

Microwave Spectrum of SiH₃CCH in the 4ν₁₀ State

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The microwave spectrum of silyl acetylene in the 4ν₁₀ state has been investigated from 29 to 79 GHz. After an assignment by graphical methods deduced from approximate analytical formulas, molecular constants have been determined through an analysis by direct diagonalization. Some slight anomalies appear. A comparison is made between the constants of the different nν₁₀ states.

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INTRODUCTION

As part of the investigation by microwave spectroscopy of the $v_{10} = n$ states of the silyl acetylene molecule (1-4), the spectrum of the 4ν₁₀ state has been observed and analyzed.

The precise location of the 4ν₁₀ state of this molecule has not been determined to our knowledge by infrared studies. But although the fundamental is low (220 cm⁻¹) (5, 6), a simple Boltzmann factor calculation shows that the population of the 4ν₁₀ state is only about 1% of that of the ground state. The weakness of the intensities of the lines is enhanced by the low dipole moment ($\mu = 0.316$ D) (7), thus involving inaccuracy and lack of resolution of the measurements.

Although approximate values of most of the constants of the $v_{10} = 4$ state could be estimated from the analysis of the lowest $v_{10} = n$ states, the assignment was far from straightforward. It was complicated by the presence of some other lines of similar intensity, likely to belong to another vibrational mode.

In this paper, the assignment and analysis concerning the $J = 1$ through 7 rotational transitions are reported for the ²⁸Si species.

EXPERIMENTAL DETAILS

The sample of SiH₃CCH, which is a rather unstable compound, was stored in liquid nitrogen. Gold-plated cells were also used when possible.

The measurements from $J = 4$ to $J = 7$, in the 49- to 79-GHz range, were performed at the University of Lille with a Stark spectrometer using phase locked klystrons as generators and 25-kHz square wave Stark modulation.

