

Negative Ion Photoelectron Spectroscopy of SiN<sup>-</sup> †

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Negative ion photoelectron spectra of SiN<sup>-</sup> have been recorded using the 355 nm (3.493 eV) and 266 nm (4.661 eV) photodetachment wavelengths. The spectra exhibit resolved vibrational features corresponding to transitions to the X <sup>2</sup>Σ<sup>+</sup> and A <sup>2</sup>Π states of SiN. Franck–Condon analyses yield the first experimental spectroscopic parameters,  $r_e$  and  $\omega_e$ , for the anion ground state, X <sup>1</sup>Σ<sup>+</sup>. We also determined the first experimental adiabatic electron affinity as 2.949 ± 0.008 eV. The anion dissociation energy  $D_0(\text{SiN}^-)$  is then obtained from the electron affinities of Si and SiN and the dissociation energy of the neutral.

## 1. Introduction

Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is a material of considerable interest because of its remarkable properties such as strength, hardness, chemical inertness, good resistance to wear and corrosion, high thermal stability, and good dielectric properties.<sup>1</sup> This combination of properties makes Si<sub>3</sub>N<sub>4</sub> a very attractive high-performance engineering material. For instance, its low density, 40% less than those of high-temperature superalloys, may offer components with lower weight and inertia, which would improve the performance of engines. Another important characteristic is the universal abundance and consequent low cost of the elements silicon and nitrogen in contrast with the short supply and increasing costs of metals for high-temperature alloys such as chromium, cobalt, nickel, and tungsten.<sup>1</sup>

Numerous studies of silicon nitride have been performed<sup>2–7</sup> to characterize many properties of the bulk, but only a few spectroscopic investigations have been carried out to study the electronic structure of its molecular subunits. In this paper we present an experimental study on the low-lying electronic states of SiN<sup>-</sup> and SiN using negative ion photoelectron spectroscopy (PES). A major advantage of anion PES over optical spectroscopy studies is that the transition selection rules are less restrictive. In principle all one-electron transitions are allowed; for instance, this enables us to access both doublet and quartet states from the photodetachment of a triplet electronic state. Moreover, mass selection allows us to unambiguously isolate the ion of interest. Anion PES has been successfully applied in our group to gain information on electron affinities, term energies, and vibrational frequencies for many diatomics such as CN,<sup>8</sup> BN,<sup>9</sup> AlP, GaP, InP, and GaAs.<sup>10</sup>

Emission spectra assigned to the SiN radical have been observed by many investigators, starting with experiments by Jevons<sup>11</sup> in 1913 and Mulliken<sup>12</sup> in 1925. The  $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$  transition, with its band origin at 24299 cm<sup>-1</sup>, has been well understood for some time. However, characterization of the lower lying A <sup>2</sup>Π state proved more difficult. Bredohl et al.<sup>13</sup> explored the emission spectrum of SiN and gave an approximate term energy ( $T_e$ ) of 8000 cm<sup>-1</sup> for the A <sup>2</sup>Π<sub>Q</sub> electronic state.

A much smaller value, 994 cm<sup>-1</sup>, was obtained by analysis of  $B\ ^2\Sigma^+ - A\ ^2\Pi$  emission by Foster<sup>14</sup> and  $A\ ^2\Pi - X\ ^2\Sigma^+$  absorption by Yamada and Hirota.<sup>15</sup> The value of  $T_e$  from the absorption experiment relied on the assignment of a band around 2000 cm<sup>-1</sup> to the 1–0 vibronic transition between the A and X states. In a subsequent experiment by Yamada et al.,<sup>16</sup> this band was reassigned to the 0–0 transition on the basis of isotope shifts, yielding  $T_e = 2032.4\ \text{cm}^{-1}$  for the A state. On the basis of this assignment, Foster<sup>17</sup> performed a global fit of term energies and vibrational frequencies of the ground and several excited states of SiN.

