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Resonant two-photon ionization spectroscopy of the 13-electron triatomic Si_2N

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Running Title: Spectroscopy of Si_2N

Abstract

Resonant two-photon ionization spectra of $^{28}\text{Si}_2\text{N}$, $^{28,29}\text{Si}_2\text{N}$, and $^{28,30}\text{Si}_2\text{N}$ have been collected between $32\,000\text{ cm}^{-1}$ and $36\,000\text{ cm}^{-1}$. A fit of the rotationally resolved spectrum of the most intense band of $^{28}\text{Si}_2\text{N}$ at $34\,314\text{ cm}^{-1}$ reveals the transition to be $^2\Sigma_u^+ \leftarrow \tilde{X}^2\Pi_{g,1/2}$. A molecular orbital analysis is made to justify the assignment. The geometric structure is determined to be linear and centrosymmetric in both the ground and excited state with $r''_0(\text{Si-N}) = 1.6395 \pm 0.0014\text{ \AA}$ and $r'(\text{Si-N}) = 1.6343 \pm 0.0014\text{ \AA}$. The ionization energy is determined to be less than 8.51 eV .

1. Introduction

Twelve of the possible $100\text{ X}_2\text{Y}$ molecules that can be formed from the second row atoms B, C, N, O, F, and their third row congeners possess 13 valence electrons. Of these, only C_2N has been investigated in the gas phase with sufficient resolution to observe the rotational structure and to unambiguously assign a conformation to the molecule. In this case it was discovered that C_2N exists as two isomers: CNC [1] and CCN [2]. Both species are clearly stable gas phase molecules. Subsequent calculations [3] have shown that these two isomers of C_2N are very nearly isoenergetic. In fact, they are so close that no definite energetic ordering is yet possible.

Not long after the investigation of CNC and CCN, Zmbov and Margrave reported the discovery of Si_2N , another 13-electron species, in the gas phase following vaporization of pure Si inside a boron nitride Knudsen cell oven [4]. By the vanishing current method they determined the ionization potential of Si_2N to be $9.3 \pm 0.3\text{ eV}$. They were also able to determine, by the third law method, the heat of atomization of this molecule to be $10.2 \pm 0.4\text{ eV}$. Not until

1993 was there any further mention of Si_2N in the literature. In that year Iraqi, Goldberg, and Schwarz [5] reported the identification of Si_2N in the gas phase again. Their neutralization-reionization mass spectrometry (NRMS) and collision induced dissociation (CID) studies indicated that, of the three possible isomers, the linear and centrosymmetric structure, SiNSi , was not produced in that experiment. Because the interpretation of their NRMS and CID results was largely based upon an assumed similarity between Si_2N and Si_2O , this conclusion can be considered tentative at best. Since this investigation, two theoretical studies of Si_2N have been carried out. Boldyrev and Simons [6] have calculated the relative energies of four different ground state symmetries of Si_2N and found that the ${}^2\Pi_g D_{\infty h}$ structure lay lowest in energy with the C_{2v} structure only 1574 cm^{-1} higher in energy. For the $\tilde{X}{}^2\Pi_g$ ground state structure, they reported a Si-N bond length of 1.643 \AA at the QCISD(T)/6-311+G* level of theory. In the most recent *ab initio* investigation, Ornellas and Iwata [7] report that the lowest energy state for Si_2N is indeed the ${}^2\Pi_g$ term. They too find that this structure is only separated from the ${}^2A_1 C_{2v}$ structure by about 1700 cm^{-1} . Both isomers could easily exist in the gas phase based on this result. In this same work, the linear SiSiN isomer was found to lie approximately 3.7 eV higher in energy, in contrast to the situation with $C_2\text{N}$.

Despite the fact that primarily *s* and *p* orbitals are involved in the bonding of X_2Y molecules, the bonding can be quite complicated. The ground state structure cannot always be determined, using Walsh's Rules, solely by the number of valence electrons [8]. The study of such molecules allows us to test and refine our ideas about bonding and to elucidate what factors are important in determining structure. Work on such molecules is also valuable because C, N, O, and Si constitute four of the eight most abundant elements in the universe [9], and simple

molecules composed of Si and N undoubtedly play an important role in the chemistry of circumstellar shells [10] and other regions of the interstellar medium. As a more practical example, a full understanding of how nitrogen interacts with a silicon surface to produce Si_3N_4 [11], an interesting material because of its hardness and inertness, cannot come until we understand the structure of the possible intermediates in the growth phase. These intermediates almost certainly involve small silicon and nitrogen containing clusters, of which Si_2N may be one. In this paper we present the first spectroscopic investigation of the triatomic molecule Si_2N and establish unambiguously that the linear centrosymmetric connectivity of Si_2N does exist in the gas phase.

