further studied all configurations obtained by distributing three electrons among the $5a_1$, $3b_2$, $2b_1$, and $1a_2$ low-lying orbitals with doublet or quartet coupling of spins.

The doublet coupling leads to twelve states: C_{2v} symmetry 2A_1 ($5a_1^1 3b_2^2 2b_1^0 1a_2^0$, structure XIV), 2A_1 ($5a_1^1 3b_2^0 2b_1^1 1a_2^0$, structure XV), 2A_1 ($5a_1^1 3b_2^0 2b_1^0 1a_2^2$, structure XVI), 2B_2 ($5a_1^1 3b_2^1 2b_1^0 1a_2^0$, structure XVII), 2B_2 ($5a_1^0 3b_2^1 2b_1^1 1a_2^0$, structure XVIII), 2B_2 ($5a_1^0 3b_2^1 2b_1^0 1a_2^2$, structure XIX), 2B_1 ($5a_1^2 3b_2^0 2b_1^1 1a_2^0$, structure XX), 2B_1 ($5a_1^0 3b_2^2 2b_1^1 1a_2^0$, structure XXI), 2B_1 ($5a_1^0 3b_2^0 2b_1^1 1a_2^2$, structure XXII), 2A_2 ($5a_1^2 3b_2^0 2b_1^0 1a_2^1$, structure XXIII), 2A_2 ($5a_1^0 3b_2^2 2b_1^0 1a_2^1$, structure XXIV), and 2A_2 ($5a_1^0 3b_2^0 2b_1^2 1a_2^1$, structure XXV). Quartet coupling of the spins leads to four states: 4A_2 ($5a_1^1 3b_2^1 2b_1^1 1a_2^0$, structure XXVI), 4B_1 ($5a_1^1 3b_2^1 2b_1^0 1a_2^1$, structure XXVII), 4B_2 ($5a_1^1 3b_2^0 2b_1^1 1a_2^1$, structure XXVIII), 4A_1 ($5a_1^0 3b_2^1 2b_1^1 1a_2^1$, structure XXIX). The optimal geometries and relative energies of all of these

structures at the SCF/6-311+G* level are presented in Fig. 1. According to the SCF/6-311+G* calculations, XXI is the global minimum but a few other structures lie within a few kcal/mol.

At SCF/6-311+G* level, XV, XVI, XVII, XX, XXI, XXII, XXV, XXVI, XXVII, and XXVIII are local minima, XIV, XIX, XXIII, XXIV, XXIX are first order saddle points, and XVIII is second order saddle point. Our search for the global minimum was subsequently expanded to C_s symmetry structures and four additional doublet ($^2A'$ and $^2A''$) and quartet ($^4A'$ and $^4A''$) structures were studied at the SCF/6-311+G* level. The $^2A''$ state collapsed to XX or XXI depending on the starting geometry. The $^2A'$ state has a local minimum with the structure XXX (Fig. 1), but this lies 19.3 kcal/mol higher in the energy than global minimum at this level. The $^4A''$ state converges to the lowest quartet structure XXVI and $^4A'$ state has a local minimum with the structure XXXI (Fig. 1) 18.2 kcal/mol higher in energy than global minimum.

Several of the lowest energy structures (XIV, XVII, XX, XXI, XXIV, XXVIII, and XXIX) identified as detailed above, have been optimized at the MP2(full)/6-311+G* level (Fig. 1) and the relative energies of the rest of the structures have been calculated at MP2(full)/6-311+G* level using UHF/6-311+G* geometry. According to our calculations, XXI and XXIV has the lowest energies at MP2 level. The XXIV (C_{2v} , 2A_2) structure is predicted to be the lowest, with the XXI (C_{2v} , 2B_1) only 0.05 kcal/mol [MP2(full)/6-311+G*] higher in energy. However, only the XXI structure is a true minimum (its geometry is shown in Fig. 1 and its simulated IR spectrum is presented in Fig. 2) while the XXIV structure is a saddle point, whose eigenvector of imaginary frequency produces an in-plane distortion. Further geometry optimization of this Si₃N structure within C_s symmetry was not successful due to poor SCF convergence. However, we do not expect structures with C_s symmetry will differ much in energy from the energy of XXIV.

Both neutral Si₂N and Si₃N species have two isomers that differ by only a few kcal/mol which is different from Si₂C, Si₃C, and Si₂O, Si₃O, where the ground state structure is well separated in energy from other structures.

Our computed adiabatic ionization energy of Si₃N is 6.3 eV and the most energetically favored dissociation energy is 73 kcal/mol into Si₂N+Si, which is much lower than the dissociation energy of Si₂N into SiN+Si (see Table I). All these number should be considered as a preliminary estimate.

