Laboratory Rotational Spectra of Silyl Isocyanide

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Abstract

The rotational spectrum of silyl isocyanide (SiH₃NC), an isomer of the well-studied silyl cyanide (SiH₃CN), has been detected in the laboratory in a supersonic molecular beam, and the identification was confirmed by observations of the corresponding rotational transitions in the rare isotopic species SiH₃¹⁵N⁴⁸C and SiH₃¹³N¹⁵C. Spectroscopic constants derived from 19 transitions between 11 and 35 GHz in the three lowest harmonically related rotational transitions in the K = 0 and 1 ladders of the normal isotopic species including the nitrogen nuclear quadrupole hyperfine constant allow the principal astronomical transitions of SiH₃CN to be calculated to an uncertainty of about 4 km s⁻¹ in equivalent radial velocity, or within the FWHM of narrow spectral features in the inner region of IRC+10216 near 200 GHz. The concentration of SiH₃CN in our molecular beam is three times less than SiH₃CN, or about the same as the corresponding ratio of the isomeric pair SiNC and SiCN produced under similar conditions. Silyl isocyanide is an excellent candidate for astronomical detection, because the spectroscopic and chemical properties are very similar to SiH₃CN, which was recently identified in the circumstellar envelope of IRC+10216 by Cernicharo et al. and of SiNC and SiCN in the same source.

Key words: ISM: molecules – line: identification – molecular data – radio lines

1. Introduction

A long-standing question in molecular astronomy is how silicon carbide (SiC) dust is formed in carbon-rich asymptotic giant branch (AGB) stars (Cherchneff 2012; Yasuda & Kozasa 2012). Following its detection, the broad unresolved absorption band at 11.3 μm attributed to solid SiC (Hackwell 1972; Treffers & Cohen 1974) has become a principal spectroscopic feature for studying the evolution of dust shells in carbon stars (see Speck et al. 2005 and references therein). Interferometric measurements of the 11.3 μm band determined that the “dust-forming region” is about five stellar radii (5R⁎, or 0.150″) from the central star in the prototypical source IRC+10216 (Monnier et al. 2000).

Radio astronomers extended the initial work on SiC in the IR by observing seven organosilanes in IRC+10216. Beginning in 1984, four silicon carbides SiC, SiCC, c-SiC₃, and SiC₄ (for a summary see McCarthy et al. 2003 and references therein); the cyanide/isocyanide pair SiCN and SiNC; and the disilicon carbide SiCSi were identified in the radio band with single antennas. Most organosilanes were shown to be present in the outer molecular envelope at a radius of about 15″ from the central star. But owing to the development in the past few years of ground-based millimeter-wave interferometers with increased angular resolution and spectral bandwidths, it is now feasible to study the inner dust-forming region of IRC+10216 where much less is known about the chemical composition than the well-studied outer molecular envelope. Observations with the Atacama Large Millimeter/submillimeter Array (ALMA) confirmed earlier indirect evidence that SiCC is also present in the inner region¹; two diatomic silicon-bearing species are present in the inner envelope (SiS and SiO; Bieging et al. 2000; Bieging 2001; Prieto et al. 2015); and there is indirect evidence from single antenna observations that SiCSi is also present in the warmer inner region as well as the outer envelope (Cernicharo et al. 2015).

To date, spectral line observations in the radio band and infrared and supporting chemical models have failed to establish the physicochemical mechanism(s) of formation of solid silicon carbide in the dust formation zone because most chemical reactions involving small silicon-bearing molecules have not been measured in the laboratory (see Cherchneff 2012), and the key silicon-bearing reactive intermediates have not yet been identified. The recent discovery of the organosilane CH₃SiH₃ in IRC+10216 by Cernicharo et al. (2017) and confirmation of the earlier tentative detection of silyl cyanide SiH₃CN by Agúndez et al. (2014) has introduced a new level of chemical complexity in the inner region of this well-studied carbon-rich AGB star. Cernicharo et al. (2017) estimated that the CH₃SiH₃ emission extends from 40R⁎ to at or near the outer envelope at 600R⁎, and a similar extent was found for SiH₃CN. Detection of CH₃SiH₃ and SiH₃CN suggests that other silicon-bearing species of comparable size, such as SiH₃NC (the isocyanide isomer of SiH₃CN), might be within reach in the laboratory and in IRC+10216.

