The Microwave Spectrum of Silylisothiocyanate, SiH_3NCS

I. Molecular Constants for the Ground State and Excited states of ν_{10}, and r_s Coordinates of Si and S

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The $J \rightarrow J+1$ transitions (J = 8, 9, 10 and 11) in the microwave spectrum of SiH_3NCS have been assigned for the vibrational ground state and for the states v_{10} = 1, 2 and 3. The results extend earlier work, giving more precise values for several of the molecular constants. Resonances in the excited vibrational states have been analysed: from these, values are deduced for the anharmonicity constant $g_{10,10}$ and the vibrational interval $v_{10} = 1 \rightarrow 2$. The spectra of molecules isotopically substituted with ^{29}Si, ^{30}Si and ^{34}S have been reassigned, and the resulting r_s coordinates are in excellent agreement with bond lengths determined by electron diffraction.

I. Introduction

Silyl isothiocyanate, SiH_3NCS, was first prepared by MacDiarmid[1]. An early study of the infrared spectrum[2] suggested that the molecule is a symmetric top. This was confirmed by more detailed analysis of the vibrational spectra by Ebsworth et al.[3], and by the microwave work of Jenkins, Kewley and Sugden[4].

Jenkins et al. measured the microwave spectra of several isotopic species of SiH_3NCS and its deuterated forms in their ground vibrational states. All except the partially deuterated molecules were found to have characteristic symmetric top spectra. They also analysed the $J = 7 \rightarrow 8$, $v_{10} = 1$ lines, where ν_{10} is the lowest degenerate vibrational fundamental, expected to be primarily an $Si-N=C$ bending mode[3]. At least five groups of lines assigned to successive vibrational levels of ν_{10} could be readily observed, with intensities suggesting that $\omega_{10} < 100$ cm^{-1}. From the observed l-doubling constant q_{10}, obtained from the $v_{10} = 1$ spectrum, Jenkins et al. deduced a value of 54 cm^{-1} using the approximate relation $q_{10} \cong 2 B_0^2/\omega_{10}$.

Recently Glidewell, Robiette and Sheldrick[5] have studied the molecular structures of SiH_3NCS and SiH_3NCO by electron diffraction. Their results confirmed the presence of a low frequency $Si-N=C$ bending mode in both molecules, and indicated a vibrational wavenumber of about 100 cm^{-1} for ω_{10} in SiH_3NCS. To our knowledge no direct observation of this mode in the infra-red or Raman spectrum has been published. We decided therefore to reinvestigate the microwave spectrum of SiH_3NCS, with particular interest in molecules in excited vibrational states of the ν_{10} mode, to see whether additional information on the vibrational potential function could be obtained.

II. Experimental

SiH_3NCS was prepared by streaming silyl bromide vapour through a tube packed with silver thiocyanate. The silyl bromide was purified before use by low temperature fractional distillation. The silver thiocyanate had been freshly precipitated and dried by prolonged pumping on a vacuum line. The SiH_3NCS thus produced was used without further purification. No microwave lines attributable to impurities were seen when fresh samples of the vapour were admitted to the absorption cell, although a few strong unidentified impurity lines appeared over the course of a few hours.

Microwave spectra were recorded on a Hewlett Packard 8560A spectrometer in the frequency range 26.5 to 39.0 GHz. The accuracy of the frequency calibration was checked by measurements of the $J = 2 \rightarrow 3$ line of OCS in its ground vibrational state[6]. All measurements were made with the sample at room temperature at a pressure of about 15 mtorr. No hyperfine structure due to the quadrupole of the ^{14}N nucleus was observed.

III. Theory

We have assigned the microwave spectra of molecules in the ground vibrational state ($v_{10} = 0$, $l_{10} = 0$) and in the excited states $v_{10} = 1$, $l_{10} = \pm 1$; $v_{10} = 2$,

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$l_{10}=0$; $v_{10}=2$, $l_{10}=\pm 2$; $v_{10}=3$, $l_{10}=\pm 1$; $v_{10}=3$, $l_{10}=\pm 3$. For brevity v_{10} and l_{10} are hereafter written simply v and l. The theoretical expressions to which the observed frequencies were fitted are given in Table 1. They are essentially those of Grenier-Besson and Amat[7], Tarrago[8] and Amat, Nielsen and Tarrago[9] except that the only l-resonance terms retained are those arising from the matrix elements $\langle v, l; J, k | H_{\text{eff}} | v, l \pm 2; J, k \pm 2 \rangle$. Levels connected by these matrix elements lie relatively close together in energy by virtue of the small size of $[A_{10} - (A\zeta)_{10} - B_{10}]$, which is found to be about 4250 MHz in this molecule. This in turn is a consequence of the size of the rotational constants ($A \sim 85000$ MHz, $B \sim 1500$ MHz) and the value of ζ, which for a chain-bending vibration is expected to lie between +0.9 and +1.0. Levels connected by other potentially important matrix elements, e. g. $\langle v, l; J, k | H_{\text{eff}} | v, l \pm 2; J, k \mp 1 \rangle$, are separated by several hundred GHz so that the effect of such terms may be considered negligible. Higher order terms such as $\langle v, l; J, k | H_{\text{eff}} | v, l \pm 4; J, k \pm 4 \rangle$ have been omitted also because their coefficients are expected to be too small to affect the calculated spectrum significantly. Throughout we follow the convention that k and l represent signed quantum numbers, and $K = |k|$.

Table 1. Theoretical expression used for the frequency of a transition with $\Delta J=1$, $\Delta k=0$, $\Delta l=0$.

$$\nu = 2B_v(J+1) - 4\,\mathrm{D_J}(\mathrm{J}+1)^3 - 2D_{JK}(J+1)k^2 + 2\eta_{10J}(J+1)kl + f(v^l; J, k)$$

where:

$$f(0^0; J, k) = 0\,;$$

for $v \neq 0$, $(k-l) \neq 0$,

$$f(v^l; J, k) = \; = \frac{q_{10}^2 (J+1)\,[(J+1)^2 - (k-1)^2]\,[(v+1)^2 - (l-1)^2]}{16\,[(k-l)(A - A\zeta - B)_v + (l-1)\Delta_v]} - \frac{q_{10}^2 (J+1)\,[(J+1)^2 - (k+1)^2]\,[(v+1)^2 - (l+1)^2]}{16\,[(k-l)(A - A\zeta - B)_v + (l+1)\Delta_v]}\,^{\dagger}$$

with $\Delta_v = [g_{10,10} + (A - B - 2A\zeta)_v]$;

for $v=1$, $(k-l)=0$,

$$f(1^1; J, k) = \pm q_{10}(J+1)\,;$$

for $v>1$, $(k-l)=0$ the levels were treated by matrix diagonalisation and no algebraic expression is appropriate.