Based on the energy ordering of the neutral Si₃N molecule at MP2(full)/6-311+G* level (Fig. 1), we studied two low-lying anionic states of Si₃N⁻: structure XXXIII (C_{2v} , 1A_1 : $1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^2 1a_2^2$) and structure XXXIII (C_{2v} , 1A_1 : $1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 4a_1^2 3b_2^2 2b_1^2$) (geometries are presented in Fig. 1). However, both of these structures are found to not correspond to local minima. The XXXII structure has two imaginary frequencies and XXXIII has one imaginary frequency. The latter structure is lower in energy and its eigenvector of imaginary frequency produces an in-plane distortion. Geometry optimization of the Si₃N⁻ starting within C_s symmetry produces the global minimum structure XXXIV (C_s , $^1A'$) structure whose geometry is pre-

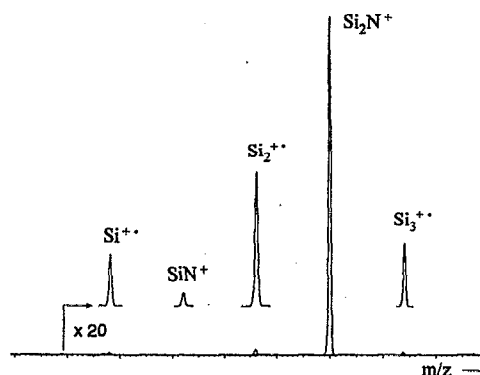


FIG. 3. Collisional activation (CA) mass spectrum of Si₃N⁺ [collision gas helium; 80% transmission (T)].

sented in Fig. 1 and the simulated IR spectrum is shown in Fig. 2. The final XXXIV geometry of Si₃N⁻ can be considered as a chain Si₁NSi₂Si₂ structure. The barrier (XXXIII structure) on the intramolecular rearrangement of the Si₃N⁻ anion from one XXXIV structure into another is not high (8 kcal/mol at MP2(full)/6-311+G*). The structure XXXV (C_{2v} , 1A_1 , $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^2 2b_2^2 5a_1^2 2b_1^2$) is a saddle point with an even lower barrier (7.5 kcal/mol) for the intramolecular rearrangement of the Si₃N⁻ anion from one XXXIV structure into another.

Our computed adiabatic EA_a(Si₃N) is predicted to be 1.4 eV. The dissociation energies [at QCISD(T) see Table I] for Si₃N⁻ into Si⁻+Si₂N is 78 kcal/mol.

We also optimized Si₂⁺, Si₂, Si₂⁻, Si₃⁺, Si₃, and Si₃⁻ (simulated vibrational spectra for Si₃⁺, Si₃, and Si₃⁻ are shown in Fig. 2), because we needed to know the energies of these species at a consistent level of accuracy for the calculations of different dissociation channels of the Si_nN neutral and ionic species. All of these silicon clusters have been previously studied experimentally^{27,28} and theoretically,²⁹ and our results for the silicon dimer and trimer agree well with the previous calculations and available experimental data.

V. MASS SPECTROMETRIC RESULTS

In order to obtain structural information, the Si₃N⁺ cations were subjected to a collisional activation (CA) experiment. The resulting fragmentation pattern, obtained upon colliding the 8 keV cluster ions with helium atoms, is shown in Fig. 3.

The base peak in the CA spectrum corresponds to the loss of a neutral silicon atom. This Si₂N⁺ fragment (m/z = 70) contributes to approximately 96% of the total intensity of the fragmentation processes.³⁰ In addition to this greatly favored dissociation process, weak signals for the losses of N, SiN, and Si₂N are observed (see the twenty fold enlarged region of Fig. 3.). The ionic fragments correspond to Si₃⁺ (m/z 84), Si₂⁺ (m/z 56), and Si⁺ (m/z 28), respectively. Furthermore the collisional activation process leads to a rather small fraction of SiN⁺ fragments (m/z 42).

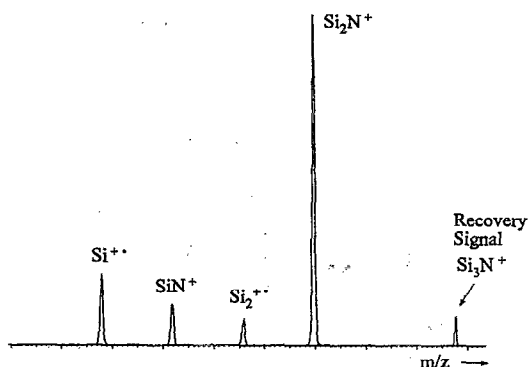


FIG. 4. Neutralization-reionization (NR) mass spectrum of Si₃N⁺ (xenon, 80% T; oxygen 80% T).

For further insight into the connectivity of the Si₃N⁺ cluster ion and to prove the existence of the neutral Si₃N molecule the cation was subjected to a neutralization-reionization experiment, and the resulting NR spectrum is given in Fig. 4.

The NR spectrum displays some distinct differences when compared to the results of the CA experiment. The presence of a recovery signal for the reionized Si₃N⁺ cations clearly demonstrates that the neutral Si₃N cluster is a viable species in the gas phase. The overall fragmentation pattern is similar to that observed in the CA process. The Si₂N⁺ ion contributes strongest to the total ion current. However, a considerably stronger fragmentation of the reionized Si₃N⁺ into Si₂⁺, SiN⁺, and Si⁺ can be found. In contrast to the CA mass spectrum (Fig. 3), no signal at *m/z* 84 that would correspond to the Si₃⁺ cation is observed at the detection limit of the machine.

