The Centrifugally Induced Pure Rotational Spectrum and the Structure of Sulfur Trioxide. A Microwave Fourier Transform Study of a Nonpolar Molecule

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The pure rotational spectrum of sulfur trioxide has been observed for the first time. A total of 25 high-J transitions could be assigned. The rotational constants, two quartic centrifugal distortion constants, and three sextic centrifugal distortion constants were determined as: $B = 10\,449.0667(23)$ MHz, $C = 5216.0330(12)$ MHz, $D_J = 9.2651(18)$ kHz, $D_{JK} = -16.3922(18)$ kHz, $H_J = -8.8(34) \cdot 10^{-3}$ Hz, $H_{JK} = -15.8(73) \cdot 10^{-3}$ Hz, and $H_{KJ} = 34.2(73) \cdot 10^{-3}$ Hz. An r_0- and an r_e-structure are presented: $r_0 = 1.4198(7)$ Å (calculated from B), $r_0 = 1.4210(7)$ Å (calculated from C), and $r_e = 1.4175$ Å.

Introduction

For nonpolar molecules the only possibility to determine highly accurate rotational constants of the ground vibrational state, and thereby the structure, is the detection of "forbidden" rotational transitions. The theory of these transitions, which are induced by centrifugal distortion, has been the subject of many investigations, see e.g. [1, 2]. Examples for nonpolar molecules with an observed rotational spectrum are molecules with T_d symmetry like methane, CH_4 [3, 4], silane, SiH_4 [5, 6], and germane, GeH_4 [7, 8], and molecules with D_{3h} symmetry like boron trifluoride, BF_3 [9–12].

Sulfur trioxide is another example of a D_{3h} molecule. Despite of its possible importance as an atmospheric species it was until now only investigated by IR spectroscopy [13–15]. This is easily understood since the rotational spectrum in the ground vibrational state is very weak, and Stark spectroscopy cannot be applied because only quadratic Stark effects occur [1, 2, 16]. Therefore Stark modulation is practically impossible. So microwave Fourier transform (MWFT) spectroscopy is predestinated to measure the pure rotational spectrum of SO_3. This technique with its high resolution and sensitivity is especially suited for transitions with a small dipole matrix element [17]. Since the spectroscopic constants of SO_3 were determined with a limited accuracy, we had to search for pure rotational transitions by use of MWFT spectroscopy over wide frequency ranges. Predictions with the spectroscopic constants of [13–15] did not give sufficiently precise positions of the lines.

Experimental

A commercial sample of SO_3 (99%, Aldrich-Chemie, Steinheim) was used without further purification. Since SO_3 decomposed to SO_2 in the spectrometer, a flow system was set up. The polyethylene terephthalate windows were slowly attacked by SO_3 and had to be replaced occasionally. The sample pressure at the entrance of the cell was typically 30 mTorr, dropping to 10 mTorr at the exit. In the Ku-band (frequency range between 12.4 and 18 GHz) we used a quadratic brass waveguide of 4 m length [18]. In the V-band (26.4–40 GHz) a 6 m long section of the circular brass waveguide described in [19] was used. The spectrometer design has been described elsewhere [18–20]. We scanned automatically in the Ku-band with a step width of 0.5 MHz [20]. The sample cell for this frequency range could be cooled down to 210 K for the recording of transitions with lower J. Microwave pulses of 1.5 to 2 μs duration corresponding to the peak power of the travelling wave tube amplifiers, 20 W for Ku-band and 10 W for V-band, were used to polarize the sample. The offset between the carrier frequency of the pulse and the molecular transition frequency was typically in the 100 to 300 kHz range.

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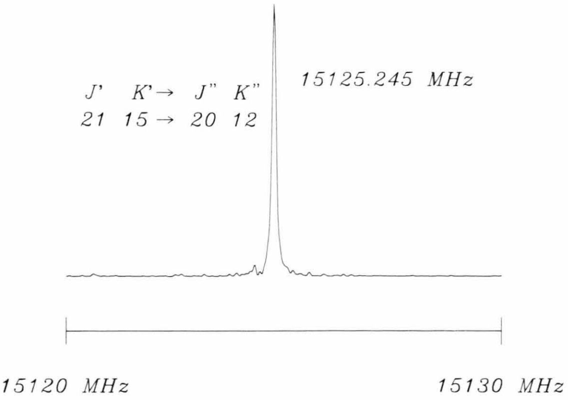


Fig. 1. A 10 MHz range out of a 50 MHz scan of the rotational power spectrum of the $J'K'-J''K''=21\ 15-20\ 12$ transition of sulfur trioxide. Pressure of the SO_3–SO_2 mixture about 20 mTorr, 210 K, polarization frequency 15 125 MHz, $16 \cdot 10^6$ averaging cycles, 1 k data points extended with 3k zeros prior to fast Fourier transformation (FFT).