Saito et al.<sup>18</sup> detected the microwave absorption spectrum of SiN, from which an equilibrium distance ( $r_e$ ) of 1.5721 Å for the ground electronic state is obtained. Naulin et al.,<sup>19</sup> through a pulsed crossed molecular beam study of the Si + N<sub>2</sub>O → SiN + NO reaction, determined the bond dissociation energy of 4.68 eV for SiN, which compares well with the Gaussian-2 theory value of 4.58 eV by Curtiss et al.<sup>20</sup>

Several calculations have been performed on the ground and excited electronic states of SiN.<sup>21–27</sup> In particular, a detailed investigation on SiN was carried out by Cai et al.,<sup>23</sup> who calculated the spectroscopic molecular parameters ( $r_e$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $\omega_e y_e$ , rotational constants ( $B_e$ ), centrifugal distortion constants ( $D_e$ ), dipole moments ( $\mu_0$ ),  $T_e$ , and dissociation energies ( $D_0$ )) for 11 bound doublet states and 10 bound quartet states of SiN. They used the internally contracted multireference configuration interaction (CMRCI) level of theory with Dunning's correlation-consistent polarization valence quadruple- $\zeta$  (cc-pVQZ) basis set to study the potential energy curves for the low-lying electronic states.

Less is known about the anion SiN<sup>-</sup>. There is no experimental determination of the electron affinity (EA). Peterson and Woods<sup>21</sup> calculated the EA of SiN as 3.33 eV using the Møller–Plesset perturbation theory with single, double, and quadruple substations (MP4SDQ). Kalcher<sup>25</sup> employed the complete active space in conjunction with the averaged coupled pair functional approach (CAS–ACPF) with the cc-pVQZ basis set to investigate trends in ground and excited electronic states of group 14, 15, and 16 mixed diatomic anions. He computed an EA of 2.862 eV and also calculated a bound excited <sup>3</sup>Σ<sup>+</sup> state of SiN<sup>-</sup> lying only 0.341 eV below the SiN <sup>2</sup>Σ<sup>+</sup> ground state. SiN and SiN<sup>-</sup> are isovalent with CN and CN<sup>-</sup>, and have the same

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ordering of electronic states. However, no calculations have found CN<sup>-</sup> to have any stable excited electronic states.

In this investigation, we used negative ion PES to examine the electronic structure of the ground and low-lying excited electronic states of SiN. The PE spectrum provides a straightforward confirmation of the A <sup>2</sup>Π state term value. We obtain the first experimental value of the EA(SiN), and using this result, we derive the SiN<sup>-</sup> dissociation energy. With the aid of a Franck–Condon (FC) simulation we determine the equilibrium bond distance and vibrational frequency of the ground electronic state of the anion SiN<sup>-</sup>. We also tentatively assigned a minor peak in the PE spectra to a transition between the first excited state of SiN<sup>-</sup> (<sup>3</sup>Σ<sup>+</sup>) and the <sup>4</sup>Π<sub>Q</sub> state, on the basis of the calculated relative energetics of these states and electronic configuration considerations.

## 2. Experiment

Details of the anion time-of-flight (TOF) PES apparatus used in this study have been described previously.<sup>28,29</sup> SiN anions are generated using a pulsed laser ablation molecular beam source. The second harmonic output (532 nm, 10–15 mJ/pulse) of a pulsed Nd:YAG laser operated at 20 Hz is focused through a 35 cm focal lens onto a rotating and translating pure silicon nitride disk (Crystallog Inc.). The resulting plasma is entrained into a pulsed supersonic beam of Ar. The gas pulse then enters a linear reflectron TOF mass spectrometer, where the negative ions are extracted perpendicular to their flow direction by a pulsed electric field and accelerated to 2.5 keV beam energy. The mass resolution  $m/\Delta m$  is approximately 2000.