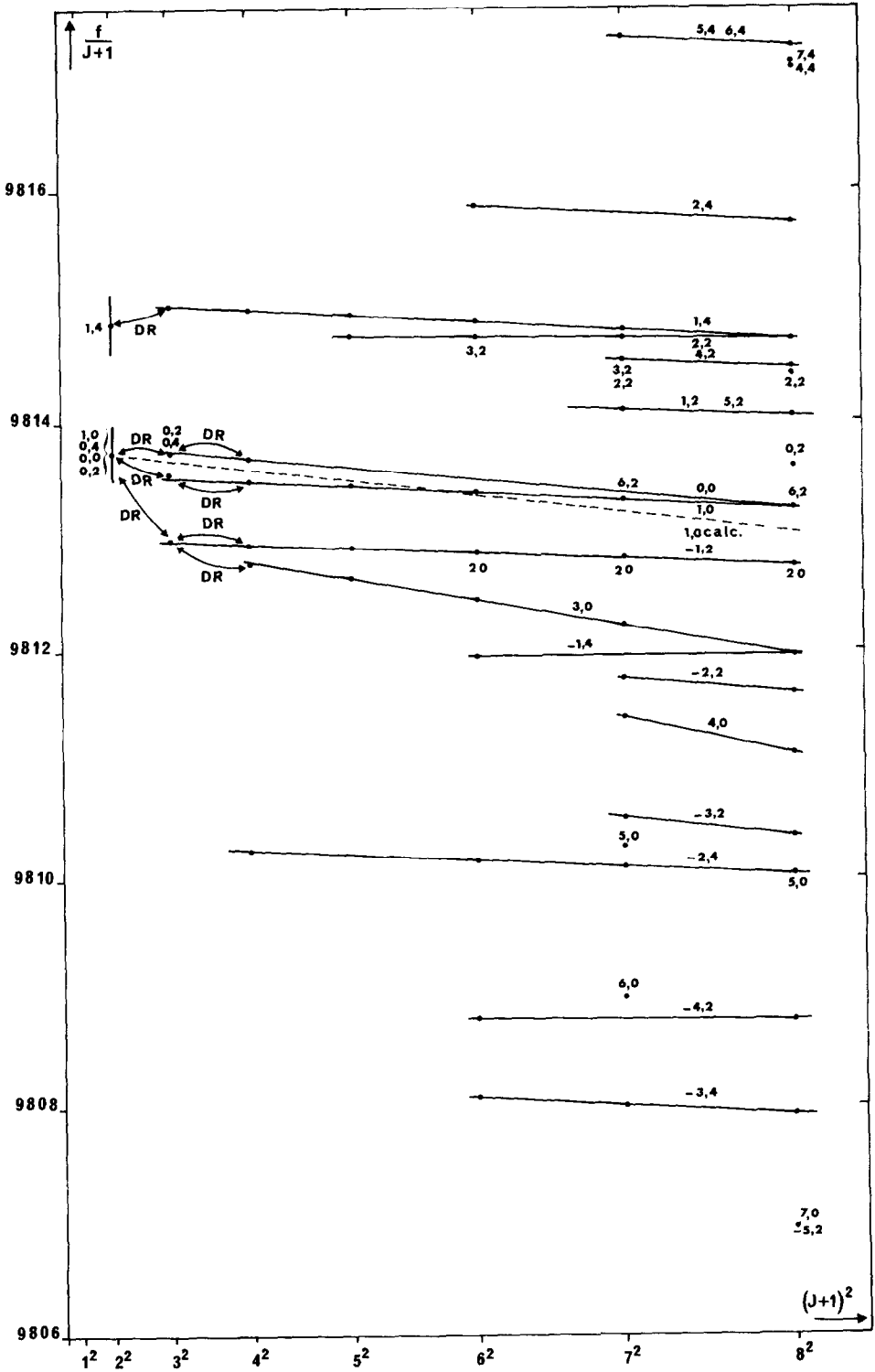


FIG. 1. Plot of $f/(J+1)$ versus $(J+1)^2$. The numbers in the figure denote K, L .

TABLE I
Matrix Elements of the Hamiltonian

$$\begin{aligned}
 \langle K, \ell | H^+ | K, \ell \rangle = & E_V + x_{\ell\ell} \ell^2 + \left[(A_V - B_V) + (A_3 - B_3) \ell^2 \right] K^2 - 2(A \zeta)_V' K \ell \\
 & + (B_V + B_3 \ell^2) J(J+1) \\
 & - D_V^V J^2 (J+1)^2 - D_{JK}^V J(J+1) K^2 - D_K^V K^4 \\
 & + H_J J^3 (J+1)^3 + H_{JJK} J^2 (J+1)^2 K^2 + H_{JKK} J(J+1) K^4 + H_K K^6 \\
 & + \eta_J^V J(J+1) K \ell + \eta_K^V K^3 \ell \\
 & + \eta_{JJ} J^2 (J+1)^2 K \ell + \eta_{JK} J(J+1) K^3 \ell + \eta_{KK} K^5 \ell
 \end{aligned}$$

with

$$\begin{aligned}
 A_V &= A_0 + A_1 v + A_2 v^2 \\
 (A \zeta)_V' &= (A \zeta)_0 + (A \zeta)_1 v + (A \zeta)_2 v^2 + (A \zeta)_3 \ell^2 \\
 B_V &= B_0 + B_1 v + B_2 v^2 \\
 D_J^V &= D_J^0 + D_J^1 v \\
 D_{JK}^V &= D_{JK}^0 + D_{JK}^1 v \\
 D_K^V &= D_K^0 + D_K^1 v \\
 \eta_J^V &= \eta_J^0 + \eta_J^1 v \\
 \eta_K^V &= \eta_K^0 + \eta_K^1 v
 \end{aligned}$$