In this paper, we report the laboratory measurements of the rotational spectrum of SiH₃NC (silyl isocyanide). While there have been several studies dedicated to the rotational spectrum of SiH₃CN, the rotational spectrum of SiH₃NC had not been measured prior to this work, although it had been observed by low-resolution IR matrix spectroscopy (Maier et al. 1998). Our laboratory measurements of SiH₃NC were guided by ab initio calculations that provided initial estimates of the rotational and hyperfine constants (Section 2), and the identification of the new species was confirmed by isotopic substitution. With our measured spectroscopic constants of SiH₃NC in hand, the rotational transitions of principal interest to radio astronomers can be calculated with sufficient accuracy to allow a deep search in IRC+10216 in the millimeter band. SiH₃NC is an excellent candidate for astronomical detection because the

¹ Prieto et al. (2015) determined that there is SiCC emission centered on the star with a size of about 3" × 5", in addition to the SiCC gas in the outer molecular envelope at a radius of about 15" from the star.
The Astrophysical Journal, 860:63 (5 pp), 2018 June 10

Lee, Gottlieb, & McCarthy

2. Ab Initio Calculations

Ab initio calculations were performed with a local version of CFOUR (Stanton et al. 2017). Geometry optimizations of SiH$_3$CN and SiH$_3$NC were conducted with the coupled-cluster method with single, double, and perturbative triple excitations, combined with Dunning’s correlation-consistent basis sets (Dunning 1989)—an approach that has been shown to provide accurate equilibrium geometries for small molecules (Bak et al. 2001). All electrons are correlated in our calculations, although they utilize basis sets without core–valence functions (cc-pVXZ, where X = D,T,Q) and with the weighted core–valence basis functions of Balabanov & Peterson (2005; cc-pwCVXZ). Harmonic frequency analysis was carried out on the optimized geometries to confirm that they are minimum energy structures. The resulting structures calculated with quadruple-$\zeta$ (VQZ) quality basis sets are shown in Figure 1.

The minimum energy structures of both isomers are closed-shell, prolate symmetric tops with $C_{3v}$ symmetry. By comparing the quantum chemical calculations on SiH$_3$CN with experimental spectroscopic constants, we determined an expected accuracy for subsequent predictions of SiH$_3$NC. These results can be found in the Appendix (Table 6). The inclusion of additional basis shells and core–valence functions act to increase the rotational constants $B_r$. The best agreement (0.03%) with the experiment was achieved at the CCSD(T)/cc-pwCVQZ level. Without the weighted core–valence functions (i.e., cc-pVQZ basis), the disparity between $B_r$ and $B_0$ increases by an order of magnitude. Comparisons of the ab initio dipole and nitrogen quadrupole moment with the values determined by Priem et al. (1998) suggest that a good agreement is reached with quadrupole–$\zeta$ quality basis, regardless of core–valence functions.

The equilibrium properties of SiH$_3$NC calculated with different basis sets are given in Table 1. The rotational constants from previous calculations (Zanchini 2000; Wang et al. 2004) are in qualitative agreement with our CCSD(T) results, with the literature $B_r$ values within $\sim$1% of our results. While the dipole moment is relatively insensitive to basis set size, the $^{14}$N quadrupole coupling constant $eQq$ changes by nearly an order of magnitude between double- and triple-$\zeta$ quality bases. The change in $eQq$ between triple- and quadruple-zeta basis is considerably smaller, although it does not appear to have converged to the complete basis set limit. The inclusion of core–valence basis functions does not have a large effect on the multipole moments. Our calculations predict that the dipole moment of SiH$_3$NC (Table 1) is comparable to that of SiH$_3$CN, which is known to be large from Stark measurements (3.44 D; Priem et al. 1998). With the nitrogen atom located closer to the center of mass in SiH$_3$NC, the quadrupole constant ($eQq(N) = -0.91$ MHz) is reduced by a factor of five relative to when the nitrogen atom is at the terminal position (SiH$_3$CN, $eQq(N) = -5.0440$ MHz). Thus, we expect that the rotational spectrum of SiH$_3$NC should be very similar to that of SiH$_3$CN—an symetric top with $\alpha$-type transitions but with more compact hyperfine structure.