The chosen ion is then selectively photodetached by a pulsed fixed-frequency Nd:YAG laser using the third (355 nm or 3.493 eV) and fourth (266 nm or 4.661 eV) harmonics. Photoelectrons are collected perpendicularly to the ion and laser beam plane, and the electron kinetic energy (eKE) distribution is determined by TOF analysis in a 1 m field-free flight tube. We calibrate the eKE scale using the PE spectra of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> at 266 nm photon wavelength, and O<sub>2</sub><sup>-</sup> at 355 nm photon wavelength. The energy resolution is 8–10 meV at 0.65 eV eKE and degrades as (eKE)<sup>3/2</sup> at higher eKE.

All PE spectra presented here are plotted as a function of the electron binding energy (eBE) defined as

$$\text{eBE} = h\nu - \text{eKE} = \text{EA} + E^{(0)} - E^{(-)} \quad (1)$$

where  $h\nu = 3.493$  or  $4.661$  eV is the photodetachment energy,  $E^{(0)}$  is the internal energy of the neutral, and  $E^{(-)}$  is the internal energy of the anion.

This anion TOF PES apparatus also yields the angular distribution of the detached photoelectrons. The PE spectra were taken at two laser polarization angles, 0° and 90°, with respect to the direction of the electron detection. This angle can be varied using a half-wave plate. The angular distribution of the photoelectrons is given by<sup>30</sup>

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[ 1 + \frac{\beta}{2}(3 \cos^2 \theta - 1) \right] \quad (2)$$

where  $\theta$  is the angle between the laser electric field and the direction of electron detection,  $\sigma_{\text{total}}$  is the total photodetachment cross section, and  $\beta$  is the anisotropy parameter, which varies from -1 to +2. Each neutral  $\leftarrow$  anion electronic transition has a characteristic  $\beta$  that can be used to distinguish peaks of

overlapping electronic transitions, and can be calculated using

$$\beta = \frac{I_{0^\circ} - I_{90^\circ}}{1/2 I_{0^\circ} + I_{90^\circ}} \quad (3)$$

where  $I_{0^\circ}$  and  $I_{90^\circ}$  are the intensities of the peak taken at  $\theta = 0^\circ$  and  $90^\circ$ .

## 3. Results

The 355 and 266 nm photoelectron spectra of SiN<sup>-</sup> taken at laser polarization angles  $\theta$  of 90° and 0° are displayed in Figure 1. The PE signal is plotted in terms of eBE. Anisotropy parameters  $\beta$  were determined for selected bands and are indicated by the solid black diamonds on the top panel of Figure 1. Peak positions are listed in Table 1.