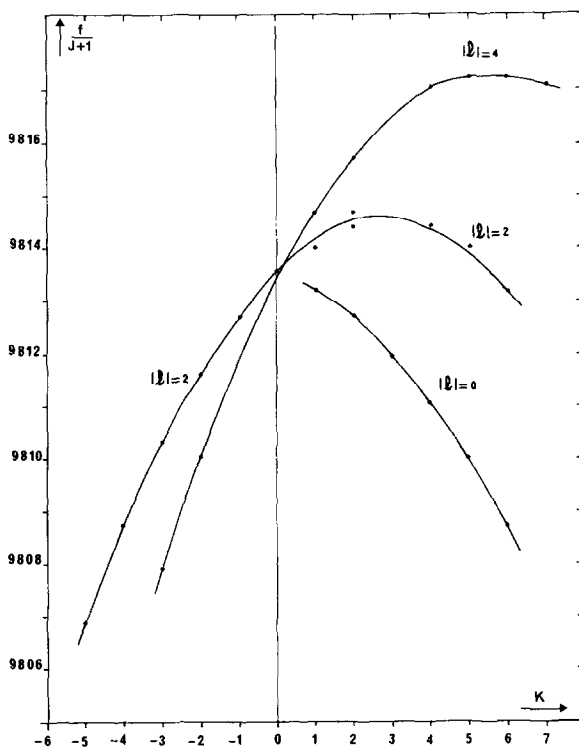
$$\begin{aligned}
 \langle K, \ell | H^+ | K \pm 2, \ell \pm 2 \rangle &= q_V \left[J(J+1) - K(K \pm 1) \right]^{1/2} \left[J(J+1) - (K \pm 1)(K \pm 2) \right]^{1/2} \\
 & \quad (v + \ell + 1 \pm 1)^{1/2} (v - \ell + 1 \mp 1)^{1/2} \\
 \langle K, \ell | H^+ | K \pm 1, \ell \mp 2 \rangle &= \left[q_{12} (2K \pm 1) + d_{12} (\ell \mp 1) \right] \left[J(J+1) - K(K \pm 1) \right]^{1/2} \\
 & \quad (v + \ell + 1 \mp 1)^{1/2} (v - \ell + 1 \pm 1)^{1/2} \\
 \langle K, \ell | H^+ | K, \ell \pm 6 \rangle &= g_6 (v + \ell + 1 \pm 1)^{1/2} (v - \ell + 1 \mp 1)^{1/2} (v + \ell + 1 \pm 3)^{1/2} (v - \ell + 1 \mp 3)^{1/2} \\
 & \quad (v + \ell + 1 \pm 5)^{1/2} (v - \ell + 1 \mp 5)^{1/2} \\
 \langle K, \ell | H^+ | K \pm 2, \ell \mp 4 \rangle &= f_{24} \left[J(J+1) - K(K \pm 1) \right]^{1/2} \left[J(J+1) - (K \pm 1)(K \pm 2) \right]^{1/2} \\
 & \quad (v + \ell + 1 \mp 1)^{1/2} (v - \ell + 1 \pm 1)^{1/2} (v + \ell + 1 \mp 3)^{1/2} (v - \ell + 1 \pm 3)^{1/2}
 \end{aligned}$$

$$\begin{aligned}
 \text{with} \quad q_V &= q_0 + f_{22} v \\
 &= q_0' + f_{22}^J J(J+1) + f_{22}^K K^2 + f_{22} v
 \end{aligned}$$

For the lower values of J the measurements were made in Utrecht. To facilitate the identification the microwave-microwave double resonance technique was used wherever possible. Two $J = 2 \leftarrow 1$ transitions were observed only indirectly as pump