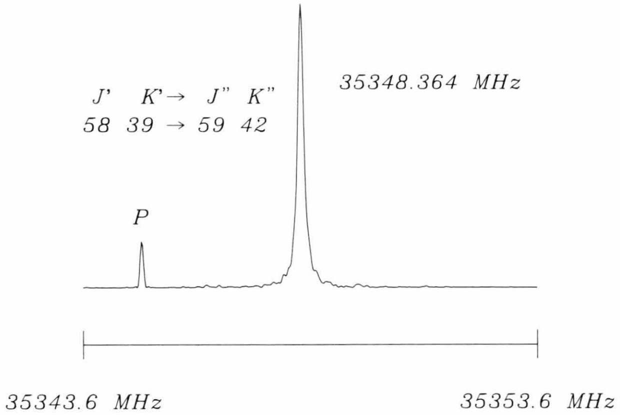


Fig. 2. A 10 MHz range out of a 50 MHz scan of the rotational power spectrum of the $J'K'-J''K''=58\ 39-59\ 42$ transition of sulfur trioxide. Pressure of the SO_3–SO_2 mixture about 20 mTorr, 293 K, polarization frequency 35 348.6 MHz, $16 \cdot 10^6$ averaging cycles, 1 k data points extended with 3 k zeros prior to fast Fourier transformation (FFT). P: Coherent perturbation caused by averager switching frequencies.

Table 1. Pure rotational transitions of sulfur trioxide, SO_3. ν_{obs} [MHz] observed transitions, ν_{calc} [MHz] calculated according to (1) and from our constants given in Table 2.