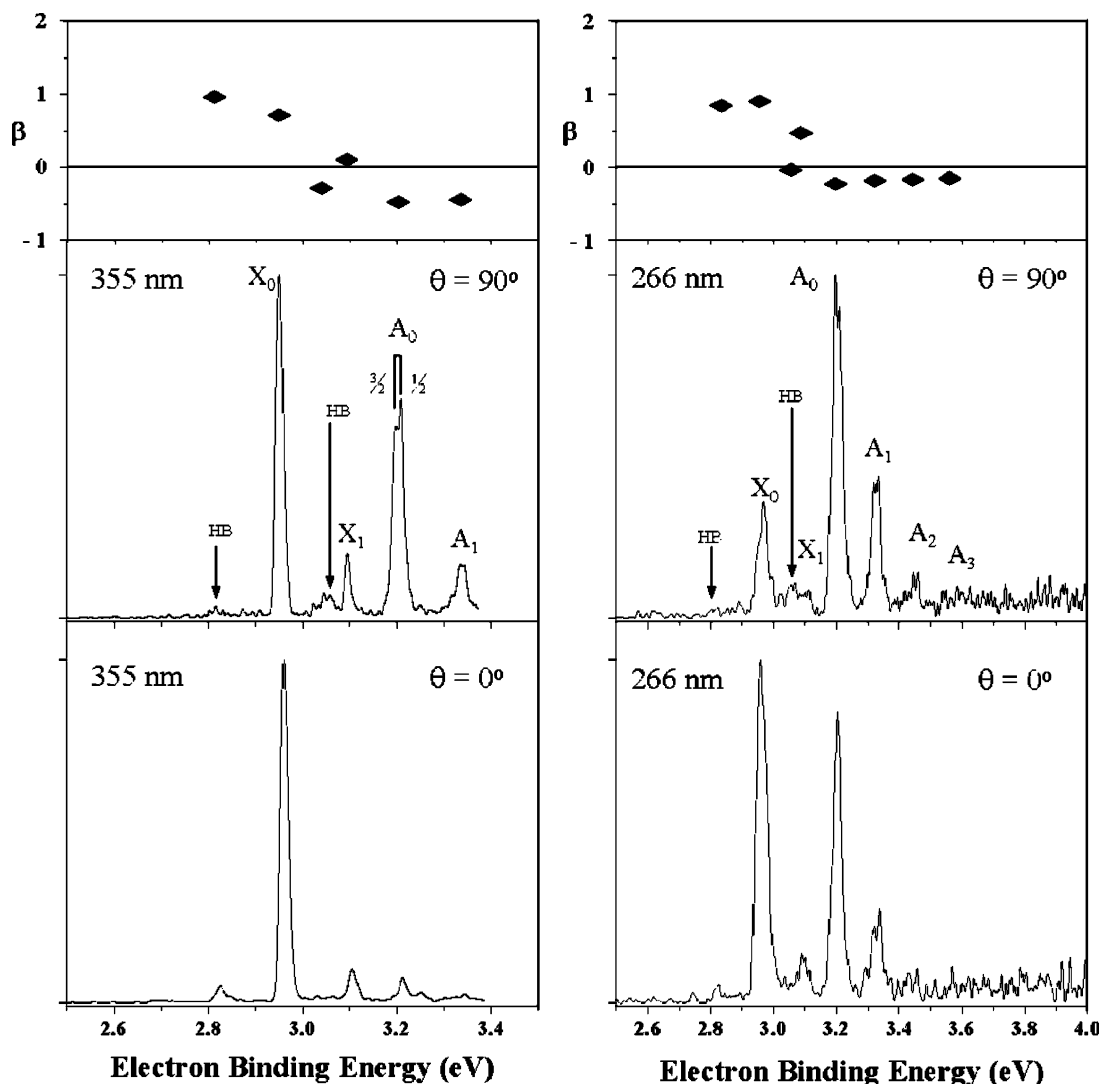
The 355 nm spectrum at 90° shows four main peaks labeled X<sub>0,1</sub> and A<sub>0,1</sub>. The two most intense peaks, X<sub>0</sub> and A<sub>0</sub>, have very different anisotropy parameters of 0.7 and -0.5, respectively, and appear to be vibrational origins of two electronic transitions, while peaks X<sub>1</sub> and A<sub>1</sub> are transitions to vibrationally excited levels within the two electronic bands. The 266 nm spectra reveal many of the same peaks seen in the 355 nm spectra but with lower resolution because of higher electron kinetic energy. Two additional peaks, A<sub>2</sub> and A<sub>3</sub>, are observed. Peaks A<sub>0</sub>–A<sub>3</sub> are equally spaced and have the same  $\beta$  parameter, and thus appear to represent a vibrational progression in a single electronic band.