TABLE II
Rotational Frequencies for $v = 4, l = 0, \pm 2, \text{ and } \pm 4$

a	
$\ell = 0$	
$f = 2(J+1) B_v - 4(J+1)^3 D_J^v - 2(J+1) K^2 D_{JK}^v + \frac{48(J+1)}{\mu^2 K^2 - \lambda^2} \left[\lambda(J+1)^2 + (2\mu - \lambda) K^2 - \lambda \right] (q_v)^2$ $+ \frac{96(J+1)}{4\sigma^2 K^2 - \pi^2} \left\{ 4K^2 \left[(q_{12})^2 (\pi - 2\rho) + 2\rho q_{12} d_{12} \right] + \pi(q_{12} - d_{12})^2 \right\}$	
with	
$\lambda = A_v - B_v - 2(A_c)_v' + x_{\ell\ell}$	$\pi = A_v - B_v + 4(A_c)_v' + 4x_{\ell\ell}$
$\mu = A_v - B_v - (A_c)_v'$	$\rho = A_v - B_v + 2(A_c)_v'$
b	
$\ell = \pm 2$	
$f = 2J(J+1) B_v - 4(J+1)^3 D_J^v - 2(J+1) K^2 D_{JK}^v + 2(J+1) K\ell \eta_J^v + 8(J+1) B_3$ $- \frac{8(J+1) \left[4(J+1)^2 - (K\ell + 2)^2 \right]}{\mu(K\ell - 4) + 6\lambda} (q_v)^2 + \frac{32(J+1) \left[q_{12} (K\ell - 1) + 3d_{12} \right]^2}{\rho(K\ell + 2) - 3\pi}$	
if $K\ell \neq -2$	$- \frac{48(J+1) \left[q_{12} (K\ell + 1) + d_{12} \right]^2}{\rho(K\ell + 2) - \pi}$
if $K\ell \neq 4$	$+ \frac{12(J+1) \left[4(J+1)^2 - (K\ell - 2)^2 \right]}{\mu(K\ell - 4) + 2\lambda} (q_v)^2$
if $K\ell = -2$ (then $K\ell \neq 4$)	$\psi^+ : + 48(J+1) f_{2,4} - \frac{96(J+1)(q_{12} - d_{12})^2}{\pi} + \frac{128(J+1)}{\mu - \lambda} g_6 q_v$ $\psi^- : - 48(J+1) f_{2,4} + 0 - \frac{128(J+1)}{\mu - \lambda} g_6 q_v$
if $K\ell = 4$ (then $K\ell \neq -2$)	$\psi^+ : + \frac{48 J(J+1)(J+2)}{\lambda} (q_v)^2$ $\psi^- : + 0$
c	
$\ell = \pm 4$	
$f = 2(J+1) B_v - 4(J+1)^3 D_J^v - 2(J+1) K^2 D_{JK}^v + 2(J+1) K\ell \eta_J^v + 32(J+1) B_3$ $+ \frac{4(J+1) \left[16(J+1)^2 - (K\ell - 4)^2 \right]}{\mu(K\ell - 16) + 12\lambda} (q_v)^2 - \frac{16(J+1) \left[q_{12} (K\ell + 2) + 6d_{12} \right]^2}{\rho(K\ell + 8) - 6\pi}$	
if $K\ell = 4$	$\psi^+ : - \frac{128(J+1)}{\mu - \lambda} g_6 q_v$ $\psi^- : + \frac{128(J+1)}{\mu - \lambda} g_6 q_v$

FIG. 2. Plot of f versus K for $J = 7$.

settings for which the signal lineshape was optimized. The accuracy of these frequencies is limited to about 0.5 MHz as indicated in Fig. 1, and they were not used for the determination of the molecular parameters.

PREDICTED FORM OF THE SPECTRUM

From a treatment of the Hamiltonian up to the fourth order in vibration and the sixth order in rotation, Amat *et al.* (8) have derived the diagonal and off-diagonal matrix elements of the vibration-rotation Hamiltonian. The usual terms and those which will be taken into account in our calculations are reproduced in Table I. Analytical expressions of the energy for a $v_E = 4$ state have been calculated from these matrix elements by a perturbation method separately for $l = 0, \pm 2, \pm 4$; and the rotational $J + 1 \leftarrow J$ transition frequencies derived from these expressions are reproduced in Table IIa, b, c. A look at these formulas gives an idea of the complexity of the spectrum and of the possible doublings which may appear; these formulas also display the linearity of the $f/(J + 1)$ versus $(J + 1)^2$ for given K, l values in the case where these perturbation calculations are valid, i.e., when no accidental degeneracies occur.