† The l-resonance terms are adapted from the general from given by Bertram[21]: see also Careless and Kroto[22].

It should be noted also that we follow the more common definition of the l-doubling constant q_t, i. e. that used by Oka[10], Morino and co-workers[11] and Cartwright and Mills[12] among many others. Thus our q_t is four times the parameter $q_0^{(t)}$ used by Amat, Tarrago et al.[7–9].

IV. Results

A summary of the molecular constants obtained is given in Table 2. In subsequent Tables the calculated frequencies are those calculated from the constants of Table 2, using the formulae of Table 1 except where otherwise indicated. We now discuss individual vibrational states in turn.

IV. 1. Vibrational Ground State Spectra

The frequencies observed for SiH$_3$NCS are given in Table 3. The assignment is straigthforward and is identical to that of Jenkins, Kewley and Sugden[4]. Although we did not include their measurements in our fit, our constants reproduce their data satisfactorily, the worst deviation being 0.29 MHz. The

Table 2. Molecular constants derived from analysis of the microwave spectrum of SiH$_3$NCS uncertainties (in paretheses) are one standard deviation and refer to the last figure quoted.

Species	v^l	B_v/MHz	D_{JK}/kHz	D_J/kHz	η_{10J}/kHz	q_{10}/MHz	$[A - A\zeta - B]$/MHz	σ/MHz[a]
^{28}SiH$_3$NC^{32}S	3^3	1545.494 (2)	35.86$_3$ (3$_3$)	0.135 (9)	47.80 (3)	2.657 (3)	4200 (assumed)	0.05
(abundant isotopic	3^1	1544.728 (1)	36.458 (7)	0.162 (4)	48.69 (3)			0.04
species)	2^2	1536.124 (2)	37.252 (11)	0.145 (7)	49.44 (3)	2.75 (3)	4200 (150)	0.05
”	2^0	1535.644 (1)	37.661 (7)	0.130 (6)	—			0.03
”	1^1	1526.335 (1)	39.184 (6)	0.116 (4)	52.151 (3)	2.783 (1)	4250 (100)	0.03
”	0^0	1516.040 (1)	41.958 (6)	0.087 (4)	—	—	—	0.02
^{29}SiH$_3$NC^{32}S	0^0	1493.640 (1)	40.50 (2)	0.089 (4)	—	—	—	0.03
^{30}SiH$_3$NC^{32}S	0^0	1472.411 (3)	39.26 (3)	0.088 (9)	—	—	—	0.04
^{28}SiH$_3$NC^{34}S	0^0	1473.556 (2)	40.01 (3)	0.089 (6)	—	—	—	0.04

[a] Standard deviation of the least squares fit to theoretical expressions of Table 1.

main reason for the small difference between their B_0 (1516.018 ± 0.008 MHz) and ours is that we have studied J values high enough for D_J to be significantly determined: Jenkins et al. were able to conclude only that $D_J < 0.3$ kHz (which is indeed the case). Their value of D_{JK}, 41.9 ± 1.0 kHz, is within experimental error the same as ours.

Spectra of some isotopic species were observed in natural abundance: $^{29}SiH_3NCS$ (5%), $^{30}SiH_3NCS$ (3%) and $SiH_3NC^{34}S$ (4%). The frequencies are given in Table 4. These assignments do not correspond to those of Jenkins et al. Even with the advantage of the Hewlett Packard spectrometer and with the more intense lines at our higher J values

Table 3. Microwave spectrum of SiH_3NCS (MHz) in the vibrational ground state.

J	$8 \rightarrow 9$		$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$	
K	obs	o−c	obs	o−c	obs	o−c	obs	o−c
0	27288.49	0.02	30320.48	0.02	33352.45	0.03	36384.38	0.02
1	27287.71	0.00	30319.62	0.00	33351.50	0.00	36383.34	−0.02
2	27285.48	0.03	30317.12	0.02	33348.74	0.01	36380.33	−0.01
3	27281.69	0.02	30312.92	0.02	33344.11	0.00	36375.31	0.01
4	27276.38	−0.01	30307.03	0.00	33337.66	0.01	36368.23	−0.02
5	27269.55	−0.04	30299.43	−0.05	33329.31	−0.03	36359.11	−0.08
6	27261.26	−0.02	30290.21	−0.04	33319.16	−0.03	36348.07	−0.04
7	27251.48	0.02	30279.34	0.00	33307.19	0.00	36335.01	−0.01
8	27240.09	−0.04	30266.74	−0.01	33293.34	0.00	36319.92	0.00
9	—		30252.50	0.02	33277.67	0.02	36302.83	0.03
10	—		—		—		36283.76	0.10
11	—		—		—		36262.74	0.22

Table 4. Microwave spectra of isotopically substituted SiH_3NCS molecules (MHz) in their vibrational ground states.