In the 355 nm spectrum, peaks X<sub>0</sub> and A<sub>0</sub> are spaced by 2010 cm<sup>-1</sup>, very close to the accepted splitting between the X <sup>2</sup>Σ<sup>+</sup> and A <sup>2</sup>Π states of SiN.<sup>16,17</sup> Moreover, peak A<sub>0</sub> appears to comprise two partially resolved peaks split by 90 cm<sup>-1</sup>, in good agreement with the spin–orbit coupling constant of -89.097 cm<sup>-1</sup><sup>15</sup> for the SiN A <sup>2</sup>Π state. The SiN<sup>-</sup> anion is predicted to have an X <sup>1</sup>Σ<sup>+</sup> ground state with no excited states lying nearby, so we assign peaks X<sub>0</sub> and A<sub>0</sub> to the vibrational origins of the X <sup>2</sup>Σ<sup>+</sup>  $\leftarrow$  X <sup>1</sup>Σ<sup>+</sup> and A <sup>2</sup>Π  $\leftarrow$  X <sup>1</sup>Σ<sup>+</sup> transitions. Since peak X<sub>0</sub> occurs at eBE = 2.95 eV, this is the approximate electron affinity of SiN. Peaks X<sub>0</sub> and X<sub>1</sub> are spaced by 1160 cm<sup>-1</sup>, while A<sub>0</sub> and A<sub>1</sub> are spaced by 1060 cm<sup>-1</sup>; these should be the vibrational fundamental frequencies of the X <sup>2</sup>Σ<sup>+</sup> and A <sup>2</sup>Π states, respectively, and are indeed very close to the literature values.<sup>17</sup>

There are two smaller peaks in the spectra at eBE = 2.81 and 3.04 eV. Each lies at 1100 cm<sup>-1</sup> lower eBE from one of the vibronic origin peaks, X<sub>0</sub> or A<sub>0</sub>, and has the same anisotropy parameter at that origin peak. These features are assigned to anion vibrational hot bands, yielding an anion vibrational frequency of approximately 1100 cm<sup>-1</sup>, and each is labeled HB in Figure 1. There appears to be an additional small feature, labeled a (see Figure 2), at slightly lower eBE than the hot band at 3.04 eV. At both wavelengths, this feature has the same anisotropy parameter as the peaks A<sub>n</sub>. Its possible assignment is discussed below.

## 4. Analysis and Discussion

To extract additional and more precise information on the anion and neutral, the PE spectrum was simulated within the Franck–Condon approximation. Within each electronic band, the vibrational transitions have intensities proportional to their FC factors,  $|\langle Y_{\nu'} | \Psi_{\nu} \rangle|^2$ , where  $\Psi_{\nu'}$  and  $\Psi_{\nu}$  are neutral and anion Morse oscillator wave functions, respectively. An anion vibrational temperature of 1000 K was assumed in the simulations.



**Figure 1.** Anion photoelectron spectra of  $\text{SiN}^-$  taken at 355 and 266 nm with the laser polarization angle  $\theta = 90^\circ$  and  $0^\circ$ . The values of the asymmetry parameters  $\beta$  are indicated by the solid black diamonds above the PE spectra for selected bands.

**TABLE 1: Franck–Condon Simulation Optimized Parameters,  $r_e$  (Å),  $\omega_e$  ( $\text{cm}^{-1}$ ), and  $T_e$  ( $\text{cm}^{-1}$ )<sup>a</sup>**

species	band	band origin	state	$r_e$	$\omega_e$	$T_e$	$T_{\text{vib}}$
$\text{SiN}^-$			$X^1\Sigma^+$	$1.604 \pm 0.005$	$1130 \pm 20$	0.000	1000
SiN	X	2.949	$X^2\Sigma^+$	$1.572^b$	$1151^b$	0.000	1000
	A	3.198	$A^2\Pi_{3/2}$	$1.642^c$	$1032^d$	$(2008 \pm 65) + \frac{1}{2}A_e^e$	1000

<sup>a</sup> The band origin is in electronvolts. <sup>b</sup> Reference 16. <sup>c</sup> Reference 15. <sup>d</sup> Reference 14. <sup>e</sup>  $A_e$  was taken from Yamada and Hirota<sup>15</sup> as  $89.097 \text{ cm}^{-1}$ .

