Spectroscopic investigation of the $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transition of HSiNCO

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The first spectroscopic observation of the previously unknown species HSiNCO has been reported. HSiNCO was generated by the fragmentation of trimethylsilylisocyanate with a high-voltage discharge source. The $0_0^0$ band of the $\tilde{A}^1A''-\tilde{X}^1A'$ transition has been recorded with full rotational resolution using laser-induced fluorescence spectroscopy and ground and excited state rotational and centrifugal distortion constants determined. Ten additional vibrational bands belonging to HSiNCO have also been observed in the laser-induced fluorescence spectrum and have been assigned based on predicted anharmonic vibrational frequencies. Due to the large change in geometry upon excitation, a number of axis-rotation peaks have been observed in the $0_0^0$ band and the axis-rotation angle ($\theta_r$) has been estimated to be $0.6^\circ \pm 0.2^\circ$. Dispersed fluorescence spectroscopy has been carried out and $v_9$ (the N–C–O out-of-plane bending mode) and a number of overtones of $v_4$ (the Si–H wagging mode) have been observed in the ground electronic state.

I. INTRODUCTION

We have recently studied the $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transition of HSIN using laser-induced fluorescence (LIF) spectroscopy. HSiNC had previously been studied using microwave spectroscopy with the hope of detecting the species in space as similar species, such as SiCN/SiNC and SiC₂, had already been observed in different regions of space. Our work on HSiNC showed that on excitation to the $\tilde{A}^1A''$ state the H–Si–N angle increased by $\approx 15^\circ$ and resulted in the observation of anomalous peaks caused by axis-rotation (or axis-switching). Similar anomalous peaks have been previously observed in the spectra of HSIF, HSICl, HSIBr, and HSII. Recent work by Dover and Evans have looked at different [H, Si, N, C, O] isomers and found a number of likely candidates for spectroscopic detection, including HSiNCO.

In this work we have extended our studies on silicon containing species and have looked at the $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transition of a previously unobserved species, HSiNCO, using laser-induced and dispersed fluorescence (DF) spectroscopy. Like HSiNC, HSiNCO has the potential of being found in space as the abundance of oxygen is similar to that of C, N, and Si in addition to the fact that HSiNCO has been predicted to be significantly more thermodynamically stable than HSiNCO.

II. EXPERIMENT

The room temperature vapor of trimethylsilylisocyanate [(CH₃)$_3$SiNCO, >95%, Fluorochem; used without further purification] was placed in a glass bubbler and a stream of argon passed through the sample at a pressure of 2 bar. This gas mixture was then expanded through a pulsed valve (General Valve, series 9) into an electric discharge source made of two stainless steel electrodes housed in Delrin. At an appropriate time, a pulsed high-voltage discharge is generated between the two electrodes via a Tesla coil. The high-voltage discharge source is similar to that used by Clouthier and co-workers.

Low (0.50 cm$^{-1}$) and medium (0.10 cm$^{-1}$) resolution LIF spectra were recorded using a 355 nm pumped tunable pulsed dye laser (Quanta-Ray PDL-3). All spectra were calibrated with lines from a neon-filled hollow cathode lamp and simultaneously recorded étalon fringes (free spectral range of 1.0 cm$^{-1}$). The LIF spectra and calibration signals were digitized on an oscilloscope (LeCroy Waverunner LT342) and captured by a personal computer using software written in LABVIEW.

High resolution spectra were recorded using a pulsed OPO laser system at the University of Bristol. The system is seeded at the idler wavelength with a narrow-linewidth, continuous wave IR diode laser, giving near transform limited bandwidth for both the idler and signal output used to excite the fluorescence. The fluorescence from the intersection of the laser and molecular beams was imaged onto an adjustable slit placed in front of a photomultiplier tube (PMT). The slit was set so that only light from the central core of the jet was collected to reduce Doppler broadening of the spectra, giving an overall resolution of 0.01–0.015 cm$^{-1}$ for the spectra recorded. The signal from the PMT was recorded via a digital oscilloscope onto a computer. To calibrate the spectra, a portion of the seeding near infrared light was directed to a wavemeter (cluster LM-007 lambdameter), with specified absolute accuracy of 0.1 ppm (equivalent to 0.01 cm$^{-1}$).
in the experimental spectral range) and a precision of 0.0001 cm\(^{-1}\). The wavemeter readings were recorded simultaneously with the spectrum on the computer. The spectra recorded on the high resolution system were significantly hotter than those on the medium resolution system; the rotational temperature for the high resolution spectrum is estimated to be 30 K.