ASSIGNMENT AND ANALYSIS OF THE SPECTRUM

The knowledge of the constants obtained for the $v_{10} = 1, 2,$ and 3 states was not enough to assign the spectrum; low J and double-resonance experiments were found

TABLE III
Observed and Calculated Frequencies for SiH₃CCH in the 4ν₁₀ State

$J+1+J$	$\frac{Kl}{ k }$	$ k $	Observed frequencies	Obs.-Calc.	$J+1+J$	$\frac{Kl}{ k }$	$ k $	Observed frequencies	Obs.-Calc.	
3 + 2	1	4	29 445.00	0.00	7 + 6	0	0	68 693.138 [*]	-0.166	
	0	2	29 441.21 [*]	-0.30		6	2		0.387	
	0	0		-0.23		1	0?		0.720	
	0	4	29 440.64 [*]	0.10		-1	2		68 689.487	-0.404
	1	0?		-0.42		2	0		68 689.487 [*]	-0.274
	2	0	0.69	3		0	68 685.510		0.170	
	-1	2	29 438.925	-0.040		-2	2		68 682.25	-0.01
4 + 3	1	4	39 259.85	0.02	4	0?	68 679.93 [*]	0.76		
	0	0	39 254.77	-0.14	-3	2?	68 673.829 [*]	1.041		
	1	0?	39 253.94 [*]	0.47	5	0?	68 671.989 [*]	0.732		
	-1	2	39 251.63 [*]	-0.22	-2	4	68 670.723	0.070		
	3	0?	39 251.00 [*]	0.67	6	0?	68 662.793 [*]	1.132		
	-2	4	39 241.0 [*]	0.2	-3	4	68 655.994	-0.175		
5 + 4	1	4	49 074.60	0.093	8 + 7	6	4	78 538.103	-0.141	
	2	2	49 073.65	-0.027		5	4		-0.057	
	1	0?	49 067.25	-0.219		7	4		78 536.892 [*]	0.611
	-1	2	49 064.50	-0.148		4	4		78 536.637 [*]	0.612
	3	0	49 063.15	0.679		2	4		78 525.727	0.134
6 + 5	2	4	58 895.176	0.056	1	4	78 517.563	0.273		
	1	4	58 889.107	0.105	2	2	78 515.57 [*]	0.341		
	3	2	58 888.318 [*]	0.238	4	2	78 515.239 [*]	0.675		
	2	2	58 888.318	0.045	1	2	78 512.216 [*]	-1.195		
	1	0?	58 880.287 [*]	0.125	5	2	78 512.216 [*]	1.243		
	2	0	58 877.025 [*]	-0.178	0	2	78 508.829	-0.050		
	-1	2	58 877.025	-0.310	6	2	78 508.829	0.506		
	3	0	58 874.594	0.461	0	0	78 505.857 [*]	0.674		
	-1	4	58 871.722	-0.182	1	0?	78 505.857 [*]	1.693		
	-2	4	58 861.032	-0.002	-1	2	78 501.777	-0.515		
	-4	2	58 852.656	-0.065	2	0	78 501.777 [*]	0.669		
7 + 6	-3	4	58 848.463	-0.152	3	0	78 495.598 [*]	-0.420		
	6	4	68 721.34 [*]	-0.32	-1	4	78 495.598 [*]	1.096		
	5	4	68 721.34	-0.20	-2	2	78 493.100 [*]	-0.545		
	2	4	68 710.574	0.032	4	0	78 489.05	0.15		
	1	4	68 703.409	0.133	-3	2	78 482.945	0.016		
	2	2	68 703.004	0.212	-2	4	78 480.294	0.276		
	3	2	68 701.600	-0.707	5	0	78 480.294 [*]	0.524		
	2	2		0.580	-4	2	78 470.056	-0.067		
	4	2	68 698.604 [*]	0.687	-3	4	78 463.403	-0.066		
	1	2		-1.102	7	0	78 455.402 [*]	-0.199		
5	2	0.877	-5	2	78 455.402	0.229				

Note. A star indicates frequencies omitted from the least-squares fit.

to be necessary to complete the Fortrat diagram for the K, l couples given in Fig 1. The D.R. arrows indicate the lines obtained by double resonance and the corresponding $J+1$ lines. For each value of J , the plot of $f/(J+1)$ versus K for every l , as given in Fig. 2 for $J=7$, was used to go further into the assignments; these curves confirm the large number of overlapping and unresolved lines observed. Many lines could not be ascribed to the $\nu_{10} = 4$ state. A direct diagonalization was then carried out using the following parameters in addition to the familiar rotation and centrifugal distortion constants: the variations x_{ll} and B_3 with the quantum number l of the vibrational