2. Experimental

The details of the resonant two-photon ionization (R2PI) apparatus used to collect the spectrum of Si_2N can be found in other publications [12] (and references therein). In this particular study, the molecules of interest were generated by pulsed laser ablation (Nd:YAG, 532 nm, 10-20 mJ/pulse) of an AlSi alloy disk (1:1 mole ratio) in the throat of a supersonic expansion of nitrogen maintained at a stagnation pressure of 120 psig. The molecules were interrogated in the extraction region of a Wiley-McLaren reflectron time-of-flight mass spectrometer by the frequency doubled output of a tunable dye laser pumped by the second harmonic of a Nd:YAG laser. A second laser source was not required for ionization. Rotationally resolved work was accomplished by the insertion of an intracavity étalon into the dye laser and by pressure scanning the cavity with Freon-12 (DuPont) from 30 torr to 650 torr. High resolution scans were calibrated by the simultaneous collection of the molecular spectrum, étalon transmission fringes, and the absorption spectrum of I_2 . A comparison with the atlas of

Gerstenkorn and Luc [13,14] followed by a correction for the Doppler shift due to the motion of the molecules toward the excitation source (+0.09031 cm⁻¹) allowed a determination of the absolute frequency of all rotational lines.

3. Results

The low resolution (0.6 cm⁻¹) spectrum of ²⁸Si₂N, shown in Fig. 1, appears simple, yet all attempts to fit the observed bands to a progression have led to irreconcilable difficulties. Either the recorded isotope shifts for ²⁸Si¹⁴N²⁹Si and ²⁸Si¹⁴N³⁰Si were found to be unreasonable for the vibrational assignment or intense features did not fit into the progression. Because of these problems, we have left the vibronic spectrum unassigned. Nevertheless, it is still possible to obtain information from this spectrum. Any R2PI experiment can place an upper limit on the ionization energy of a molecule because the sum of the energies of the excitation and ionization photons must be greater than or equal to the ionization energy of the molecule. Otherwise, no resonant enhancement can be seen. A reliable determination of this sort requires, first, that the transition in question originate in the vibrationless level of the ground state and, second, that we know only two photons are used to move from the ground state to the ion state. Because it is unlikely that in a supersonic jet the most intense band in the observed spectrum results from a vibrationally hot level, we are confident in making the first assertion about the 34 314 cm⁻¹ band. As discussed in Section 4, we are also confident that only two photons are used to produce the ions. Twice the transition frequency of this band, corrected for the field ionization effect, leads to a determination of the ionization energy of Si₂N as less than 8.51 eV. This is significantly less than the value of 9.3 ± 0.3 eV determined by Zmbov and Margrave [4].

A scan over the intense $34\,314\text{ cm}^{-1}$ band with better laser resolution (0.07 cm^{-1}) revealed the rotational structure displayed in Fig. 2. As can be seen, the width of individual lines in this spectrum is greater than that expected given the resolution of the excitation source. This is due to a power broadening process caused by our use of the same wavelength to both excite and ionize the molecules. Presumably the ionization step has a lower cross-section than the excitation process such that efficient ionization could only be achieved at laser fluences which led to power broadening. This problem could have been avoided if a two-color ionization scheme had been available to us when these data were collected.

In the rotationally resolved spectrum the lines fan out rather symmetrically on either side of the band origin, indicating a very slight geometry change upon excitation. If such an excitation could be considered as simply a Hund's case (a) - case (a) or case (c) - case (c) transition, one would expect to see rotational lines fanning out in the P and R branches with roughly equal separations while the lines of the Q-branch would all fall at nearly the same frequency. This is not the case for the spectrum displayed in Fig. 2. Close inspection of this band reveals that the lines far from the band origin are spaced by three times the separation of the lines close to the band origin. This is the classic structure of a $^2\Sigma$ (b) - $^2\Pi$ (a) transition with $B'' \approx B'$, unresolved spin rotation splitting in the $^2\Sigma$ state, and unobservable lambda doubling in the $^2\Pi$ state [15,16]. There are four branches, the lines of which can be fit to the well known formulae for the P_{11} , $Q_{11} + P_{21}$, $R_{11} + Q_{21}$, and R_{21} branches as listed in reference 16. The observed line positions are shown in Table 1, and the residuals of their fit to these formulae are shown in parentheses. The rotational constants determined from this fit, along with their 1σ

error limits, are $B' = 0.11280 \pm 0.00020 \text{ cm}^{-1}$ and $B'' = 0.11208 \pm 0.00019 \text{ cm}^{-1}$. The band origin is at $34\,314.2880 \pm 0.0058 \text{ cm}^{-1}$.