The ground state vibrational manifold was investigated using DF spectroscopy. DF spectra were obtained by fixing the wavelength of the dye laser to the \( ^2Q_1 \) branch of the \( 0^0_0 \), \( 5^1_0 \), and \( 8^2_0 \) bands in the LIF spectrum and imaging the resultant fluorescence onto the entrance slit of a 0.5 m scanning monochromator (Acton Research SpectraPro 2500i) fitted with a 1800 lines/mm grating blazed at 500 nm. The wavelength-resolved fluorescence signals were detected with an air cooled charge coupled device camera (PI-MAX system). The monochromator was calibrated to an estimated accuracy of \( \pm 2 \) cm\(^{-1}\) using known emission lines from a mercury lamp.

**III. CALCULATIONS**

A theoretical investigation of HSiNCO and a number of [H, Si, N, C, O] isomers has been previously undertaken by Dover and Evans.\(^5\) However, for this work some additional calculations were required. First, to look at the excited state of HSiNCO and its energy the Symmetry-Adapted Cluster-Configuration Interaction (SAC-Cl) method, as implemented in the GAUSSIAN03 suite of programs, was used.\(^9,10\) For these calculations geometry optimization was carried out using the “level 2” method and the aug-cc-pVDZ basis set; then, using the optimized geometry, a single point calculation was carried out using the “level 3” method and the aug-cc-pVTZ basis set. Second, MP2 harmonic and anharmonic vibrational frequencies for both the ground and excited electronic states of HSiNCO were calculated for the optimized MP2 structure using GAUSSIAN03 with an aug-cc-pVTZ basis set.\(^9,11\)

**IV. RESULTS AND DISCUSSION**

**A. Identity of the observed species**

Figure 1 shows a portion of low resolution LIF scan of the band system which was recorded between 18 500 and 22 500 cm\(^{-1}\) when a trimethylsilisilisocyanate/argon mixture was passed through the high-voltage discharge source. A number of bands were observed to have a similar structure. The strongest of these bands, at 20 346 cm\(^{-1}\), was assigned as the \( 0^0_0 \) band and as no other bands with this structure were observed to the red of this band. Figure 2(a) shows a medium resolution spectrum of the \( 0^0_0 \) band. The band structure of the \( 0^0_0 \) band bears a strong resemblance to that observed in the \( \tilde{A}^1A''-\tilde{X}^1A' \) electronic spectra of the halosilylenes and HSiNC which have been studied previously.\(^1,3,4\) This resemblance was a good starting point in identifying the spectral carrier as that of another pseudohalosilylene, in this case HSiNCO. Given the precursor used, some of the possible species formed in the discharge could be those discussed in our theoretical study on the [H, Si, N, C, O] isomers.\(^5\) Simulations of the \( 0^0_0 \) band based on predicted rotational constants of both the ground and excited states of the most energetically stable [H, Si, N, C, O] isomers gave a clear indication that HSiNCO is the most likely carrier of the signal (see supplementary material for the simulation plots).\(^12\) The predicted structure of HSiNCO in its ground and excited \( \tilde{A}^1A'' \) electronic states are given in Table I. Like the halosilylenes and HSiNC, there is a significant increase in the H–Si–X angle in going from the ground state to the \( \tilde{A}^1A'' \) electronic state. The LIF spectrum of HSiNCO was relatively clean with few bands from different molecules being observed (see Fig. 1).

**B. Rotational analysis**

Since HSiNCO is heavier than HSiNC the degree of rotational structure resolved is significantly less at low to medium resolution. However, from Fig. 2(a) it is clear that anomalous peaks [marked with a diamond in Fig. 2(a)] similar to that seen for HSiNC, are present which may be attributed to axis-rotation. The assignment of these peaks is much clearer than that found with HSiNC, as the level of contamination in the spectra recorded for HSiNCO is significantly less than that observed for HSiNC.\(^1\) The level of resolution achieved in this case was not suitable for analysis of the rotational structure and therefore, the LIF spectrum of HSiNCO was investigated further at high resolution at the University of Bristol.