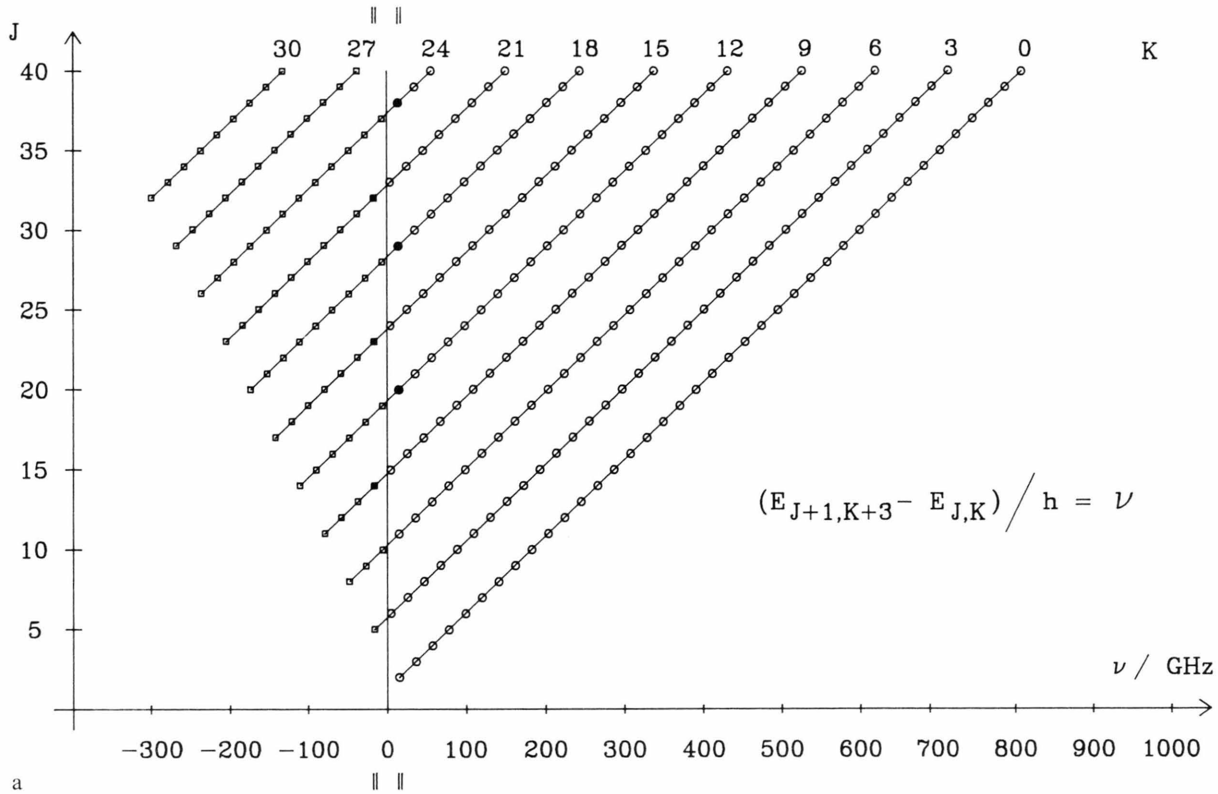
J'	K'	J''	K''	ν_{obs}	ν_{calc}	$\nu_{obs-calc}$
14	9	15	12	16 155.1510	16 155.1472	0.0038
23	15	24	18	16 293.4249	16 293.4353	−0.0104
32	21	33	24	16 246.3345	16 246.3441	−0.0096
41	27	42	30	15 946.0488	15 946.0571	−0.0083
50	33	51	36	15 325.8168	15 325.8194	−0.0026
59	39	60	42	14 320.2347	14 320.2323	0.0024
21	15	20	12	15 125.2448	15 125.2380	0.0068
30	21	29	18	15 093.8975	15 093.8875	0.0100
39	27	38	24	15 289.8987	15 289.8904	0.0083
48	33	47	30	15 780.2635	15 780.2623	0.0012
57	39	56	36	16 630.7234	16 630.7285	−0.0051
66	45	65	42	17 905.4270	17 905.4289	−0.0019
27	18	28	21	26 762.3653	26 762.3674	−0.0021
36	24	37	27	26 607.7741	26 607.7766	−0.0025
53	36	52	33	26 647.9836	26 647.9884	−0.0048
22	15	23	18	37 215.3368	37 215.3329	0.0039
31	21	32	24	37 187.1925	37 187.1762	0.0163
40	27	41	30	36 911.0706	36 911.0644	0.0063
49	33	50	36	36 320.0260	36 320.0204	0.0056
58	39	59	42	35 348.3635	35 348.3690	−0.0055
22	15	21	12	36 035.0250	36 035.0335	−0.0085
31	21	30	18	36 017.7986	36 017.8053	−0.0067
40	27	39	24	36 233.1882	36 233.1998	−0.0116
49	33	48	30	36 748.0192	36 748.0187	0.0005
58	39	57	36	37 627.7270	37 627.7186	0.0084

The transient emission signal was heterodyned down into an IF band around 30 MHz and sampled at a rate of 100 MHz. 1 k data points of the transient emission were taken. Typical averaging times were 5 minutes ($16 \cdot 10^6$ pulses). Each line was measured several times with differing polarization frequencies. Further we proved the signal to originate from a "nonpolar" molecular species by reducing the microwave power: This resulted in a monotonous decrease of the transient emission intensity. For polar molecules, like SO_2, this would not occur.

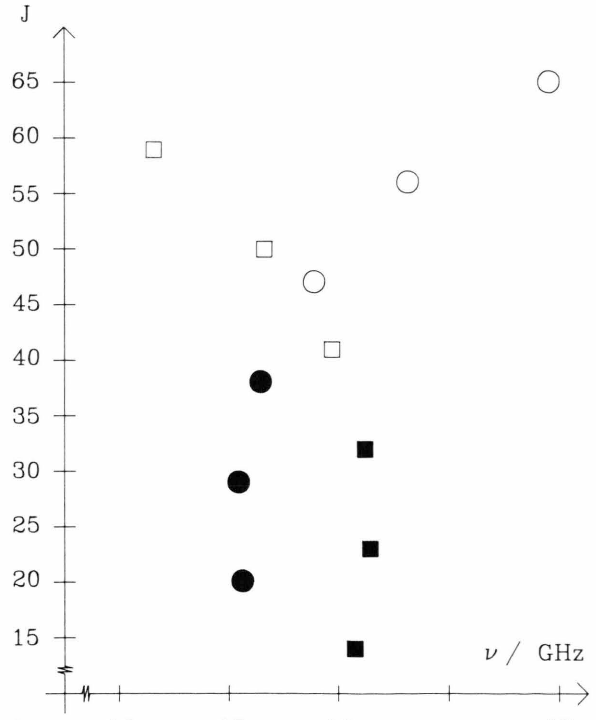
The Fourier transform algorithm was used to get a first survey of the spectrum. More accurate frequencies were obtained by least squares fits to the time domain signals [21].