3. Laboratory Measurements

The Fourier-transform microwave (FTMW) cavity spectrometer used in this work is described in previous publications (McCarthy et al. 2000). SiH$_3$NC and SiH$_3$CN were synthesized in situ using a mixture of SiH$_4$ ($\sim$0.1%) and CH$_3$CN ($\sim$0.1%) heavily diluted in Ne. For detection of the rare isotopic species, either CH$_3^{13}$CN or CH$_3C^{15}$N were used in place of CH$_3$CN. The gas mixture was introduced into the spectrometer via a pulsed valve with an electrical discharge nozzle (McCarthy et al. 2000). A high voltage discharge (1.4 kV) initiates a series of chemical reactions by fragmenting the precursor gases. A sufficient number of collisions occur prior to the adiabatic expansion to efficiently produce a mixture of new stable and transient species. At the orifice of the discharge nozzle, the products are rapidly cooled by adiabatic expansion in the confocal Fabry–Perot cavity, achieving a rotational temperature of $\sim$2 K near the center of the cavity.

Table 1

| Basis Set        | $A_e$ (MHz) | $B_e$ (MHz) | $\mu_{e\nu}$ (D) | $eQq$ (MHz) |
|------------------|-------------|-------------|------------------|-------------|
| cc-pVDZ          | 83,714.42   | 5460.07     | -3.22            | -0.09       |
| cc-pVTZ          | 85,004.89   | 5639.51     | -3.17            | -0.91       |
| cc-pVQZ          | 86,263.47   | 5705.69     | -3.15            | -1.00       |
| cc-pwCVQZ        | 84,459.22   | 5512.48     | -3.15            | -0.29       |
| cc-pwCVTZ        | 85,631.70   | 5674.15     | -3.12            | -0.87       |
| cc-pwCVQZ$^a$    | 85,575.16   | 5688.45     | -3.17            | -0.91       |

Note.

$^a$ The basis set used to predict the SiH$_3$NC equilibrium rotational constants.

Figure 1. Ab initio equilibrium molecular structures for SiH$_3$CN (top) and SiH$_3$NC (bottom). Values in red were obtained with a cc-pVQZ basis, while the calculated values in black include core–valence basis functions (cc-pwCVQZ). Bond lengths are given in Å, and angles in degrees. See the Appendix for analogous calculations of SiH$_3$CN.
On the basis of our new ab initio calculations, a search for the fundamental rotational \((J_K = J_0 = 0)\) transition of SiH\(_3\)NC was centered near 11,380 MHz. Three unidentified, closely spaced (∼300 kHz) features were found at approximately 11,387 MHz (Figure 2). The intensity and line shape of these features were unaffected by a small external permanent magnet, implying that the species has a closed-shell ground state. The lines required the presence of both SiH\(_4\) and CH\(_3\)CN, and were not observed when the electrical discharge was absent. Thus, the unknown species is almost certainly a closed-shell, silicon-containing molecule with closely spaced splittings characteristic of nitrogen quadrupole hyperfine structure. Subsequent searches revealed features at integer multiples of 11,386 MHz, i.e., at 22,774 and 34,161 MHz, as expected for SiH\(_3\)NC. In all 19 transitions, with well-resolved hyperfine and \(K = 0\) and 1 (albeit weak) structure, were ultimately observed. The \(K = 1\) transitions were approximately three times weaker than the corresponding \(K = 0\) lines, consistent with what is expected at a rotational temperature of 2 K—for this reason, no attempt was made to search for the \(J_K = 3\) \(2\) transition near 34 GHz. A standard symmetric top Hamiltonian with one hyperfine nucleus was used to analyze the observed frequencies. The fitting was performed with the SPFIT suite of programs (Pickett 1991). The assignments and model differences are summarized in Table 2 and the derived spectroscopic constants in Table 5.