A fit of the observed lines as a ${}^2\Sigma \leftarrow {}^2\Pi$ transition confirms that the Si_2N molecule is linear, but does not reveal whether the molecule is structured as SiSiN or SiNSi . This uncertainty can be resolved if we consider why, as shown in Table 1 and Fig. 2, successive lines in any one branch had to be fit by omitting every other possible value for J . If both ${}^{28}\text{Si}$ nuclei ($I=0$) are located in equivalent positions, as they are in the structure SiNSi , then full account must be taken of the effect of nuclear spin on the symmetry of rotational levels in both the ground and excited states. An atomic arrangement in which two such identical nuclei are placed in equivalent positions requires that the total wavefunction (including the nuclear wavefunction) be totally symmetric upon interchange of the ${}^{28}\text{Si}$ nuclei; thus, only symmetric rotational levels exist because there are no antisymmetric nuclear wavefunctions in the case of nuclei with $I=0$ [15]. When the ef parity selection rules for electric dipole radiation are taken into account ($e \leftrightarrow e$ and $f \leftrightarrow f$ for P and R branches; $e \leftrightarrow f$ for Q branches) [17] it is found that every other rotational transition is expected to be missing from the spectrum in Fig. 2 if it arises from the SiNSi isomer. This constitutes unmistakable proof that the atoms in Si_2N are in the centrosymmetric arrangement, SiNSi .

Based upon the J assignments of the first lines observed in the rotationally resolved spectrum, it is possible to assign the transition as either ${}^2\Sigma_u^+ \leftarrow {}^2\Pi_{g, 1/2}$ or ${}^2\Sigma_g^- \leftarrow {}^2\Pi_{u, 1/2}$. Because the rotational structure of the band would be the same in the two cases, either assignment is consistent with the observed spectrum and, therefore, either assignment is equally valid. An unambiguous choice between the two is not possible based only on the observed rotationally

resolved spectrum. As discussed in the next section, a consideration of the molecular orbitals makes one choice more reasonable than the other. Knowing now that the structure of the molecule is linear and centrosymmetric allows the determination of the Si-N bond lengths in the ground and excited states. These values are $r''_0(\text{Si-N}) = 1.6395 \pm 0.0014 \text{ \AA}$ and $r'(\text{Si-N}) = 1.6343 \pm 0.0014 \text{ \AA}$.

The observed isotope shift for the $34\,314 \text{ cm}^{-1}$ band is larger than expected for an origin band [18,19], assuming the calculated ground state vibrational frequencies of either Ornellas and Iwata [7] or those of Boldyrev and Simons [6] to be acceptable. The observed shift in this band is $\nu(^{28}\text{Si}_2\text{N}) - \nu(^{28,30}\text{Si}_2\text{N}) = +4.73 \pm 0.6 \text{ cm}^{-1}$. In fact, the vibrational frequencies would have to more than double upon excitation for this change to be reasonable. This value does turn out to be reasonable if it is assumed that one quantum of symmetric stretch similar in frequency to the calculated ground state value is excited in the upper state. For this reason, we cannot determine the true origin of this band system because we do not know the vibrational frequency of the upper state. A summary of the spectroscopic information gathered about Si_2N in this study is provided for easy reference in Table II.

4. Discussion

Despite the inherent limitations of the molecular orbital concept, molecular orbital diagrams can provide a useful starting point for understanding the chemical bonding in a molecule such as SiNSi . To aid in achieving such an understanding, a molecular orbital diagram for SiNSi is presented in Fig. 3. In this diagram the low energy $2s$ orbital of nitrogen is assumed to be core-like and uninvolved in the bonding. Hybridization has been allowed between the $3s$ and $3p$ orbitals of silicon, particularly in orbitals of σ_u symmetry. The resulting molecular

orbitals and their occupation by electrons are shown in the figure along with a graphical representation of the atomic orbital basis functions contributing to each molecular orbital.