Unfortunately due to the reduced intensity of the transitions with the high resolution system only the strongest subbands of the \( 0^0_0 \) band were studied. This reduction in the intensity also meant that detection of the axis-rotation peaks was not possible at high resolution.

The linewidth of the high resolution system (\( \approx 0.015 \) cm\(^{-1}\)) is an order of magnitude better than the medium resolution system allowing the \( Q \) branches for the strongest subbands to be almost fully resolved. The high resolution spectra also revealed asymmetric top splittings which...
were not apparent in the medium resolution spectra. Figure 2(b) shows the high resolution spectrum of the subband centered on the \( ^1Q_1 \) branch of the \( 0^0 \) band of HSiNCO.

Assignment of the spectrum was relatively straightforward. The \( 0^0 \) band is a C-type band and the assigned lines were fitted to Watson’s \( S \)-reduced Hamiltonian with an \( I' \) representation using Pickett’s spectral fitting program SPFIT.\(^{13}\) Transitions with \( K''_J=0, 1, 2, \) and 3 were assigned with \( J' \) values up to 23 for the strongest branches. Where the intensity of the LIF signal was strong enough to achieve good rotational resolution of the \( Q \) branches, these lines were included in the fit. In cases where there was a degree of uncertainty in the assignments (due to lines being overlapped or not fully resolved), care was taken to weight them suitably. The resulting constants for the ground and the excited \( \tilde{X}^1A^+ \) electronic states are given in Table II (the line list can be found in the supplementary material).\(^{12}\) Ab initio determined values are also given in Table II. The calculated values of the \( B \) and \( C \) rotational constants are in good agreement with those observed, while the predicted values of the \( A \) rotational constants are slightly lower than those observed; however, the predicted change in \( A \) in going from the ground to the excited state is very similar to the observed change. This agreement between the predicted and observed values of the rotational constants further confirms that HSiNCO is the likely carrier of the observed signal. The SAC-CI transition energy (\( T_0 \)) is in very good agreement with the observed value, while the MP2 method underestimates the transition energy by \( \approx 4000 \text{ cm}^{-1} \), which is probably due to the limitations in the single-reference nature of the MP2 method.\(^{14}\)

As seen with the halosilylenes and HSiNC, the centrifugal distortion constant \( D_K \) is significantly large.\(^{1,3,4}\) In this case, the value of \( D_K \) is \( \approx 10\% \) that of the \( A \) rotational constant, which is similar to that observed for HSiNC.\(^{1}\) Anomalously large values of \( D_K \) have also been seen in HNCO and HNCS, where the reason for the large value of \( D_K \) has been explained by a strong coupling between the in-plane bending vibrations (e.g., the H–N–C or N–C–O in-plane bending modes) with the rotation about the axis of the least moment of inertia.\(^{15}\) It can be easily seen how a similar process could be occurring in both HSiNC and HSiNCO.

### Table II. Rotational constants for the lowest vibrational level in the ground (\( \tilde{X}^1A^+ \)) and excited (\( \tilde{A}^1A^+ \)) electronic states of HSiNCO (all values in \( \text{cm}^{-1} \)).

<table>
<thead>
<tr>
<th>State</th>
<th>Constant</th>
<th>This work(^a)</th>
<th>MP2(^b)</th>
<th>SAC-CI(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tilde{X}^1A^+ )</td>
<td>A</td>
<td>4.131 56(32)</td>
<td>3.396 6</td>
<td>3.204 8</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.091 479(17)</td>
<td>0.091 3</td>
<td>0.091 4</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.089 326(17)</td>
<td>0.088 8</td>
<td>0.088 9</td>
</tr>
<tr>
<td></td>
<td>( D_J \times 10^7 )</td>
<td>-1.16(39)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D_K \times 10^5 )</td>
<td>-3.21(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D_K )</td>
<td>0.011 653(31)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tilde{A}^1A^+ )</td>
<td>A</td>
<td>5.723 41(22)</td>
<td>4.936 9</td>
<td>5.123 7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.090 556(16)</td>
<td>0.089 9</td>
<td>0.089 9</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.089 001(16)</td>
<td>0.088 4</td>
<td>0.088 4</td>
</tr>
<tr>
<td></td>
<td>( D_J \times 10^7 )</td>
<td>-1.28(36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D_K \times 10^5 )</td>
<td>-2.64(93)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D_K )</td>
<td>0.018 277(22)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_0 )</td>
<td></td>
<td>20 346.339 51(56)</td>
<td>16 386 20</td>
<td>9 195</td>
</tr>
<tr>
<td>No. of lines</td>
<td></td>
<td>220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Numbers in parentheses are 1\(\sigma\) uncertainties in units of the last significant digit.