| \(J' - J^0\) | \(K' - K^0\) | \(F' - F^0\) | Frequency (MHz) | O-C (kHz) |
|---|---|---|---|---|
| 1 \(-\) 0 | 0 \(-\) 0 | 1 \(-\) 1 | 11,387.240 | 0 |
| 2 \(-\) 1 | 1 \(-\) 1 | 2 \(-\) 1 | 22,774.305 | -3 |
| 0 \(-\) 0 | 2 \(-\) 2 | 3 \(-\) 2 | 22,774.614 | -1 |
| 1 \(-\) 0 | 3 \(-\) 2 | 4 \(-\) 2 | 34,161.494 | 3 |
| 2 \(-\) 1 | 3 \(-\) 3 | 4 \(-\) 3 | 34,161.665 | 3 |
| 0 \(-\) 0 | 4 \(-\) 4 | 5 \(-\) 5 | 34,161.713 | 5 |
| 1 \(-\) 0 | 5 \(-\) 5 | 6 \(-\) 6 | 34,161.713 | 5 |
| 3 \(-\) 2 | 1 \(-\) 1 | 2 \(-\) 2 | 32,851.948 | 1 |
| 2 \(-\) 1 | 2 \(-\) 2 | 3 \(-\) 3 | 21,901.174 | 0 |
| 0 \(-\) 0 | 3 \(-\) 3 | 4 \(-\) 4 | 21,901.417 | 7 |
| 1 \(-\) 0 | 4 \(-\) 4 | 5 \(-\) 5 | 21,901.831 | 0 |
| 3 \(-\) 2 | 1 \(-\) 1 | 3 \(-\) 3 | 32,851.441 | 1 |
| 2 \(-\) 1 | 3 \(-\) 3 | 4 \(-\) 4 | 32,851.519 | 1 |
| 0 \(-\) 0 | 4 \(-\) 4 | 5 \(-\) 5 | 32,851.519 | 3 |

Notes.

* Calculated with the spectroscopic constants from Table 5.
* Blended lines.

| \(J' - J^0\) | \(K' - K^0\) | \(F' - F^0\) | Frequency (MHz) | O-C (kHz) |
|---|---|---|---|---|
| 1 \(-\) 0 | 0 \(-\) 0 | 1 \(-\) 1 | 10,950.495 | 0 |
| 2 \(-\) 1 | 1 \(-\) 1 | 2 \(-\) 2 | 21,900.836 | -5 |
| 0 \(-\) 0 | 2 \(-\) 2 | 3 \(-\) 3 | 21,901.127 | 0 |
| 1 \(-\) 0 | 3 \(-\) 3 | 4 \(-\) 4 | 21,901.417 | 7 |
| 2 \(-\) 1 | 4 \(-\) 4 | 5 \(-\) 5 | 21,901.831 | 0 |
| 3 \(-\) 2 | 1 \(-\) 1 | 3 \(-\) 3 | 32,851.441 | 1 |
| 2 \(-\) 1 | 3 \(-\) 3 | 4 \(-\) 4 | 32,851.519 | 1 |
| 0 \(-\) 0 | 4 \(-\) 4 | 5 \(-\) 5 | 32,851.519 | 3 |
| 1 \(-\) 0 | 5 \(-\) 5 | 6 \(-\) 6 | 32,851.702 | -4 |
| 2 \(-\) 1 | 6 \(-\) 6 | 7 \(-\) 7 | 32,851.948 | 2 |
| 3 \(-\) 2 | 7 \(-\) 7 | 8 \(-\) 8 | 32,851.984 | -5 |
| 4 \(-\) 4 | 8 \(-\) 8 | 9 \(-\) 9 | 32,852.006 | 6 |
| 2 \(-\) 2 | 9 \(-\) 9 | 10 \(-\) 10 | 32,852.383 | -2 |

Notes.