J	$8 \rightarrow 9$		$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$		$12 \rightarrow 13$	
$^{29}SiH_3NCS$										
K	obs	o−c	obs	o−c	obs	o−c	obs	o−c	obs	o−c
0	26885.26	−0.01	29872.47	0.02	32859.63	0.02	35846.75	0.00	38833.89	0.02
1	26884.56	0.02	29871.68	0.04	32858.73	0.01	35845.79	0.01	38832.80	−0.01
2	26882.35	0.00	29869.20	−0.01	32856.05	0.00	35842.84	−0.02	38829.64	−0.01
3	26878.72	0.01	29865.15	−0.01	32851.57	−0.02	—		38824.35	−0.04
4	26873.53	−0.07	—		—		35831.22	0.02	38816.96	−0.06
5	26867.04	0.00	—		—		35822.51	0.06	38807.61	0.07
6	—		—		—		35811.73	−0.03	38795.95	0.00
$^{30}SiH_3NCS$										
K										
0					32392.59	0.02	35337.26	0.01	38281.89	−0.02
1					32391.69	−0.02	35336.29	−0.02	38280.88	−0.01
2					32389.12	0.01	—		38277.81	−0.01
3					32384.80	0.00	—		38272.77	0.05
4					—		35322.19	0.02	—	
5					—		35313.64	−0.06	—	
6					—		35303.35	0.02	—	
$SiH_3NC^{34}S$										
K										
0	26523.73	−0.01	29470.76	−0.01	32417.80	0.04	—		38311.69	0.01
1	26523.10	0.07	29469.96	−0.01	32416.90	0.02	35363.75	−0.02	38310.65	0.01
2	26520.89	0.02	29467.53	−0.03	32414.15	−0.09	35360.88	−0.01	38307.43	−0.09
3	26517.29	0.02	29463.57	0.01	32409.84	0.00	35356.13	0.04	38302.34	0.03
4	—		29457.96	0.00	—		35349.33	−0.04	38295.08	0.05
5	—		29450.78	0.02	—		35340.70	−0.02	—	
6	—		29441.86	−0.10	32386.10	0.03	35330.21	0.05	38274.23	0.00

we did not find it easy to identfy these weak spectra among the many unassigned lines from molecules in high vibrational states, so it is understandable that incorrect assignments could have been made in the earlier work. We are confident that our present assignments are correct in view of the excellent fits over five J values and the very reasonable values obtained for the centrifugal distortion constants of all species.

Spectra of the ^{13}C and ^{15}N substituted species are expected to occur very close to those of the abundant isotopic species, and they could not be observed because of the extensive K-structure of the abundant species.

IV. 2. The State $v=1, l=\pm 1$

The frequencies observed are given in Table 5. The fit to the equation of Grenier-Besson and Amat[7] is good, with the exception of the lines with $K=4$, $|k-l|=5$ which appear to be perturbed. These lines were accordingly given zero weight in the fit.

Our constants predict the frequencies of the $J=7\rightarrow 8$ lines in general agreement with the measurements of Jenkins, Kewley and Sugden[4]. We do not make detailed comparisons between their constants and ours as they used earlier and less complete theoretical expressions to fit their frequencies. It is however worth noting that they assign the doublets of given $|k-l|$ in the opposite sense to us. For example, the doublet with $|k-l|=6$ comprises lines at 24401.33 MHz and 24396.19 MHz. Jenkins et al. assign the former as a $K=7$ line and the latter as a $K=5$ line, whereas our constants predict the $K=5$ line at 24401.26 MHz and the $K=7$ line at 24396.26 MHz. Our assignment is established unambiguously by two factors. Firstly, within each doublet of given $|k-l|$ the line higher in frequency always has the greater intensity, indicating that it possesses the lower of the two possible K values. The second and conclusive factor is that we observe in each $J\rightarrow J+1$ group the two lines of highest $|k-l|$, i. e. with $|k-l|=J$ and $J+1$ respectively, in the expected position. These two lines were not recorded in the $J=7\rightarrow 8$ group[4].

IV. 3. The States $v=2, l=0$ and $v=2, l=\pm 2$

The B rotational constants of these states are very similar, so that their microwave transitions lie close together in the spectrum and the series of lines overlap one another (see Fig. 1). The lines belonging to the $l=0$ state can be picked out because their pattern recalls that of the $v=0$, $l=0$ state. Lines

Table 5. Microwave spectrum of SiH_3NCS (MHz) in the state $v_{10}=$, $l_{10}=\pm 1$.

J		8 → 9		9 → 10		10 → 11		11 → 12	
K	$\lvert K-l\rvert$	obs	o−c	obs	o−c	obs	o−c	obs	**o−c**
1	0	27498.99	0.01	30554.37	0.04	33609.68	0.02	36665.00	0.05
1	0	27448.96	0.08	30498.70	0.03	33548.44	0.01	36598.17	0.01
0	1	27473.36	−0.01	30525.78	−0.01	33578.21	0.05	36630.77	0.31
2	1	27473.20	0.12	30525.74	0.10	33578.20	0.00	36630.72	−0.04
1	2	27471.89	0.00	30524.20	0.00	33576.44	−0.02	36628.66	−0.01
3	2	27470.35	0.03	30522.55	0.02	33574.75	0.02	36626.94	0.02
2	3	27468.90	0.00	30520.89	0.01	33572.82	−0.01	36624.71	−0.02
4	3	27466.23	−0.03	30518.03	0.02	33569.78	0.04	36621.47	0.02
3	4	27464.48	0.01	30515.98	0.02	33567.40	−0.03	36618.83	−0.02
5	4	27460.83	0.01	30511.95	−0.01	33563.10	0.03	36614.17	0.00
4	5	*27479.49	0.88	*30510.40	0.94	*33561.27	0.99	*36612.09	1.03
6	5	27453.97	−0.01	30504.35	0.00	33554.70	0.00	36605.02	−0.01
5	6	27451.28	−0.06	30501.36	−0.02	33551.36	−0.04	36601.35	−0.03
7	6	27445.45	0.00	30495.17	−0.02	33544.62	0.00	36594.01	−0.01
6	7	27442.70	0.05	30491.67	−0.07	33540.74	−0.05	36589.77	−0.04
8	7	27436.15	0.07	30484.44	−0.02	33532.80	−0.02	36581.10	−0.04
7	8	27432.52	−0.04	30480.47	−0.05	33528.38	−0.07	36576.34	−0.01
9	8	—		30472.17	0.00	33519.26	−0.03	36566.37	−0.02
8	9	27421.00	−0.05	30467.73	0.00	33514.38	−0.01	36561.02	0.01
10	9	—		—		33504.08	0.03	36549.73	−0.03
9	10	—		30453.31	−0.07	33498.68	0.08	36543.84	0.06
10	11	—		—		33481.17	0.09	36524.74	0.06
11	12	—		—		—		36504.03	0.34

* Perturbed transition, omitted from fit.