TABLE IV
 Constants for SiH₃CCH in the 4ν₁₀ State (in MHz)

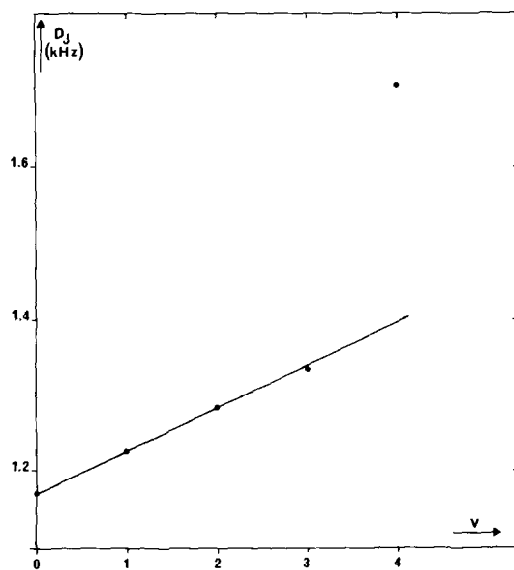
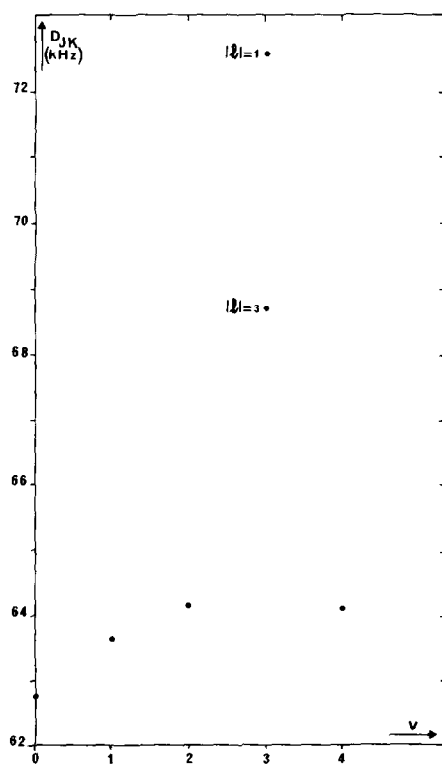
B _v	4906.958 (12)	with :	
B ₃	-0.0049 (5)	H _{JJJ}	<u>0</u>
D _J ^v	0.00170 (11)	H _{JJK}	<u>0.0000003</u>
D _{JK} ^v	0.0641 (5)	H _{JKK}	<u>0.0000013</u>
η _J ^v	0.17805 (47)	η _{JK}	<u>0</u>
x _{ℓℓ}	105900 (1270)	q _v	<u>1.8979</u>
(Aζ) _v ^v	76460 (410)	A _v =A ₀	<u>84700</u>

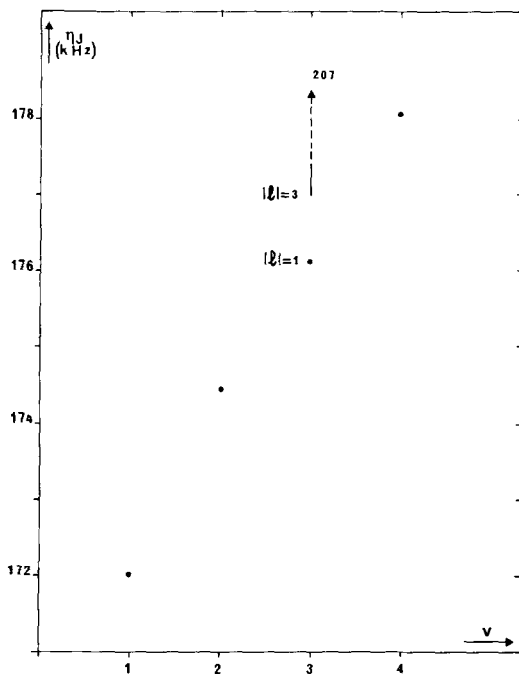
energy and the rotational constants B_v , respectively; the coefficient n_J of the diagonal term in $KIJ(J+1)$ of the third-order energy; and the Coriolis coupling constant ζ .