In the depiction of the molecular orbitals, the $1\sigma_g$ orbital remains unchanged from the core-like $2s$ orbital of nitrogen. The $1\sigma_u$ and $1\pi_u$ orbitals have good overlap between the atomic centers and are strongly bonding, while the $2\sigma_g$ and $2\sigma_u$ orbitals lie near the energy of the $3s$ orbital of atomic Si and are mainly non-bonding in character. The higher energy $1\pi_g$ and $3\sigma_g$ orbitals have little or no contribution from nitrogen atomic orbitals and are expected to lie near the energy of the silicon $3p$ orbital and to be mainly non-bonding in character. Finally, the $2\pi_u$ and $3\sigma_u$ orbitals have nodal planes bisecting the Si-N and N-Si bonds and are strongly anti-bonding in character.

If the 13 valence electrons of Si_2N are placed into the orbitals of Fig. 3, we are left with the configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2 2\sigma_u^2 1\pi_g^1$. This configuration can result only in a ${}^2\Pi_g$ term, leading to the conclusion that the rotationally resolved transition in this work must be assigned as ${}^2\Sigma_u^+ \leftarrow {}^2\Pi_{g,1/2}$ rather than ${}^2\Sigma_g^- \leftarrow {}^2\Pi_{u,1/2}$. This is in perfect analogy to the work on isovalent CNC [1] in which it was also shown that the ground state was ${}^2\Pi_g$. The observation of an excited ${}^2\Sigma_u^+$ state in this work is consistent with excitation of a $2\sigma_u$ electron to the $1\pi_g$ orbital. The resulting configuration of $2\sigma_u^1 1\pi_g^2$ produces terms of ${}^2\Sigma_u^+$, ${}^4\Sigma_u^-$, ${}^2\Sigma_u^-$, and ${}^2\Delta_u$. The last two of these terms were observed in the case of CNC while only the first has yet been observed in SiNSi. The fact that the Si-N bond length changes by only $+0.0052 \text{ \AA}$ upon excitation is consistent with this molecular orbital picture as well because the $2\sigma_u$ and $1\pi_g$ orbitals are essentially non-bonding in character. The observed transition involves moving an electron from a non-bonding orbital to a non-bonding orbital, both localized on the Si atoms. It is interesting to note that the bond length

reported for the 12-electron $^1\Sigma_g^+$ species AlOAl [20] is 1.64 Å, almost exactly the same as in Si₂N. The removal of the non-bonding $1\pi_g$ electron in moving from Si₂N to Al₂O apparently makes little difference in the bonding, as judged by the bond length. It is worth pointing out that if this molecular orbital picture of Si₂N is a reasonably good description of the bonding, the ionization energy of the molecule would not be expected to differ radically from the ionization energy of atomic silicon. This is because the electron removed from Si₂N to form the ion is presumably the π_g electron which is mainly Si 3*p* in character. The ionization energy of atomic Si is 8.149 eV [21] while that of Si₂N is less than 8.51 eV. The close agreement of these numbers is good evidence that what is being observed in Si₂N is truly an ionization process involving only two photons.

The two *ab initio* studies of Si₂N [7,6] agree that the $^2\Pi_g$ state should be the ground state and that the C_{2v} isomer lies not much higher in energy. Ornellas and Iwata report that this energy difference only amounts to about 1700 cm⁻¹. As Ornellas and Iwata point out, it may be difficult to quench the bent molecule to the linear molecule in a supersonic expansion because the 2A_1 potential energy surface of C_{2v} Si₂N correlates to neither surface that results when the $^2\Pi_g$ state of Si₂N is bent. The linear centrosymmetric isomer may be thermodynamically more stable than the bent molecule, but if the barrier to conversion is high enough both isomers may be present in our experiment. If indeed our low resolution spectrum contains transitions originating from more than one isomer of Si₂N, this may partly explain our difficulty in assigning the vibrational spectrum. More bands will have to be rotationally resolved to confirm this possibility. Indeed, it will be informative to do so because in C₂N it is the two linear isomers

CNC and CCN that are nearly isoenergetic [3] rather than the bent and linear forms as predicted for Si₂N.