This value was chosen to reproduce the hot band intensities in the PE spectra, and it does not have any effect on the determination of the energetics and molecular parameters. Such a high vibrational temperature is not uncommon in laser ablation experiments in which conditions are optimized for the production of diatomic anions, as was seen in our previous study of  $\text{C}_2^-$ .<sup>31</sup>

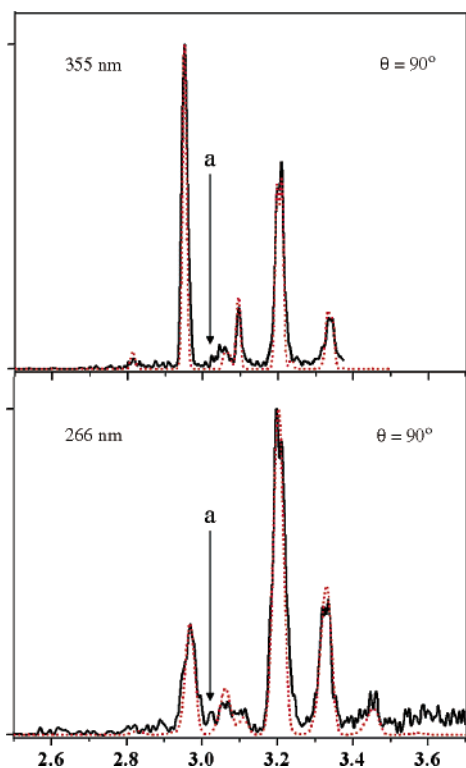
For each anion and/or neutral state, the parameters that determine these wave functions are  $r_e$ , the equilibrium bond length,  $\omega_e$ , the harmonic vibrational frequency, and  $\omega_e x_e$ , the anharmonicity. All of these parameters are known for the neutral X and A states,<sup>16–18</sup> and were fixed at those values (see Table 1) in the simulations. The experimental spin–orbit coupling constant<sup>15</sup>  $A_e = -89.097 \text{ cm}^{-1}$  was used for the  $A^2\Pi$  state, as was the experimental value of  $2032 \text{ cm}^{-1}$  for the term value of this state. Thus, only the anion parameters needed to be varied: the bond length, vibrational frequency, and EA( $\text{SiN}$ ).

Our assignment described in section 3 indicated only a single hot band transition associated with each of the two photodetachment bands, so that the anion anharmonicity cannot be extracted from our simulations. We thus estimated  $\omega_e x_e$  for  $\text{SiN}^-$  to be  $4.3 \text{ cm}^{-1}$  by scaling it to that of the neutral using the Morse function formula:

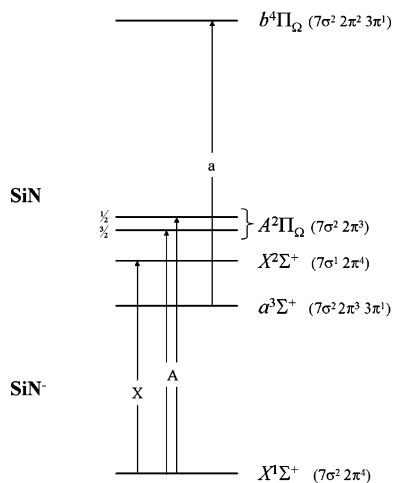
$$\frac{\omega_e x_e^{(-)}}{\omega_e x_e^{(0)}} = \frac{(\omega_e^{(-)})^2 D_e^{(0)}}{(\omega_e^{(0)})^2 D_e^{(-)}} \quad (4)$$

where  $D_e^{(0)}$  and  $D_e^{(-)}$  are the neutral and anion dissociation energies (the determination of  $D_e^{(-)}$  is discussed below). The simulated PE spectra are shown in Figure 2, and best fit anion parameters are displayed in Table 1.