* Calculated with the spectroscopic constants from Table 5.
* Blended lines.
Table 4

|  |  | \(J' - J''\) |  |  |  |
|---|---|---|---|---|---|
|  |  |  | Frequency |  | O–C |
|  |  |  | (MHz) |  | (kHz) |
| 1 − 0 | 0 − 0 | 11,321,343 |  | −2 |
| 2 − 1 | 0 − 0 | 26,642,310 |  | 2 |
| 3 − 2 | 0 − 0 | 33,963,353 |  | −1 |
|  |  |  | 33,963,864 |  | 1 |

Note. \(eQq\) were calculated with the spectroscopic constants from Table 5.

Table 5

| Parameter       | \(\text{SiH}_3\text{NC}\) | \(\text{SiH}_3\text{N}^\text{3}\) | \(\text{SiH}_3\text{N}^\text{4}\) |
|-----------------|--------------------------|---------------------------|--------------------------|
| \(B\) \(\times 10^3\) | 5693.73300(43) | 5475.36068(69) | 5660.67605(59) |
| \(D_1\) | 1.716(28) | 1.619(44) | 1.793(38) |
| \(D_{1K}\) | 0.08736(28) | 0.08244(47) | 0.08473(39) |
| \(eQq\) | −0.8765(26) | −0.8803(40) | −0.8803(40) |

Note. Constants given in MHz. Values in parentheses represent 1σ uncertainty.

We also estimated the relative abundances of \(\text{SiH}_3\text{CN}\) and \(\text{SiH}_3\text{NC}\) under similar experimental conditions by using the calculated CCSD(T)/cc-pwCVQZ dipole moment of \(\text{SiH}_3\text{NC}\) and the experimental value for \(\text{SiH}_3\text{CN}\) (3.44 D; Priem et al. 1998), and on the assumption the rotational temperature (2 K) is the same for both species. By comparing the difference in relative line intensities of the same transition \((J_k = 1_0 – 0_0, F = 2 – 1)\), we estimate that \(\text{SiH}_3\text{CN}\) is approximately three times more abundant than \(\text{SiH}_3\text{NC}\) in our discharge source.

4. Discussion

The laboratory measurements and calculations provide overwhelming evidence that \(\text{SiH}_3\text{CN}\) is the carrier of the lines shown in Figure 2. The measured frequency of the triplet of lines in Figure 2 is within 0.1% of that calculated with the equilibrium rotational constants \((B_h)\) at the CCSD(T)/cc-pwCVQZ level of theory (Table 1). The relative intensities and frequency separations of the closely spaced triplet is characteristic of \(^{14}\text{N}\) quadrupole hyperfine structure in the lowest rotational transition, and is the only triplet pattern observed in the 200 MHz wide search range. Assays confirmed that the carrier: (1) contains Si and N, (2) is a closed-shell molecule, and (3) is only observed when there is an electrical discharge through the stable precursor gases \(\text{CH}_3\text{CN}\) and \(\text{SiH}_4\). The observed \(eQq\) for \(\text{SiH}_3\text{NC}\) is much smaller than that of \(\text{SiH}_3\text{CN}\), as expected when the nitrogen atom is near the center of mass rather than at the terminal position. The theoretical value of \(eQq\) for \(\text{SiH}_3\text{CN}\) agrees to better than 5% with the measured constant. The observed \(K\) rotational structure is that of a symmetric top with \(C_3\) symmetry, and the frequency separation of the \(K = 0\) and 1 lines is comparable to that of \(\text{SiH}_3\text{CN}\). Isotopic substitution provides the final piece of evidence in support of the identification: the \(\text{SiH}_3\text{N}^{13}\) and \(\text{SiH}_3\text{N}^{15}\) isotopic species were synthesized when \(^{13}\text{C}\) or \(^{15}\text{N}\) were substituted for either \(^{12}\text{C}\) or \(^{14}\text{N}\) in the \(\text{CH}_3\text{CN}\) precursor, and the rotational lines of the rare isotopic species were at the expected isotopic shifts in frequency.