VI. DISCUSSION

According to our calculations, Si₂N, Si₂N⁻, and Si₃N form two stable isomers (linear and cyclic) that differ in energy only by few kcal/mol, so both may coexist in the gas phase. The Si₂N⁺, Si₃N⁺, and Si₃N⁻ clusters form only one very stable structure, so these species should have a single isomer in the gas phase.

The theoretical results predict the most stable Si₃N⁺ cluster to possess a planar rhombic C_{2v} structure [MP2(full)/6-311+G*]. In this ¹A₁ state, the three silicon atoms do not have identical Si-N bond lengths. Rather, two of the silicon atoms are bonded equivalently (*R*_e(Si-N)=1.720 Å), and the third silicon atom is coordinated to the nitrogen atom by a considerably longer bond (1.894 Å). The results of the mass spectroscopic experiments can be rationalized by comparing the relative abundance's of the fragment ions with the theoretically derived reaction energies (see Table I). The calculated values predict the fragmentation process of Si₃N⁺ into Si₂N⁺ and Si to be highly favored energetically. This decomposition pathway is favored over the next lowest lying reaction channel (fragmentation into Si₂N and Si⁺) by 45 kcal/mol [the Δ*E* values are all taken from the results at QCISD(T) calculations]. The

process Si₃N⁺→Si₂N⁺+Si can be viewed upon as a simple silicon atom evaporation from the cluster molecule Si₃N⁺. All other fragmentation channels were calculated to be significantly higher in energy. These results are in excellent agreement with the experimental behavior of this ion as the Si₂N⁺ ion accounts for 96% of the total ion current in the CA process. Nitrogen extrusion from Si₃N⁺ to produce the cyclic Si₃⁺ (C_{2v}, ²B₁) requires 60 kcal/mol more than the Si₂N⁺+Si formation. The CA spectrum displays only a very weak signal for this process. In the lower mass region of the spectrum, signals for Si₂⁺, SiN⁺, and Si⁺ are observed. The reaction energies for these processes were calculated to lie 92, 143, and 45 kcal/mol higher in energy than the corresponding lowest channel. The "strong" abundance of the Si₂⁺ signal relative to Si⁺ and SiN⁺, can be rationalized by an additional contribution of secondary fragmentation reactions of Si₃⁺ and Si₂N⁺ that can form Si₂⁺ upon collisional activation.

The weak SiN⁺ signal agrees well with the energetic predictions as this reaction channel requires 143 kcal/mol more than the Si₂N⁺ formation. The extrusion of a nitrogen cation that leads to the formation of the cyclic Si₃ species (C_{2v}, ¹A₁), requires 251 kcal/mol more energy than process 1 and cannot be detected at all. Thus, the overall fragmentation pattern is in satisfying agreement with the expectation based on the theoretical values.

The Si₂N radical was found to form two different isomers that differ in energy only by a few kcal/mol. The linear SiNSi structure was predicted to be the global minimum, whereas the cyclic structure lies only 4.5 kcal/mol higher.

The NR spectrum gives rise to a relatively small intensity for the survivor ion; this observation points towards quite unfavorable Franck-Condon factors for the charge transfer processes.^{30,31} The lowest energy requiring fragmentation of Si₃N is, in analogy to the cationic cluster molecule, silicon atom extrusion accompanied by formation of the Si₂N radical. The reaction energy for the formation of Si₂N and Si was calculated to be only 73 kcal/mol. The next accessible reaction channel (Si₃N→Si₂+SiN) requires 53 kcal/mol more than this process. Thus, again in agreement with the experimental results, the reionized Si₂N⁺ species represents the major dissociation pathway. In contrast to the fragmentation in the CA process, the NR spectrum does not give rise to Si₃⁺ ions. This observation points to the fact that the NR spectrum may be viewed as a superposition of the two mass spectra of Si⁺ and Si₂N⁺.

VII. CONCLUSIONS

The cationic and neutral Si₃N cluster molecules have been characterized by mass-spectrometric techniques. Their fragmentation behavior in high energy collision experiments corresponds well with the theoretical predictions. High-level *ab initio* calculations have been used to describe the energetic and structural features of these new molecules. In addition, all experimentally observed ionic and neutral fragment molecules (Si₂N, SiN, Si₃, Si₂) have been theoretically characterized and their vibrational spectra are reported in order to assist their future infrared spectroscopic characterization.

According to our calculations, the Si₂N and Si₃N molecules form two isomeric structures that differ by a few kcal/mol which may coexist in the gas phase, while the other clusters (Si₂C, Si₃C, Si₂O, and Si₃C) possess one preferred structure.

Upon completion of this work, we have ascertained that Morse and Brugh have determined³² that ground electronic state of Si₂N has linear structure with the ²Π_g ground electronic state. Their preliminary equilibrium bond length $R_e(\text{Si-N})$ is 1.639 Å is very close to our value $R_e(\text{Si-N})=1.631$ Å at MP2(full)/6-311+G* and $R_e(\text{Si-N})=1.643$ Å at QCISD/6-311+G* levels.

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