The PE spectrum yields the first experimental determination of the SiN adiabatic electron affinity,  $2.949 \pm 0.008 \text{ eV}$ , slightly



**Figure 2.** Anion photoelectron spectra of SiN<sup>-</sup> taken at 355 nm with  $\theta = 0^\circ$  and 266 nm with  $\theta = 90^\circ$ . The FC-simulated (dotted) PE spectra are superimposed on the experimental ones.



**Figure 3.** Energy level diagram for SiN<sup>-</sup>/SiN as derived from ab initio, DFT, and experimental investigations.

higher than the value of 2.8632 eV recently calculated by Kalcher.<sup>25</sup> The resulting energetics for the anion and neutral states, along with the dominant molecular orbital configurations, are shown in Figure 3. Our FC analysis also yields the first experimental determination of the molecular constants for the anion SiN<sup>-</sup>. In particular, using  $r_e = 1.572066 \pm 0.000041 \text{ \AA}$ <sup>18</sup> for the SiN ground state and  $r_e = 1.641879 \pm 0.000020 \text{ \AA}$ <sup>16</sup> for the A <sup>2</sup>Π state, in combination with the bond changes for the  $X^2\Sigma^+ + e^- \leftarrow X^1\Sigma^+$  and  $A^2\Pi_\Omega + e^- \leftarrow X^1\Sigma^+$  electronic transitions determined from the FC simulation, we obtain  $r_e(\text{SiN}^-) = 1.604 \pm 0.005 \text{ \AA}$ . Note that while one can generally only extract the absolute value of the bond length change  $|\Delta r_e|$  from FC analysis, the observation of transitions to two neutral electronic states with known bond lengths removes any ambiguity in  $r_e$  for the anion. Finally, from the FC analysis, we also determined  $\omega_e(\text{SiN}^-) = 1130 \pm 20 \text{ cm}^{-1}$ ; this was optimized

to reproduce the position of the hot band in the PE spectrum. The molecular parameters obtained from the PE spectrum simulation are also in very good agreement with Kalcher's calculations ( $r_e = 1.6045 \text{ \AA}$  and  $\omega_e = 1120 \text{ cm}^{-1}$ ).<sup>25</sup>

The lowest dissociation asymptote of SiN<sup>-</sup> is Si<sup>-</sup> ( $3p^3, ^4S_{3/2}$ ) + N ( $2p^3, ^4S_{3/2}$ ); therefore, from a thermodynamic cycle we can derive the dissociation energy difference between SiN<sup>-</sup> and SiN employing the relation  $D_0(\text{SiN}^-) - D_0(\text{SiN}) = \text{EA}(\text{SiN}) - \text{EA}(\text{Si})$ . Using the EA(SiN) value of 2.949 eV determined in this study together with the EA(Si) value of 1.3895 eV measured by Blondel et al.,<sup>32</sup> we obtain  $D_0(\text{SiN}^-) - D_0(\text{SiN}) = 1.560 \pm 0.008 \text{ eV}$ . In addition, using the  $D_0(\text{SiN})$  value of  $4.68 \pm 0.14 \text{ eV}$  derived by Naulin et al.<sup>19</sup> from a crossed molecular beam study, we derive the dissociation energy of SiN<sup>-</sup> as  $6.24 \pm 0.14 \text{ eV}$ .