As was done for the analysis of the other ν_{10} excited states, the sextic centrifugal constants in H have been constrained to the $v=0$ values. The A rotational value has also been fixed to the value $A = 84\,700$ MHz obtained from infrared measurements and used in the $\nu_{10} = 1, 2, 3$ analysis. Any new value of this constant would involve a parallel shift of the anharmonic constant x_{ll} and the product $(A\zeta)_v^v$. The variation $(A\zeta)_3$ of $(A\zeta)_v^v$ with l has been neglected. As in the $2\nu_{10}$ state, the coefficient q_v of the off-diagonal terms $\langle K, l|H|K \pm 2, l \pm 2 \rangle$ could not be determined, because the contribution of these terms does not operate as a doubling for $Kl = 1$ like for the $v = 2n + 1$ states; a linear variation with v was assumed, so that q_v was constrained to the value $q_{v=4} = q_{v=3} + [(q_{v=3} - q_{v=1})/2]$. The terms depending on this constant, appearing in the analytical formulas as perturbation terms, were very sensitive to small variations of $A\zeta$ and x_{ll} , involving sometimes discontinuities; these two constants had to be determined independently in a first step, involving starting values for the final calculation. As the contribution of the $\langle K, l|H|K \pm 1, l \mp 2 \rangle$ elements is weak and had been shown not to be determinable independently of some other constants such as η_J , the q_{12} and d_{12} coefficients of these terms have been fixed to zero. As no doublets seemed to appear, due to the $\langle K, l|H|K, l \pm 6 \rangle$ element linking the $(K, l) = (\pm 1, \pm 4)$ and $(\pm 1, \mp 2)$ levels, the g_6 parameter was fixed to zero. The η_{JK} diagonal parameter was indeterminate.

The observed lines are listed in Table III. Many unresolved or too inaccurate lines had to be omitted from the calculations (denoted with a star in Table III). The analysis of the remaining lines shows a satisfactory agreement between experimental and theoretical frequencies.

However, many of the $l = 0$ lines are missing in the assignment, and the remaining ones, which are very sensitive to weak variations of the constants, show discrepancies

FIG. 3. Variation of D_J with v .FIG. 4. Variation of D_{JK} with v .

FIG. 5. Variation of η_J with v .

higher than the experimental error. In particular the straight line assigned to the $K = 1, l = 0$ couple on the Fortrat diagram of Fig. 1 displays a higher slope than the calculated one; all the attempts to modify the constants for an increase of the calculated slope led to sets of constants inconsistent with the analysis of the $|l| = 2$ and $|l| = 4$ lines. An analysis of the $l = 0$ spectrum separately, according to the procedure used for the $v_{10} = 3$ state (4), yielded indeterminable parameters.

So, as for the spectrum in the $3\nu_{10}$ state, some anomalies appear, which cannot be accounted for in terms of an internal interaction in the $4\nu_{10}$ state. These anomalies may be due to interactions with other vibrational modes; according to the infrared values of Refs. (5, 6), many states or combination states may be involved (8, 9).

The constants derived from this analysis are given in Table IV. Their values are consistent with those obtained for $v = 0$ and $v_{10} = 1, 2, 3$, except for B_3 , which becomes negative in the $v_{10} = 4$ state. A variation with v of the most significant parameters can be obtained. Figures 3, 4 and 5 show the variations of D_J , D_{JK} , and η_J . The values of the D_J and D_{JK} constants for $v_{10} = 4$ are respectively higher and lower than the expected ones, whereas η_J seems to follow a linear law. The anomalies observed for $v_{10} = 3$ (4) appear strongly on the D_{JK} and η_J plots. The variation of the rotational B constant is theoretically given by $B_v = B_0 + B_1v + B_2v^2 + B_3l^2$. Application of this expression to the $n\nu_{10}$ states yields $B_1 \cong 19.85$, $B_2 \cong -0.07$ MHz, with the ground state value $B_0 = 4828.6651$ MHz; B_3 varies with the different v_{10} states.

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