\(^b\)Calculated at the MP2 level of theory using the aug-cc-pVTZ basis set.

\(^c\)SAC-CI calculation. This work.

\(^d\)Overall standard deviation of fit (in \( \text{cm}^{-1} \)).
TABLE III. Vibrational assignments and the harmonic and anharmonic vibrational frequencies for the ground ($\tilde{X}$ $^1A'$) and the excited ($\tilde{A}$ $^1A''$) electronic states of HSiNCO calculated at the MP2/aug-cc-pVTZ level of theory (all values in cm$^{-1}$).

<table>
<thead>
<tr>
<th>State</th>
<th>Vibrational mode (symmetry)</th>
<th>Assignment</th>
<th>MP2 (harmonic)$^a$</th>
<th>MP2 (anharmonic)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{X}$ $^1A'$</td>
<td>$v_1$ ($a'$)</td>
<td>N–C–O antisymmetric stretch</td>
<td>2309.6</td>
<td>2274.1</td>
</tr>
<tr>
<td></td>
<td>$v_2$ ($a'$)</td>
<td>Si–H stretch</td>
<td>2093.4</td>
<td>2017.0</td>
</tr>
<tr>
<td></td>
<td>$v_3$ ($a'$)</td>
<td>N–C–O symmetric stretch</td>
<td>1408.3</td>
<td>1406.9</td>
</tr>
<tr>
<td></td>
<td>$v_4$ ($a'$)</td>
<td>Si–H in-plane wag</td>
<td>885.9</td>
<td>869.8</td>
</tr>
<tr>
<td></td>
<td>$v_5$ ($a'$)</td>
<td>Si–N stretch</td>
<td>641.2</td>
<td>625.7</td>
</tr>
<tr>
<td></td>
<td>$v_6$ ($a'$)</td>
<td>N–C–O in-plane bend</td>
<td>568.2</td>
<td>563.7</td>
</tr>
<tr>
<td></td>
<td>$v_7$ ($a'$)</td>
<td>Si–N–C in-plane bend</td>
<td>101.1</td>
<td>94.1</td>
</tr>
<tr>
<td></td>
<td>$v_8$ ($a'$)</td>
<td>N–C–O out-of-plane bend</td>
<td>637.9</td>
<td>634.2</td>
</tr>
<tr>
<td></td>
<td>$v_9$ ($a'$)</td>
<td>Si–N–C out-of-plane bend</td>
<td>157.6</td>
<td>145.2</td>
</tr>
</tbody>
</table>

$\tilde{A}$ $^1A''$

| $v_1$ ($a'$) | N–C–O antisymmetric stretch | 2347.8 | 2308.8 |
| $v_2$ ($a'$) | Si–H stretch | 2218.8 | 2115.8 |
| $v_3$ ($a'$) | N–C–O symmetric stretch | 1433.9 | 1429.5 |
| $v_4$ ($a'$) | Si–H in-plane wag | 690.9 | 675.7 |
| $v_5$ ($a'$) | Si–N stretch | 643.8 | 634.6 |
| $v_6$ ($a'$) | N–C–O in-plane bend | 597.5 | 595.5 |
| $v_7$ ($a'$) | Si–N–C in-plane bend | 107.6 | 107.4 |
| $v_8$ ($a'$) | N–C–O out-of-plane bend | 571.4 | 575.9 |
| $v_9$ ($a'$) | Si–N–C out-of-plane bend | 132.8 | 135.1 |

$^a$Unscaled frequencies.