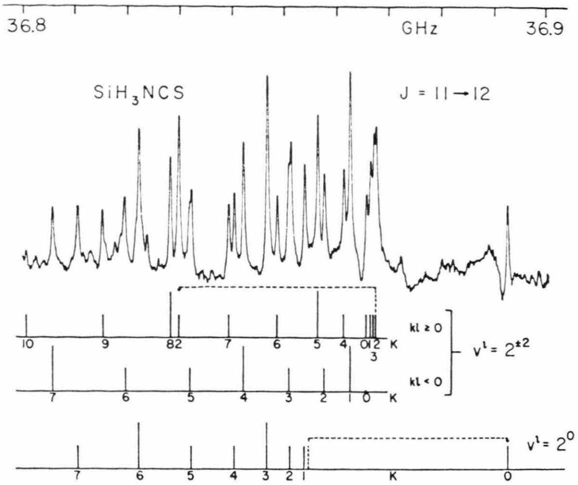

Fig. 1. Experimental recording of the $v=2$, $l=0$ and ± 2, $J=11 \rightarrow 12$ spectra. Assignments are indicated below the trace; for the transitions perturbed by the strong resonance, the unperturbed positions and the shifts induced are shown as broken lines. The height of the line below each transition indicates its spin statistical weight but takes no account of the other factors affecting the calculated intensity.

with $K=3, 6, \ldots$ etc. have enhanced intensity from their double statistical weight (as for the vibrational ground state) and D_{JK} is comparable with that in the other vibrational states. The $K=0$ line is not in its expected position in the pattern: a line of appropriate intensity and Stark effect was observed shifted upwards in frequency by several MHz from the expected position. The shift is 17.2 MHz for the $J=8 \rightarrow 9$ transition, increasing progressively with J to 34.4 MHz for the $J=11 \rightarrow 12$ transition. If this is assigned to $K=0$, it is clear that the $K=0$ levels of the $v=2$, $l=0$ state are involved in a strong resonance. Here we use the term "strong" resonance to distinguish large effects of this kind from the effects produced by the q-dependent terms of Table 1 which are usually described as "l-resonance" terms. The latter contribute typically ~ 1 MHz to the frequencies.

Once the $l=0$ lines have been identified, the spectrum of the $l=\pm 2$ state is easily assigned. Taking the $K=0$ line as origin, two branches are expected with kl positive and negative respectively (see Table 1). The values of D_{JK} and η_{10J} are such that lines for which $kl<0$ are always lower in frequency than the K = 0 line, while the branch with $kl>0$ forms a high-frequency "head" before turning round and setting off to low frequency. In addition the statistical weights are a powerful aid to assignment. The branch with $kl<0$ shows enhanced intensity for the lines with $K=1, 4, 7, \ldots$ etc., while the branch with $kl>0$ shows enhanced intensity for the lines with $K=2, 5, 8, \ldots$ etc., except for an anomaly in the case of $K=2$. In each $J \rightarrow J+1$ group the line with $K=2$, kl positive, for which $|k-l|=0$, does not have the double intensity predicted from its statistical weight. Also an extra line is observed shifted downwards in frequency from this line: the downwards shift matches the upwards shift of the $K=0$ line in the $v=2$, $l=0$ spectrum for the same J values. This establishes the cause of the strong resonance.

The $K=0$ level of $v=2$, $l=0$ is nondegenerate and of A_1 or A_2 rovibrational symmetry as J is even or odd. The $K=2$, $|k-l|=0$ level of $v=2$, $l=\pm 2$ is doubly degenerate in the absence of perturbations, the two components being of A_1 and A_2 rovibrational symmetry[13]. Thus the $K=0$ level of $v=2$, $l=0$ can always interact with one level of this $A_1 A_2$ pair but not the other. In consequence one of the two microwave transitions involving the $K=2$, $|k-l|=0$ levels of $v=2$, $l=\pm 2$ is observed in its normal position while the other is shifted by an amount mirroring the shift of the $K=0$ line of $v=2$, $l=0$.

The strong resonance takes place through the l-resonance matrix element mentioned earlier, since the levels concerned differ by ± 2 in K and ± 2 in l. It was analysed by diagonalising the appropriate 2×2 matrix for each value of J, leading to fairly precise values for the l-doubling constant q_{10} in the $v=2$ state and for the energy separation of the unperturbed positions of the resonating levels. These constants were then used in the analysis of the remaining lines in the spectra of the $v=2$, $l=0$ and ± 2 states since all other l-resonances are weak enough to be handled by second-order perturbation theory as in Tarrago's formulae[8]. The results are collected in Tables 6, 7 and 8. One line for each $J \rightarrow J+1$ group was significantly perturbed further, the $K=4$, $|k-l|=2$ line of $l=\pm 2$. These lines were given zero weight in the fit. A tentative explanation for the perturbation is given in Section V.4(a).

The strong resonance observed in the $v=2$ spectrum is similar in origin to that in the $v_8=2$ spectrum of CH$_3$CN observed by Bauer[14] and analysed by Bauer and Maes[15], although there the resonance is between two levels of E symmetry.

Table 6. Microwave spectrum of SiH_3NCS (MHz) in the state $v_{10}=2$, $l_{10}=0$.

J	$8 \rightarrow 9$		$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$	
K	obs	o−c	obs	o−c	obs	o−c	obs	o−c
1	27640.53	−0.01	30711.56	−0.05	33782.58	−0.07	36853.50	−0.16
2	27638.52	0.01	30709.32	−0.03	33780.13	−0.04	36850.92	−0.03
3	27635.19	0.07	30705.64	0.05	33776.07	0.05	36856.46	0.03
4	27630.42	0.05	30693.49	−0.04	33770.25	0.03	36840.10	0.00
5	27624.17	−0.10	30685.25	0.00	33762.75	−0.02	36831.94	−0.03
6	27616.79	−0.02	30675.47	0.01	33753.66	0.01	36822.04	0.02
7	27607.99	−0.01	30664.14	−0.02	33742.88	0.00	36810.26	−0.01
8	27597.82	−0.01	30651.34	−0.01	33730.45	0.00	36796.72	0.00
9	—		—		33716.38	0.01	36781.38	0.03
10	—		—		33700.59	−0.04	36764.21	0.03
11	—		—		—		36745.19	−0.01

Table 7. Microwave spectrum of SiH_3NCS (MHz) in the state $v_{10}=2$, $l_{10}=\pm 2$.