Cyanide (−CN) and isocyanide (−NC) isomer pairs have received a great deal of attention in molecular astronomy, largely owing to the anomalously high abundance of HNC in cold dark clouds and its formation via ion–molecule reactions involving HCNH+ (Loison et al. 2014). In the outer molecular envelope of IRC+10216, the abundances of the −CN isomers of the cyanopolyynes HCN, HC3N, and HCN are 100–1000 times higher than the corresponding −NC isomers (Bieging & Nguyen-Quang-Rieu 1988; Guelin et al. 2004; Agúndez et al. 2014). Perhaps more relevant to the work here are the metal-bearing cyanides/isocyanide pairs MgCN/MgCN and SiCN/SiNC, which are among the more abundant metal-bearing molecules in IRC+10216. Both pairs have been observed in the outer envelope of IRC+10216 (Ziurys et al. 1995; Guelin et al. 2004), but have significantly different abundances despite comparable heats of formation \((\Delta H)\). The MgNC/MgCN ratio of ~20 was rationalized by Ziurys et al. (1995) on the basis of \(\Delta H\) of MgNC, which is lower than MgCN by 950 K (Senent et al. 2012). However, the same argument does not apply to SiCN and SiNC because the column densities of the two silicon-bearing species are comparable, despite a relative \(\Delta H\) that is similar to MgNC/MgCN. Only one other cyanide/isocyanide isomeric pair (HCN/HNC) has been observed in the inner envelope of IRC+10216.

Close to the photosphere, the abundance of HNC is fairly high and the HCN/HNC ratio is about 10, but the ratio increases rapidly with distance from the star (Cernicharo et al. 2013). Lacking possible analogs in the inner envelope like that of SiCN/SiNC, estimation of the SiH3CN/SiH3NC ratio in the inner envelope awaits detection of SiH3NC.

There are no apparent obstacles for detection of SiH3NC in IRC+10216: the dipole moments, rotational partition functions, and spectroscopic constants of SiH3NC and SiH3CN are similar. We did not extend the measurements of SiH3NC to higher frequencies, instead the effect of neglecting high-order centrifugal distortion terms was estimated by referring to SiH3CN, which has been measured both in the centimeter and millimeter bands (Prien et al. 1998). We fit the four spectroscopic constants in the truncated Hamiltonian used to analyze SiH3NC (see Table 2) to the centimeter-wave measurements of SiH3CN alone, and compared the frequencies of SiH3CN calculated with this Hamiltonian to the measured ones in the millimeter band. The estimated uncertainty in the calculated frequencies of SiH3CN at 200 GHz—i.e., near the highest frequency where SiH3CN was observed in IRC+10216 (Cernicharo et al. 2017)—is about 4 km s−1, or a fraction the FWHM of the features observed in the inner region of IRC+10216 with ALMA (Cernicharo et al. 2013).

Because silicon carbide films are synthesized in the laboratory from \(\text{CH}_3\text{SiH}_3\) and other substituted methyl silanes \((\text{CH}_3)_n\text{SiH}_{4–n}\), it is worth considering whether solid SiC is formed by the same chemical mechanism in the laboratory and the inner envelope of a carbon-rich AGB star. Silicon carbide films are synthesized in the laboratory by the process known as hot wire chemical vapor deposition (HWCVD; Zaharias et al. 2006; Shi 2017). Three main processes occur in HWCVD: (1) formation of initial reactive species by activation of the precursor gas \((\text{CH}_3\text{SiH}_3)\) on a metal filament surface heated to \(\lesssim 2000\) K; (2) chemical reactions in the gas phase.

2 The term “metal bearing” used here refers to a gasous molecule in an evolved star that contains Al, Ti, Fe, Si, or Mg. We prefer “metal bearing” because in terrestrial chemistry “refractory” refers to a solid whose melting point (fusion temperature) is \(\gtrsim 1850\) K (e.g., solid silicon carbide (SiC) or carborundum whose melting point is 3100 K).
between the reactive species and the abundant precursor CH₃SiH₃; and (3) reactions on the substrate surface at temperatures near 600–700 K. Although the temperatures are comparable in the inner envelope and HWCVD, the gas density in HWCVD is 10⁻³⁻¹⁰⁴ times higher than in the photosphere of the central star in IRC+10216 and 10⁵⁻¹⁰⁹ times higher still than the dust-forming region (Agúndez et al. 2012). Another source of uncertainty in the analogy with HWCVD is whether the gas-phase reactions that occur in the inner envelope of the carbon star are the same as those in the laboratory reactor. Nevertheless, it is striking that the gas-phase precursor (CH₃SiH₃), synthesized product (solid SiC), and temperatures are roughly the same in HWCVD and the inner envelope of IRC+10216.