C. Vibrational analysis

The observed band system has been assigned to the $\tilde{A}$ $^1A''$-$\tilde{X}$ $^1A'$ electronic transition of HSiNCO. This transition corresponds to the promotion of an electron from a nonbonding s orbital on the silicon atom to an unoccupied out-of-plane 3p orbital also located on the silicon. HSiNCO is a bent, planar molecule with $C_s$ symmetry. There are seven $a'$ vibrational modes labeled $v_1$ (N–C–O antisymmetric stretch), $v_2$ (Si–H stretch), $v_3$ (N–C–O symmetric stretch), $v_4$ (Si–H in-plane wag), $v_5$ (Si–N stretch), $v_6$ (N–C–O in-plane bend), and $v_7$ (Si–N–C bend), as well as two $a''$ vibrational modes labeled $v_8$ (N–C–O out-of-plane bend) and $v_9$ (Si–N–C out-of-plane bend). Harmonic and anharmonic vibrational frequencies obtained from the ab initio calculations on the $\tilde{A}$ $^1A''$ electronic state of HSiNCO are given in Table III.

In the LIF spectrum, as well as the $0^0_0$ band, ten additional vibrational bands of HSiNCO have been identified. At low resolution these bands consist of partially resolved subbands with prominent Q branches (see Fig. 1). Each observed vibrational band was fitted using the spectral fitting program PGOPHER. For each band, a rough fit was first obtained by fitting the Q branches and floating the origin frequency only. Once the rough fit was complete, a more accurate fit was obtained by adding in any rotational lines that were sufficiently resolved in the low resolution spectrum and the excited state rotational constants $A'$ and $B'$ were floated together with the origin frequency. This process was not very accurate as the number of rotationally resolved lines in the low resolution spectra was very few. However, in most cases the rough fitting of the Q branches gave a reasonable fit. In all cases the ground state parameters were fixed to those obtained from the high resolution fit of the $0^0_0$ band, while the centrifugal distortion constants of the excited states were fixed to those obtained from the rotational analysis of the $0^0_0$ band (see Table II). The assignments, band origins, offset from the $0^0_0$ band, MP2 anharmonic frequencies, and approximate values of $A'$ and $B'$ for each band are given in Table IV. The band at an offset of 153 cm$^{-1}$ has been tentatively assigned as $v_8$; however, there is a significant difference between the observed value and the MP2 anharmonic frequency, which is carried through to the band at an offset of 284 cm$^{-1}$ which has been assigned as $2v_9$. The bands at 21 575, 21 623, and 22 139 cm$^{-1}$ have a number of possible assignments and these are also listed in Table IV.

D. Dispersed fluorescence spectra

The DF spectra obtained for HSiNCO are similar to that observed for HSINC, adding further to the argument that the identity of the spectral carrier is indeed HSiNCO. The fluorescence signal of HSiNCO is an order of magnitude stronger than that found for HSINC so DF spectra were accessible from other prominent bands in the LIF spectrum. DF spectra were recorded by pumping the $\nu Q_1$ branch of the $0^0_0$, $5^0_0$, and $8^0_0$ bands of HSiNCO in the $\tilde{A}$ $^1A''$ electronic state [see Figs. 3(a)–3(c)]. The DF spectrum for the $0^0_0$ band [Fig. 3(c)] is quite simple and only contains a short $v_4$ (Si–H in-plane wagging mode) progression. For the $5^0_0$ band [Fig. 3(a)], the DF spectrum is more complicated than that of the $0^0_0$ band as there are two separate progressions present. As in the DF spectrum of the $0^0_0$ band there is a progression of $v_4$ which is the dominant feature of the spectrum; however, there is a second smaller progression which can be attributed to a combination of $n$-quanta of $v_4$ ($n=0–4$) with one quanta of $v_5$ (the N–C–O out-of-plane bending mode). For the $8^0_0$ band [Fig. 3(b)], the DF spectrum is quite simple and consists of a single progression which can be attributed to a combination
Assignment (symmetry) | Band origin | Offset from $0^0_0$ band | MP2$^a$ | $A'$ | $B'$ | rms error
--- | --- | --- | --- | --- | --- | ---
$0^0_0$ ($a'$) | 20 346.34 | 0.0 | 0.0 | 5.723 | 0.089 8 | ---
$7^0_2$ ($a'$) | 20 457.03(47)$^b$ | 99.63 | 107.4 | 4.439(58)$^b$ | 0.090 7(54)$^b$ | 0.094
$9^0_2$ ($a'$) | 20 508.98(14) | 152.73 | 135.1 | 6.954(17) | 0.090 3(16) | 0.389
$5^0_2$ ($a'$) | 20 580.27(34) | 223.94 | 212.3 | 4.404(93) | 0.090 19(38) | 0.088
$8^0_3$ ($a'$) | 20 640.08(30) | 284.18 | 269.3 | 6.043(36) | 0.090 3(34) | 0.816
$5^0_3$ ($a'$) | 20 934.28(19) | 577.94 | 575.9 | 6.024(33) | 0.090 22(22) | 0.054
$5^0_3$ ($a'$) | 20 991.06(21) | 634.76 | 634.6 | 6.763(26) | 0.090 4(24) | 0.593
$8^0_4$ ($a'$) | 21 514.66(16) | 1158.46 | 1152.8 | 6.499(20) | 0.090 20(19) | 0.047
$5^0_4$ ($a'$) | 21 575.44(37)$^c$ | 1220.01 | 1213.2 | 7.730(96) | 0.090 0(40) | 0.890
$5^0_4$ ($a'$) | --- | --- | --- | --- | --- | ---
$7^0_5$ ($a'$) | 21 623.28(32)$^d$ | 1266.93 | 1261.1 | 5.794(88) | 0.090 20(36) | 0.083
$5^0_5$ ($a'$) | --- | --- | --- | --- | --- | ---
$4^0_5$ ($a'$) | --- | --- | --- | --- | --- | ---
$5^0_5$ ($a'$) | 22 139.65(32)$^e$ | 1783.35 | 1787.4 | 5.708(39) | 0.090 17(36) | 0.089
$6^0_5$ ($a'$) | --- | --- | --- | --- | --- | ---
$5^0_5$ ($a'$) | --- | --- | --- | --- | --- | ---