J	$8 \rightarrow 9$		$9 \rightarrow 10$		$10 \rightarrow 11$		$11 \rightarrow 12$	
	obs	o−c	obs	o−c	obs	o−c	obs	o−c
$K=0$	27649.58	0.09	30721.51	0.05	33793.40	0.03	36865.25	0.03
K (kl positive)								
1	27650.38	0.08	30722.21	−0.07	33794.28	0.09	36866.03	0.04
2	27650.62	−0.06	30722.92	0.06	33795.02	0.00	36867.09	−0.04
3	27649.78	0.00	—		—		36866.72	0.05
4	*27645.65	−0.84	*30717.40	−0.90	*33789.17	−0.94	*36860.89	−1.02
5	27642.16	0.04	30713.43	0.02	33784.73	0.04	36856.00	0.05
6	27636.44	−0.02	30707.11	0.00	33777.77	0.04	36848.35	0.01
7	—		—		33769.25	0.07	36839.07	0.07
8	27621.18	0.01	30690.09	−0.02	33759.00	−0.02	36827.90	0.00
9	—		30679.33	−0.06	33747.16	−0.06	36814.99	−0.04
10	—		—		—		36800.35	−0.02
11	—		—		—		36783.91	−0.03
K (kl negative)								
1	27647.13	−0.02	30718.86	−0.03	33790.54	−0.03	36862.16	−0.04
2	27643.35	−0.06	30714.71	−0.04	33786.00	−0.04	36857.22	−0.06
3	27638.35	0.03	30709.18	0.08	33779.90	0.06	36850.53	0.01
4	27631.77	−0.11	30701.84	−0.11	33771.89	−0.08	36841.85	−0.10
5	27624.17	0.08	30693.31	0.02	33762.47	0.01	36831.60	0.02
6	27614.87	−0.08	30683.01	−0.14	33751.13	−0.17	36819.22	−0.19
7	27604.54	0.07	—		—		36805.44	0.00
8	27592.57	−0.07	—		33724.01	−0.04	36789.70	0.01
9	—		—		33708.00	0.04	36772.18	0.04
10	—		—		33690.32	0.08	—	

* Perturbed transition, omitted from fit.

IV.4. The States $v=3$, $l=\pm 1$ and $v=3$, $l=\pm 3$

Consideration of the energy level expression for a symmetric top [9] shows that if in the $v=2$ state the levels $K=0$, $l=0$ and $|k-l|=0$, $l=\pm 2$ are virtually coincident, it follows that $g_{10,10} \cong 2(A\zeta)_{10} - (A_{10}-B_{10})$. Further, if this is the case then the levels with $|k-l|=0$ will also lie close together for higher values of v. Thus for $v=3$ the levels $K=1$, $|k-l|=0$ of the $l=\pm 1$ state, a pair of $A_1 A_2$ symmetry, lie close to $K=3$, $|k-l|=0$ of the $l=\pm 3$ state, another $A_1 A_2$ pair. The $l=\pm 1$ pair are however split by the normal l-doubling interaction even in the absence of a strong resonance. The problem can be resolved into two 2×2 matrices, one for the A_1 levels and the other for the A_2 levels. The formalism for this is the same as for the interaction between $l=\pm 1$ and $l=\pm 3$ levels in the $v=3$ state

Table 8. Analysis of the strong resonance between lines with $K=0$, $l=0$ and $K=2$, $l=2$, $|K-l|=0$ in the $v_{10}=2$ state of SiH_3NCS. All frequencies in MHz.

$K=0$, $l=0$		Without l-resonance terms		With l-resonance terms	
J	obs	calc	o−c	calc	o−c
$8 \rightarrow 9$	27658.45	27641.22	17.23	27658.36	0.09 [a]
$9 \rightarrow 10$	30735.58	30712.36	23.22	30735.48	0.10 [a]
$10 \rightarrow 11$	33813.54	33783.48	30.06	33813.47	0.07 [a]
$11 \rightarrow 12$	36892.20	36854.56	37.64	36892.17	0.03 [a]
$K=2$, $l=2$					
J	obs	calc	o−c	calc	o−c
$8 \rightarrow 9$	27650.62	27650.68	− 0.06	—	—
	27633.54	27650.68	−17.14	27633.54	0.00
$9 \rightarrow 10$	30722.92	30722.86	0.06	—	—
	30700.0 [b]	30722.86	−22.9 [b]	30699.75	0.2 [b]
$10 \rightarrow 11$	33795.02	33795.02	0.00	—	—
	33765.03	33795.02	−29.99	33765.03	0.00
$11 \rightarrow 12$	36867.09	36867.13	− 0.04	—	—
	36829.52	36867.13	−37.61	36829.52	0.00

Derived constants

$$q = 2.75 \pm 0.03 \text{ MHz}$$

$$4\,[g_{10,10} + A - B - 2A\zeta] = -1220 \pm 60 \text{ MHz}$$

[a] The constants have been chosen to fit the $l=2$ lines and leave a small systematic error in the $l=0$ lines, because the latter are incompletely modulated even at high Stark voltages and could not be measured particularly accurately.

[b] Overlapped by $K=4$, $l=0$ and by $K=7$, $l=2$, kl positive.

of a linear molecule which is discussed by, for example, Winnewisser and Winnewisser [16]. (Indeed, the strong resonance within the $v=2$ state discussed above is exactly analogous to the $\Sigma - \Delta$ interaction in the $v=2$ state of a linear molecule: all symmetric top rovibrational levels for which $k=l$ behave in a manner analogous to the levels of corresponding v and l in a linear molecule [17].)

In the observed spectrum (see Fig. 2) the main group of lines of the $v=3$, $l=\pm 1$ state is readily assigned through its similarity to the $v=1$, $l=\pm 1$ spectrum. The l-doublets of $v=3$, $l=\pm 1$ are also easily assigned, but they are shifted appreciably from their expected positions relative to the central group of lines by the strong resonance discussed in the preceding paragraph.