Our laboratory detection of SiH₃NC suggests that fragments of CH₃SiH₃, SiH₃CN, and SiH₃NC might be key reactive intermediates in the formation of solid SiC dust in circumstellar envelopes. The rotational spectra of most of these organosilane fragments have not been measured in the laboratory, although some have been observed trapped in cold matrices by low-resolution IR spectroscopy. Kaiser & Osamura (2005) and Bennett et al. (2005) considered seven possible derivatives of CH₃SiH₃ with the elemental composition [C, H, Si] where x = 3, 4, 5, and provided calculations of their dipole moments and rotational constants. To date, the rotational spectrum of only one fragment (CH₃SiH₃) has been measured in the laboratory (Bailleux et al. 1997), but the lowest rotational transition (0 01 − 0 00) of the six remaining candidates are predicted to lie within range of our sensitive FTMW spectrometer used to observe SiH₃NC. Although the dipole moments of the [C, H, Si] fragments are modest (µ ≤ 1 D; Bak & Osamura 2005), they are comparable to the recently detected parent molecule CH₃SiH₃ (0.7 D), and the dipole moments of fragments of SiH₃CN and SiH₃NC (x = 1, 2, 3) are expected to be much larger. Another intriguing candidate for detection is HNCSI, a small silicon-bearing species observed in abundance in a solid Ar matrix (Maier et al. 1998). The rotational spectrum of HNCSI has not yet been measured, but accurate quantum chemical predictions of its structure and spectroscopic properties are available (Thorwirth & Harding 2009), and a laboratory search would appear straightforward.

Software: SPFIT (Pickett 1991), CFOUR (Stanton et al. 2017).

### Appendix

#### Ab Initio Calculations on Cyanosilane

The calculations on SiH₃CN (Table 6) were used to determine the expected accuracy for predicting SiH₃NC. The calculations on SiH₃CN were used to determine the expected accuracy for predicting SiH₃NC. All calculations were performed at the all-electron CCSD(T) level. The overall trend with increasing basis size and inclusion of weighted core-valence basis functions (Section 2) is increasing rotational constant Bᵣ with the number of basis functions. The excellent agreement between the experimental and ab initio value with the quadruple-ξ quality basis is consistent with the benchmarking performed by Bak et al. (2001). The inclusion of core-valence basis functions (cc-pCVQZ) yields the best agreement between theory and experiment with Bᵣ within 0.03% of Bᵣ. The dipole moment and ¹⁴N quadrupole coupling constant is also in qualitative agreement with the experimentally determined values (Priem et al. 1998), providing confidence in our calculations of SiH₃NC.

### Table 6

| Basis Set          | Aᵣ (MHz) | Bᵣ (MHz) | Bᵣ - Bₑ (MHz) | Dipole Moment (D) | eQq (N) (MHz) |
|--------------------|----------|----------|----------------|------------------|---------------|
| cc-pVDZ            | 83,593.78 | 4813.18  | −159.83        | −3.25            | −4.08         |
| cc-pVTZ            | 84,865.07 | 4940.02  | −32.99         | −3.38            | −5.16         |
| cc-pVQZ            | 86,023.03 | 4990.37  | 17.37          | −3.45            | −5.27         |
| cc-pwCVZD          | 84,256.93 | 4847.73  | −125.27        | −3.23            | −4.45         |
| cc-pwCVTZ          | 85,415.44 | 4957.13  | −15.88         | −3.12            | −5.10         |
| cc-pwCVQZ          | 85,368.29 | 4971.61  | −1.39          | −3.46            | −5.11         |

#### Notes

1. Bₑ corresponds to the experimental rotational constant (4973.005714 MHz) determined by Priem et al. (1998).
2. The basis set used to predict the SiH₃NC equilibrium rotational constants.

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