In Fig. 1 we present a comparatively low J transition measured in the Ku-band and in Fig. 2 a high J transition measured in the V-band.

The observed line frequencies are given in Table 1. Under ν_{obs} the mean value of several measurements is given. The mean square deviation never exceeded 5 kHz. Due to the presence of three equivalent oxygen atoms with spin zero, only states with $K=3n$ (n an integer or zero) are symmetry allowed in the ground vibrational state. Further the selection rules $\Delta J=0$, ± 1 and $\Delta K= \pm 3$, with J the angular momentum quantum number and K its projection quantum number onto the molecular symmetry axis, reduce the number of transitions in the microwave region. As illustrated in Fig. 3 only $\Delta J=-1$, $\Delta K=-3$, and $\Delta J=+1$, $\Delta K=+3$ transitions have been observed.



a



b

Fig. 3. "Fortrat diagrams" for the observable rotational transitions. In Fig. 3a positive and negative frequencies are given, corresponding to $\nu = (E_{J+1,K+3} - E_{J,K})/h$. For positive ν, J designates the lower energy level. These transitions are marked with circles. For negative ν, J designates the higher energy level. These transitions are marked with squares. In Fig. 3b only positive values of the frequency ν are used. There a small Ku-band section of Fig. 3a has been enlarged. In Fig. 3a this frequency range is indicated by two sets of markers ||. All the transitions given in Fig. 3b have been observed (compare with Table 1); the filled circles and squares designate transitions shown in Figs. 3a and 3b. Although the observed transitions originate from different K-subbranches of Fig. 3a, they are arranged in a regular way.

The regularities in the frequency positions given in Fig. 3 b and Table 1 as "series" are consequences of the values of B and C, of spin statistics, selection rules and the accessible frequency range. They lead to the step widths of $\delta J = 9$ and $\delta K = 6$ in the observable "series".

Assignment and Analysis

As a starting point for the present investigation we have used the rotational constants and quartic centrifugal distortion constants given in [15] to predict the spectrum. The sextic centrifugal distortion constants were not known and set to zero. Based on this prediction we tentatively assigned quantum numbers to several observed lines in the Ku-band, until internal consistency was reached. The difference between initially predicted and finally observed frequencies was between 50 and 300 MHz. It was then relatively easy to assign further lines in V-band. The results are given in Table 1.

To confirm our assignment we can state that we found only the lines of SO_3 of Table 1 and lines of SO_2 given in [22] in our Ku-band search, which covered a band of 2.5 GHz in steps of 500 kHz. Further, the theoretically predicted line strengths (compare [1, 2, 11]) are in accordance with the experimental results. The strongest observed transitions are therefore $J'K'-J''K'' = 41\ 27 - 42\ 30$ at 210 K and $49\ 33 - 48\ 30$ at 293 K.

The transition frequencies were analyzed using the oblate symmetric top energy expression and the planarity conditions relating the centrifugal distortion constants [23]. We set the planarity defect of the centrifugal distortion constants to zero in accordance with the experimental results of BF_3 [11]:

$$\begin{aligned} E = {} & BJ(J+1) + (C-B)\,K^2 - D_J J^2 (J+1)^2 \\ & - D_{JK} J(J+1)\,K^2 + (2D_J + 3D_{JK})\,K^4/4 \\ & + H_J J^3 (J+1)^3 + H_{JK} J^2 (J+1)^2 K^2 \\ & + H_{KJ} J(J+1) K^4 - (3H_J + 4H_{JK} + 5H_{KJ})\,K^6/6\,. \end{aligned} \tag{1}$$

In the fit 25 lines with J between 14 and 66 have been included (see Table 1). The standard deviation of the fit, 8 kHz, is on the order of the experimental error quoted above.

The results are compared in Table 2 with the results of the IR investigations. Constants combined with $J^n \cdot K^m$, where $n+m$ has the same value, are highly correlated as given in Table 3. This is due to the type of experimentally accessible transitions. No other types of transitions are within the region of our MWFT spectrometers from 4 to 40 GHz.

Table 2. Rotational constants, quartic centrifugal distortion constants and sextic centrifugal distortion constants of sulfur trioxide.