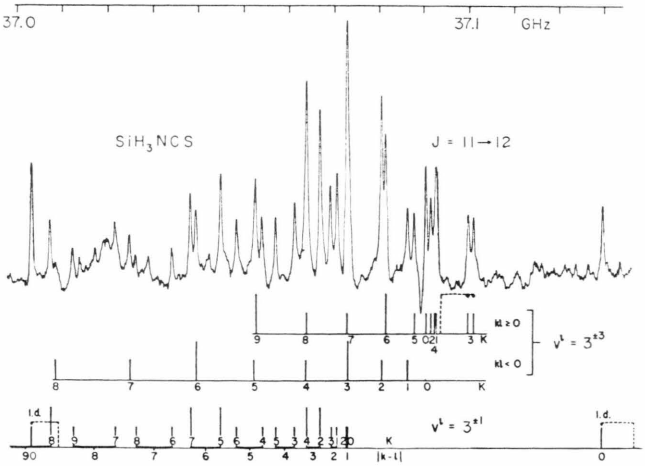

Fig. 2. Experimental recording of the $v=3$, $l=\pm 1$ and ± 3, $J=11 \rightarrow 12$ spectra. Assignments are indicated below the trace; for the transitions perturbed by the strong resonance, the unperturbed positions and the shifts induced are shown as broken lines. l-doublets are labelled "l.d.". The height of the line below each transition indicates its spin statistical weight but takes no account of the other factors affecting the calculated intensity.

The lines of $v=3$, $l=\pm 3$ can then be identified and assigned. The $K=3$, $|k-l|=0$ transitions are shifted and split by the strong resonance, the $A_1 A_2$ degeneracy being removed. As with the $v=2$ states, the strong resonance was analysed by exact diagonalisation of the appropriate 2×2 matrices. For the group of four E levels with $|k-l|=1$ (i. e. $K=0$ and $K=2$, kl positive of $l=\pm 1$; $K=2$ and 4, kl positive of $l=\pm 3$) diagonalisation of the hamiltonian also gave results a little different from those obtained by perturbation theory, but all remaining lines could be fitted to the theoretical expressions of Table I with perturbation treatment of the l-resonances. In fact the $|k-l|=1$ lines cannot be measured accurately since they all occur in congested regions of the spectrum: the two lines of the $l=\pm 1$ state overlap one another and are also blended with the strong $K=3$, $|k-l|=6$ line of

$l=\pm 3$, while the $K=2$ and 4, kl positive, lines of $l=\pm 3$ occur in the band head where they are not clearly resolved from one another or from the $K=1$, kl positive, line of this state.

The results are collected in Tables 9, 10 and 11. Because of the large number of lines in the spectra, many lines are blended and most of the relatively larger discrepancies between observed and calculated frequencies can be traced to this cause. In particular, most of the higher K lines of the $v=3$, $l=\pm 3$ spectrum are obscured by the extensive $v=3$, $l=\pm 1$ spectrum.

Table 9. Microwave spectrum of SiH_3NCS (MHz) in the state $v_{10}=3$, $l_{10}=\pm 1$.

	J	8 → 9		9 → 10		10 → 11		11 → 12	
K	$\lvert K-l\rvert$	obs	o−c	obs	o−c	obs	o−c	obs	o−c
0	1	27804.78	0.14	30894.05	0.13	33983.34	0.17	37072.61	0.24
2	1	27804.65	0.11	30893.94	−0.07	33983.29	−0.20	37072.61	−0.40
1	2	27803.08	−0.02	30892.15	−0.05	33981.21	−0.06	37070.19	−0.09
3	2	27801.66	0.02	30890.65	0.01	33979.65	0.02	37068.60	0.00
2	3	27800.26	0.01	30889.01	−0.02	33977.74	−0.02	37066.41	−0.04
4	3	27797.80	−0.02	30886.38	0.00	33974.95	0.04	37063.44	0.03
3	4	27796.09	−0.01	30884.42	0.00	33972.66	−0.03	37060.91	−0.01
5	4	27792.77	0.03	30880.76	0.03	33968.73	0.05	37056.61	0.01
4	5	27790.66	0.02	30878.39	0.04	33966.07	0.05	37053.70	0.05
6	5	27786.42	0.05	30873.66	0.02	33960.93	0.05	37048.15	0.07
5	6	27783.83	−0.04	30870.81	−0.02	33957.75	0.00	37044.59	−0.03
7	6	27778.68	−0.02	30865.12	0.01	33951.49	0.00	37037.84	0.00
6	7	27775.69	−0.09	30861.79	−0.05	33947.77	−0.10	37033.80	−0.04
8	7	—		30855.11	−0.02	33940.49	−0.02	37025.84	−0.01
7	8	27766.40	0.02	30851.45	0.05	33936.46	0.08	37021.33	0.02
9	8	—		30843.65	−0.04	33927.88	−0.05	37012.09	−0.03
8	9	27755.66	−0.01	30839.52	0.02	33923.34	0.05	37007.09	0.06
10	9	—		—		33913.72	−0.02	36996.64	−0.01
9	10	—		—		33908.64	0.05	36991.00	0.00
10	11	—		—		—		36973.19	−0.04

Table 10. Microwave spectrum of SiH_3NCS (MHz) in the state $v_{10}=3$, $l_{10}=\pm 3$.

J	8 → 9		9 → 10		10 → 11		11 → 12	
	obs	o−c	obs	o−c	obs	o−c	obs	o−c
$K=0$	27818.17	0.02	30908.86	0.00	33999.49	−0.02	37090.03	−0.06
K (kl positive)								
1	27819.85	0.00	30910.66	−0.03	34001.41	−0.04	37092.25	0.12
2	27819.85	−0.01	30910.66	0.12	34001.41	0.33	37091.10	−0.37
3 [a]	—		—		—		—	
4	27819.21	0.28	30910.36	0.42	34000.84	−0.12	37092.25	0.26
5	27815.57	0.00	30906.20	0.01	33996.80	0.00	—	
6	27810.93	−0.01	30901.02	0.01	33991.05	−0.02	37081.09	−0.03
K (kl negative)								
1	27815.04	0.01	30905.39	−0.03	33995.69	−0.07	37085.95	−0.12
2	27810.68	0.10	30900.49	0.00	33990.31	−0.04	37080.19	0.04
3	27804.79	−0.03	30894.05	−0.05	33983.34	0.01	37072.57	0.08
4	27797.83	0.08	30886.38	0.13	—		—	
5	27789.32	−0.07	30876.95	−0.02	33964.58	0.08	37052.20	0.21
6	27779.72	−0.02	30866.24	0.00	33952.69	−0.02	37039.09	−0.04
7	—		30854.08	0.00	33939.29	−0.04	37024.51	−0.03
8	—		30840.49	0.01	—		—	

[a] Perturbed by strong resonance; see Table 11.