Owing to the relatively small amounts of SiN<sup>-</sup> produced in the ion source, the PE spectra are not entirely noise-free, even at 355 nm where there is virtually no background from stray photoelectrons. There are small features in the PE spectra that are not fit by the above simulations. The most reproducible of these is labeled "a" at eBE = 3.04 eV in the 355 nm PE spectra shown in Figure 2. There are no other neutral states of SiN accessible from the anion ground state in this energy range.<sup>17,23</sup> This feature may arise from photodetachment of the  $a^3\Sigma^+$  excited state of SiN<sup>-</sup>, calculated by Kalcher<sup>25</sup> to lie 0.341 eV below the detachment threshold. The molecular orbital configuration of this state is  $\dots 7\sigma^2 2\pi^3 3\pi^1$ . The anisotropy parameter for peak "a" is similar to that for the main progression  $A_{0-n}$ , suggesting that the photodetachment transition involves removal of an electron from the same orbital as in the  $A^2\Pi \leftarrow X^1\Sigma^+$  transitions, namely, the  $2\pi$  orbital. Detachment of this electron from the  $a^3\Sigma^+$  state produces the <sup>4</sup>Π neutral state, as shown in Figure 3. The calculation by Cai et al.<sup>23</sup> found  $T_e = 2.83 \text{ eV}$  for the  $b^4\Pi$  state, and using this along with Kalcher's energy yields eBE = 3.17 eV for the  $b^4\Pi \leftarrow a^3\Sigma^+$  photodetachment transition, remarkably close to peak "a". Unfortunately, we did not observe the  $A^2\Pi + e^- \leftarrow a^3\Sigma^+$  transition that would allow us to determine unequivocally the term energies of the triplet anion and neutral quartet state.

Finally, it is worthwhile to compare the experimental findings for SiN<sup>-</sup>/SiN with those for the isovalent molecules CN<sup>-</sup>/CN. The EA of CN,  $3.862 \pm 0.004 \text{ eV}$ ,<sup>8</sup> is considerably higher than EA(SiN) found here. The dissociation energies of CN<sup>-</sup>, 10.31 eV,<sup>33</sup> and CN, 7.76 eV,<sup>33</sup> are much higher than  $D_0(\text{SiN}^-)$  and  $D_0(\text{SiN})$ . CN<sup>-</sup> is a closed shell anion with an X <sup>1</sup>Σ<sup>+</sup> ground state, while CN has an X <sup>2</sup>Σ<sup>+</sup> ground state and low-lying A <sup>2</sup>Π and B <sup>2</sup>Σ<sup>+</sup> states. While the state ordering is the same as in SiN,  $T_e$  for the A state of CN, 9235 cm<sup>-1</sup>, is considerably higher than the term value for the A state in SiN, 2032 cm<sup>-1</sup>. A simple molecular orbital picture might lead one to expect a decrease in bond order from 3 to 2.5 upon photodetachment from either CN<sup>-</sup> or SiN<sup>-</sup> accompanied by an increased  $r_e$ . In fact, the bond length for detachment to the X <sup>2</sup>Σ<sup>+</sup> state decreases in both cases:  $\Delta r_e = -0.005 \text{ \AA}$  for CN<sup>-</sup> and  $-0.032 \text{ \AA}$  for SiN<sup>-</sup>. In CN<sup>-</sup>, the very small bond length change was attributed to the nonbonding character of the  $\sigma$  highest occupied molecular orbital (HOMO) from which detachment occurs to form the neutral X <sup>2</sup>Σ<sup>+</sup> state.<sup>8</sup> It thus appears that the  $7\sigma$  HOMO in SiN<sup>-</sup> has some antibonding character.

## 5. Conclusions

The anion photoelectron spectra of SiN<sup>-</sup> have been recorded at 355 and 266 nm photodetachment wavelengths. We obtained the first experimental spectroscopic parameters for the anion

ground state,  $r_e = 1.604 \pm 0.005 \text{ \AA}$  and  $\omega_e = 1130 \pm 20 \text{ cm}^{-1}$ . We determined the adiabatic electron affinity of SiN as  $2.949 \pm 0.008 \text{ eV}$  and the SiN<sup>-</sup> dissociation energy as  $6.24 \pm 0.14 \text{ eV}$ . The PE spectra also confirm the most recent literature values of the term value for the SiN A <sup>2</sup>Π state,  $2032 \text{ cm}^{-1}$ . Finally, we tentatively assigned a small spectral feature to the transition between the anion first excited electronic state ( $a \text{ } ^3\Sigma^+$ ) and the  $b \text{ } ^4\Pi$  state of SiN.

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