Both *ab initio* studies also calculated Si-N bond lengths that are reasonably close to those found in this study. Boldyrev and Simons report $r_c(\text{Si-N}) = 1.643 \text{ \AA}$ at the QCISD(T)/6-311+G* level and Ornellas and Iwata report $r_c(\text{Si-N}) = 1.646 \text{ \AA}$ at the CCSD(T)/DZP level of theory, with both being slightly larger than the experimentally determined value of $r_0 = 1.6395 \pm 0.0014 \text{ \AA}$. All of the Si-N bond length values, theoretical and experimental, are larger than the SiN ground state bond length of 1.575 \AA [22], indicating that the bonds in Si₂N cannot be considered to have the same bond order of 2.5 expected for SiN.

5. Conclusion

An R2PI spectrum of the linear and centrosymmetric isomer of the 13-electron triatomic Si₂N has been collected. A rotationally resolved scan over the most intense band and an analysis of the molecular orbitals involved in the bonding have shown the ground state to be $\tilde{X}^2\Pi_{g,1/2}$ with a Si-N bond length of $1.6395 \pm 0.0014 \text{ \AA}$. The excited electronic state probed in this experiment is of $^2\Sigma_u^+$ symmetry with a bond length of $1.6343 \pm 0.0014 \text{ \AA}$. We plan future studies of this molecule aimed at explaining the vibrational spectrum. We also plan dispersed fluorescence studies of this molecule to help determine if we do indeed have two isomers present in the molecular beam. Rotationally resolved studies are also planned for the 12-electron species SiNAl and the 11-electron species Al₂N for which we have also found spectra in this same spectral region.

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TABLE I. Rotational line positions of the $34\,314\text{ cm}^{-1}$ band of $^{28}\text{Si}^{14}\text{N}^{28}\text{Si}$ in wavenumbers with the residuals ($\times 10^3$) of their fit to the formulae of reference 16 shown in parentheses.

J	P_{11}	$Q_{11}+P_{21}$	$Q_{21}+R_{11}$	R_{21}
0.5			34 314.459(30)	
1.5		34 314.073(20)		34 315.201(20)
2.5	34 313.574(42)		34 314.661(0)	
3.5		34 313.864(12)		34 315.890(16)
4.5	34 312.887(20)		34 314.909(11)	
5.5		34 313.677(13)		34 316.608(10)
6.5	34 312.181(27)		34 315.111(30)	
7.5		34 313.464(5)		34 317.292(3)
8.5	34 311.550(4)		34 315.375(14)	
9.5				34 318.009(12)
10.5	34 310.903(3)		34 315.634(9)	
11.5				34 318.716(10)
12.5	34 310.262(2)			
13.5				
14.5	34 309.635(8)			

TABLE II. Molecular constants for the ground and excited state of $^{28}\text{Si}^{14}\text{N}^{28}\text{Si}$. Numbers shown in parentheses are the 1σ error limits in the last two decimal places.

	$\tilde{X}^2\Pi_{g,1/2}$	$^2\Sigma_u^+$
T_0	0 cm^{-1}	$34\,314.2880(58) - x$
B	$B_0 = 0.11208(19) \text{ cm}^{-1}$	$B = 0.11280(20) \text{ cm}^{-1}$
$r(\text{Si-N})$	$r_0 = 1.6395(14) \text{ \AA}$	$r = 1.6343(14) \text{ \AA}$
$\Delta\nu^a$	-	$+4.73(60) \text{ cm}^{-1}$

^aThe reported isotope shift is the value of $\nu(^{28}\text{Si}_2\text{N}) - \nu(^{28,30}\text{Si}_2\text{N})$.

FIGURE CAPTIONS:

Figure 1. A portion of the low resolution resonant two-photon ionization spectrum of $^{28}\text{Si}^{14}\text{N}^{28}\text{Si}$ collected under one-color R2PI conditions by frequency doubling the output of a dye laser and scanning without an excimer laser for ionization.

Figure 2. Rotationally resolved scan over the $34\,314\text{ cm}^{-1}$ band of $^{28}\text{Si}^{14}\text{N}^{28}\text{Si}$ with the four observed branches labeled. Note that alternate values of J in each branch have been omitted to obtain a satisfactory fit. The lines have a width greater than the linewidth of the excitation source because of a power broadening effect as discussed in the text.

Figure 3. Molecular orbital diagram for SiNSi graphically showing the atomic orbital basis functions that contribute to each molecular orbital. The number of electrons assigned to each orbital in the ground state of Si_2N is shown by vertical arrows. The atomic orbitals for Si and N are drawn on an energy scale which places their ionization limits at the same energy, which is off the top of the figure.