Table 11. Analysis of the strong resonance between lines with $K=1$, $l=1$, $|k-l|=0$ and $K=3$, $l=3$, $|k-l|=0$ in the $v_{10}=3$ state of SiH_3NCS. All frequencies in MHz.

$K=1$, $l=1$ (l-doublets)		Without l-resonance between $l=1$ and $l=3$		With l-resonance between $l=1$ and $l=3$	
J	obs	calc	o−c	calc	o−c
$8\rightarrow 9$	27849.84	27852.68	−2.84	27849.84	0.00
	27754.44	27757.03	−2.59	27754.43	0.01
$9\rightarrow 10$	30943.35	30947.30	−3.95	30943.35	0.00
	30837.48	30841.02	−3.54	30837.47	0.01
$10\rightarrow 11$	34036.50	34041.88	−5.38	34036.54	−0.04
	33920.33	33924.97	−4.64	33920.29	0.04
$11\rightarrow 12$	37129.30	37136.42	−7.12	37129.40	−0.10
	37003.00	37008.88	−5.88	37002.88	0.12
$K=3$, $l=3$					
J	obs	calc	o−c	calc	o−c
$8\rightarrow 9$	27823.23 [a]	27820.44	2.79	27823.27	−0.04 [a]
		27820.44	2.79	27823.03	0.20 [a]
$9\rightarrow 10$	30915.49	30911.49	4.00	30915.45	0.04
	30915.11	30911.49	3.62	30915.04	0.07
$10\rightarrow 11$	34007.94	34002.52	5.42	34007.86	0.08
	34007.15	34002.52	4.63	34007.20	−0.05
$11\rightarrow 12$	37100.64	37093.50	7.14	37100.52	0.12
	37099.35	37093.50	5.85	37099.51	−0.16

Derived constants

$$q=2.657\pm 0.003 \text{ MHz}$$

$$8\,[g_{10,\,10}+A-B-2A\,\zeta]=7100\pm 400 \text{ MHz}$$

[a] Two components not resolved.

IV.5. Higher Vibrational States

The spectra of the $v=4$ and $v=5$ states were recorded. That of the $v=4$ region could be partially assigned. The region is complex, since spectra of $v=4$ states with $l=0$, $l=\pm 2$ and $l=\pm 4$ all overlop. Strong resonances are expected between all of the $|k-l|=0$ lines, of which there are five altogether. These could not all be identified, and since many lines of the various spectra were lost through overlapping the analysis of the $v=4$ and $v=5$ states was not pursued. Preliminary measurements of the $v=4$, $l=0$, $K>0$ lines showed that B_v is about 1553.27 MHz and D_{JK} about 36.1 kHz, in line with the values for the vibrational states analysed in detail.

V. Discussion

V.1. Molecular Constants

The variation of the constants q_{10}, η_{10J}, D_{JK} and D_J with vibrational state is reasonably smooth. The rotational constant B_v is also well-behaved: the equation

$$B_v/\text{MHz}=1505.119+11.294\,(v+1)-0.373\,(v+1)^2+0.120\,l^2,$$

chosen to fit the rotational constants of the lowest four vibrational levels exactly, predicts B_v to be 1544.447 MHz for $v=3$, $l=\pm 1$ and 1545.407 MHz for $v=3$, $l=\pm 3$ in fair agreement with the observed values of 1544.728 MHz and 1545.494 MHz respectively. The values of $[A_{10}-(A\zeta)_{10}-B_{10}]$ are essentially the same in the $v=1$ and $v=2$ states, and a value of 4200 MHz was assumed in the analysis of the $v=3$ states. If we assume that $A=2.80\pm 0.05\text{ cm}^{-1}$ (a range which would encompass most of the silyl groups studied [18]) and ignore the separate vibrational dependence of A and $A\zeta$, then ζ_{10} is found to be 0.931 ± 0.002. This is a most reasonable magnitude for the zeta constant of this $Si-N=C$ bending mode.

V.2. r_s Coordinates

The ground state rotational constants listed in Table 2 can be used to calculate r_s coordinates for the Si and S atoms in the principal axis system of the abundant isotopic species. The results are: Si, 2.2489 Å (same coordinate from either ^{29}Si or ^{30}Si substitution); S, 2.2189 Å. Since the spectra of ^{13}C and ^{15}N substituted molecules were not identified the r_s structure of the skeleton could not be completed at this stage of the work. The Si . . . S distance of 4.467_8 Å is however in excellent agreement with the sum of the Si – N, N = C and C = S bonded distances determined by electron diffraction, which is 4.467 Å (r_a values of original study [5] converted to r_g). The Si ... S distance obtained by Jenkins et al.[4] was 4.485 Å, in poor agreement with the electron diffraction results: this discrepancy is now removed.

V.3. The Magnitude of $g_{10,10}$

Assuming normal vibration-rotation theory the term values of the ν_{10} mode are given by

$$G(v,l) = \omega_{10}(v+1) + x_{10,10}(v+1)^2 + g_{10,10}\, l^2 + \dots$$

$g_{10,10}$ can be estimated from the microwave results, since in the $v=2$ states the difference between the $K=0$ levels of $l=\pm 2$ and $l=0$ is $4\,g_{10,10}$, while in the $v=3$ states the corresponding difference between $K=0$ of $l=\pm 3$ and $l=\pm 1$ is $8\,g_{10,10}$. The analyses of the strong resonances in Tables 8 and 11 give for $v=2$,

$$g_{10,10} = A\zeta - [A - A\zeta - B] - 1220/4\ \text{MHz} \cong 2.45 \pm 0.05\ \text{cm}^{-1},$$

and for $v=3$,

$$g_{10,10} = A\zeta - [A - A\zeta - B] + 7100/8\ \text{MHz} \cong 2.51 \pm 0.05\ \text{cm}^{-1},$$

where we have again taken A to be $2.80 \pm 0.05\ \text{cm}^{-1}$.

It is interesting that both here and in CH_3CN [15] g_{tt} for the lowest bending mode is roughly equal to $A\zeta^2$. The formula given by Mills [19] for g_{tt} in a symmetric top contains, besides contributions from cubic and quartic anharmonic constants, the term $A\zeta_t^2$. It seems that in highly prolate tops such as SiH_3NCS and CH_3CN the $A\zeta_t^2$ term is the dominant contribution to g_{tt}, at least for the low frequency bending modes for which $\zeta \cong +1$.