$^a$Unscaled frequencies values based on anharmonic calculation at the MP2 level of theory using the aug-cc pVTZ basis set.
$^b$Numbers in parentheses are 1σ uncertainties in units of the last significant digit
$^c$Multiple assignments possible.
$^d$Alternative assignment.

of $n$-quanta of $v_4$ ($n=0−4$) with one quanta of $v_5$. For comparison, the predicted harmonic and anharmonic frequencies for the fundamental vibrational modes of HSiNCO in its ground electronic state are given in Table III. Using the obtained DF data it is possible to carry out an anharmonic analysis on the $v_4$ vibrational mode of HSiNCO in its ground electronic state. To do this the standard power series expression was used. The DF data from the $0^0_0$ and $5^0_1$ bands have been used to estimate $\omega_4$ and $x_{44}$ (see the supplementary material).

**E. Axis-rotation**

In Fig. 2(a) it is shown that a number of features in the $0^0_0$ band have been attributed to axis-rotation peaks resulting from the large change in the H–Si–N angle on excitation. Originally this phenomenon was discussed by Hougen and Watson and results in the observation of “forbidden” transitions involving $\Delta K=0$ and $\pm 2$. There are not enough data for accurate determination of the equilibrium geometries for the two electronic states examined in this study; therefore, to prove that the peaks assigned as axis-rotation peaks are real, the spectrum has been simulated using the JB95 program (JB95). In the JB95 program axis-rotation about the $\varphi$, $\theta$, and $\chi$ angles can be made (Euler angle inertial frame reorientation); for this work only the angle $\theta$ in the excited state was altered. Figure 4 shows an expanded view of a region in Fig. 2(a) where the axis-rotation peaks occur. An iterative approach based on comparing the simulated spectrum with the

![FIG. 3. The DF spectra obtained by exciting the strong $^1Q_1$ branch of the (a) $5^0_0$, (b) $5^0_1$, and (c) $0^0_0$ vibrational band of the $\bar{A}^1A'^-\bar{X}^1A'$ transition of HSiNCO. The spectra were recorded by averaging 5000 laser shots using a slit width of 170 μm.](image)

![FIG. 4. An expanded view of the axis-rotation region of the medium resolution spectrum of the $0^0_0$ band between 20 343 and 20 351 cm$^{-1}$. Section (a) shows the simulated spectrum with a rotational temperature of $\sim$8 K and an axis-rotation angle of 0.6°. Section (b) shows the experimental spectrum.](image)
experimental spectrum was taken to obtain an estimate of the axis-rotation angle ($\theta_T$) of $0.6^\circ \pm 0.2^\circ$.