V.4. The Vibrational Intervals of ν_{10}

The results presented here suggest that the potential function of ν_{10} must be close to that of a (two-dimensional) harmonic oscillator, because of the smooth variation of the molecular constants with vibrational state and the fact that normal vibration-rotation theory is well obeyed despite the low wavenumber of the vibration. (This may be contrasted with the case of SiH_3NCO, where the potential function is certainly very anharmonic and the vibration-rotation constants have an anomalous vibrational dependence [20].) In this respect we support the conclusions of the electron diffraction study [5]. However, the electron diffraction estimate of 100 cm^{-1} for ω_{10} appears to be unsatisfactory, since several pieces of evidence in the microwave spectrum point to a value between 55 and 60 cm^{-1}. These are:

(a) The value of q_{10}. If cubic anharmonic contributions to q_{10} are small, as they seem to be in most molecules of this type [21], the formula $q_{10} \cong 2B_0^2/\omega_{10}$ used by Jenkins, Kewley and Sugden [4] should hold fairly well. With our data of Table 2 ω_{10} is estimated to be 55 cm^{-1} in agreement with the result of Jenkins et al.

(b) The value of D_{JK}. If D_{JK} is calculated from the harmonic force field, the result is extremely sensitive to the SiNC bending force constant and rather insensitive to the remainder of the force field (which is in any case reasonably well determined from the known vibrational wavenumbers and zeta constants). When the force field is adjusted to reproduce the experimental D_{JK} for the vibrational ground state exactly ω_{10} is then predicted to be 56 cm^{-1}.

(c) Microwave intensity measurements. Intensity measurements were carried out on the $K=0$ lines of the $l=0$ states and the l-doublets of the $l=1$ states. The results were rather inaccurate because the sample slowly decayed in the cell during the experiments, but the estimated value of ω_{10} was $65 \pm 15\ \text{cm}^{-1}$.

(d) A chance resonance between the $v=1$, $l=\pm 1$ and $v=2$, $l=\pm 2$ states. It is tempting to identify the levels which perturb the $K=4$, $|k-l|=5$ levels of the $v=1$ state as $K=4$, $|k-l|=2$ of $v=2$, $l=\pm 2$. The frequency shifts of the appropriate lines for the same $J \rightarrow J+1$ transition are opposite in sign and virtually equal in magnitude (Tables 5 and 7). The levels concerned have the same k but differ by three in l, and thus have the same rovibrational symmetry [13]: e. g. $k=+4$, $l=-1$ of $v=1$ would interact with $k=+4$, $l=+2$ of $v=2$. The interaction term would have to be of quite high order in the hamiltonian, so that we may presume the levels coincide fairly closely. Assuming again the values of A and $A\zeta$ used earlier, the difference between the $K=0$ levels of $v=2$, $l=\pm 2$ and $v=1$, $l=\pm 1$ is calculated to be $62.6 \pm 1.2\ \text{cm}^{-1}$. Making use of $g_{10,10} = 2.45 \pm 0.05\ \text{cm}^{-1}$, we estimate also that the interval $v=1$, $l=\pm 1 \rightarrow v=2$, $l=0$ is $52.8 \pm 1.4\ \text{cm}^{-1}$.

In isolation the attribution of this resonance between two different vibrational states might be somewhat tenuous, but added to the other evidence it appears quite plausible. This resonance, and the strong resonances discussed in Sections IV. 3 and IV. 4, are illustrated by an energy level diagram (Figure 3).

VI. Conclusions

We consider that the microwave spectrum of SiH_3NCS in vibrationally excited states of the SiNC bending mode provides good evidence that the potential function of this mode exhibits only small anharmonicity and that the vibrational intervals are around 55 cm^{-1}. Although the vibrational wavenumber is low, and consequently the vibrational amplitude is large, the microwave spectra are satisfactorily fitted using conventional vibration-rotation theory. Our results largely confirm the earlier work of Jenkins, Kewley and Sugden[4] on the $v_{10} = 0$ and 1 states, but the new data are much more extensive. The reassignment of the spectra of species isotopically substituted at Si and S removes a previous discrepancy between microwave r_s coordinates and electron diffraction bond lengths. On the other hand, the shrinkage effects observed in the electron diffraction experiment seem to require a vibrational wavenumber of ~ 100 cm^{-1} for ν_{10} instead of ~ 55 cm^{-1} as found here: this disagreement remains unexplained.

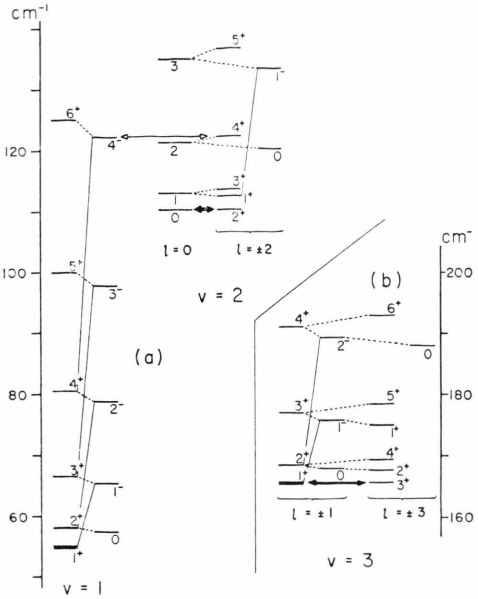

Fig. 3. Part of the energy level diagram of the ν_{10} manifold of SiH_3NCS, constructed from the molecular constants given in the text and Tables. Individual levels are labelled by K, the superscript giving the sign of kl for $l \neq 0$. J structure is not shown. Broken lines indicate l-resonance interactions involving q_{10}. (a) $v=1$ and $v=2$ levels. The strong resonance within $v=2$ [see Section IV. 3] is indicated by a solid arrow, the weak resonance between $v=1$ and $v=2$ [see Section V. 4(d)] by a light arrow. (b) $v=3$ levels (note displacement of vertical scale). The strong resonance [see Section IV. 4] is indicated by a solid arrow.

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