As mentioned previously, SAC-CI calculations were carried out on both the ground and excited electronic states. The structural data obtained from these calculations were put through the procedure originally described by Hougen and Watson to see if they agreed with the experimentally determined axis-rotation angle. The SAC-CI structural data gave an axis-rotation angle of $\sim 0.3^\circ$, which is significantly different from the experimentally determined value of $0.6^\circ$. As there are no other similar systems available for comparison, it is very difficult to assess the validity of this result; however, the difference between the theoretical and experimental values of $\theta_T$ for HSINC was only 20% and therefore there is enough of a difference for HSINCO to consider what may be causing it.1

Assuming the experimental data obtained were of good quality then the obvious reason for the discrepancy in the axis-rotation angle could be the poor prediction of the H–Si–N angle in the excited state. However, analysis of this angle shows that in order for the predicted axis-rotation angle to match the observed value the H–Si–N angle would need to change by over 30° in going from the ground to the excited electronic state, which is a significant increase over that observed in the halosilylenes and HSINC and is therefore unlikely. The most likely scenario is that $\theta_T$ is dependent on the H–Si–N angle as well as the Si–N–C or N–C–O angles.

There has been some debate over the linearity or nonlinearity of the N–C–O group in a number of species, with the typical N–C–O angle being between 160° and 180°. The calculations on HSINCO only predict minor deviations from a linear geometry for the N–C–O group. For HSINCO, variation of the N–C–O angle does not seem to result in any significant changes to the predicted axis-rotation angle, unless for extreme angle changes, for example, an N–C–O angle of 90°, which are unrealistic. The dependency of the axis-rotation angle to the N–C–O angle therefore may be ruled out, as it would seem unlikely that the $ab\ initio$ methods used would be so wrong in the prediction of this angle in either electronic state.

If we now focus on the Si–N–C angle, the $ab\ initio$ results suggest that there is an approximate $+5^\circ$ change in the Si–N–C angle in going from the ground state to the $\tilde{A} \ A^\prime$ excited state. By varying the Si–N–C angle in the excited state and keeping the other structural parameters fixed, the axis-rotation angle predicted by experiment can be achieved by a Si–N–C angle change of $-13.6^\circ$. This angle change relates to an excited state Si–N–C angle of 132° compared to the predicted value of 151°. It is possible that the $ab\ initio$ methods are overestimating the Si–N–C angle by $\sim 19^\circ$; therefore, it is essential that further work is carried out in order to accurately determine the geometry of HSINCO in both the ground and $\tilde{A} \ A^\prime$ electronic states.

**V. CONCLUSION**

In this work, we have completed the first spectroscopic study of the $\tilde{A} \ A^\prime$-$\tilde{X} \ A^\prime$ transition of HSINCO. This is the first observation of HSINCO of any kind. Together with the $ab\ initio$ work carried out on HSINCO and the similarity of the spectrum to HSINC and other halosilylenes we are confident in the assignment of the observed spectra. A number of vibrational bands have been observed in the ground state and the first $A^\prime$ electronic excited state and have been tentatively assigned based on the $ab\ initio$ results. Detailed rotational analysis has been carried out on the $0_0^+$ band of the $\tilde{A} \ A^\prime$-$\tilde{X} \ A^\prime$ transition resulting in the evaluation of rotational and quartic centrifugal distortion constants of both states.

The most interesting aspect of the spectrum is the appearance of the forbidden transitions corresponding to $\Delta K_a = 0$ and $\pm 2$. These peaks are known as “axis-rotation” peaks and they arise because of the significant change in the H–Si–N angle in going from the ground state to the excited state. The determination of the axis-rotation angle has been carried out in two ways: An iterative approach based on simulation of the LIF spectrum and by using the Hougen and Watson method with SAC-CI predicted structures of HSINCO. The axis-rotation angle was estimated to be $0.6^\circ \pm 0.2^\circ$ from the observed spectrum. However, the value of $\theta_T$ based purely on the SAC-CI result predicts an axis-rotation angle of only $0.3^\circ$. The structural dependence of the axis-rotation angle has been explored and the discrepancy between the observed and predicted values of $\theta_T$ is probably a result of poor prediction of the H–Si–N and Si–N–C angles in both ground and excited electronic states.

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