	This work	Ortigoso et al. [15]	Henfrey et al. [14]
B/MHz	10 449.0667(23)	10 449.085(51)	10 449.3(3)
C/MHz	5 216.0330(12)	5 217.0 [a]	5 219.7 [b]
D_J/kHz	9.2651(18)	9.282(23)	9.0(3)
D_{JK}/kHz	−16.3922(18)	−16.4(6)	−16.2(14)
H_J/kHz	− 8.8(34)		
$H_{JK}/10^{-3}$ Hz	−15.8(73)		
$H_{KJ}/10^{-3}$ Hz	34.2(73)		

[a] C was calculated from the B value of Kaldor [13] using the calculated inertial defect [24].

[b] C was calculated from the B value using a refined value for the calculated inertial defect.

Table 3. Correlation matrices of the molecular parameters of SO_3 from the least squares fit [a].

	B	C	D_J	D_{JK}	H_J	H_{JK}	H_{KJ}
B	1000						
C	−999	1000					
D_J	908	−912	1000				
D_{JK}	−902	908	−999	1000			
H_J	145	−139	183	−163	1000		
H_{JK}	−117	111	−150	130	−999	1000	
H_{KJ}	85	−79	112	−92	997	−999	1000

[a] All values are multiplied by 1000.

Discussion

In our discussion we will concentrate on two topics: the discussion of the fact that the intensities in the centrifugally induced rotational spectrum of $^{32}SO_3$ appear to be definitely lower than in the corresponding spectrum of $^{11}BF_3$ also measured at our laboratory [12], and the discussion of the structure.

We start with the comparison of the intensities. They depend on the transition dipole matrix element (compare [1, 2]) and on the Boltzmann population differences between the upper and the lower state. From the latter, the SO_3 intensities should be clearly higher, since in BF_3 all K-levels are symmetry allowed albeit with differing spin weights, which spreads the population over considerably more states. Furthermore the relative abundance of ^{32}S is larger than the abundance of ^{11}B. Actually our observation was that the SO_3 intensities were clearly lower under comparable conditions. This indicates that in SO_3 the effective

Table 4. Inertial defect, r_0-structure, equilibrium rotational constants and r_e-structure of SO_3 [a, b].

	This work	Preceding work
Δ [c]	0.15764(3) amu Å^2	0.148 amu Å^2 [24]
r_0 [d]	1.4198(7) Å	
r_0 [e]	1.4210(7) Å	
B_e	10 483.1 MHz	10 483.1 MHz [15]
$2C_e$	10 483.4 MHz	
r_e [f]	1.4175 Å	1.4173 Å [15]

[a] A conversion factor for 505 379 MHz amu Å^2 was used.

[b] The uncertainties result from Gaussian error propagation and do not include systematic errors.

[c] Inertial defect $\Delta = I_{cc} - 2I_{bb}$.

[d] Calculated from $2I_{bb}$.

[e] Calculated from I_{cc}.

[f] The uncertainty cannot be calculated since, unfortunately, the uncertainties of the α_i-values in (3) and (4) have not been given in [15, 24].

dipole moment parameter Θ_x^{xx} [1, 2], which enters into the expression for the transition matrix elements, is smaller than in BF_3, either because SO_3 is stiffer or because the bond moments are smaller. (The index x refers to an axis perpendicular to the threefold axis.)

We now turn to the discussion of the structure. First it is instructive to compare the value of the inertial defect $\Delta = I_{cc} - 2I_{bb}$, now determined with high precision, to the calculated value presented in [24] (see Table 4). The value of C presented in [15] was calculated from B using the inertial defect given in [24]. The discrepancy of about 1 MHz with our experimental value combined with the high values of K explain the poor agreement of the initial prediction with the observed spectrum.

SO_3 is planar with an interbond angle $2\pi/3$. Thus only one parameter, the bond length (S–O) completely describes the structure within the rigid rotor model. This distance can be calculated according to

$$r = \sqrt{(2I_{bb}/(3M_O))} \quad \text{or} \quad r = \sqrt{(I_{cc}/(3M_O))} \tag{2}$$

with I_{gg} = moment of inertia ($g = b, c$), M_O = mass of oxygen.

By inserting the experimental rotational constants, r_0-values are obtained (see Table 4). Their difference is due to vibrational effects documented by the non-zero value of the inertial defect (see above).

To eliminate these vibrational effects on the structure we calculated equilibrium values for the rotational constants B_e and C_e [25]:

$$B_e = B_0 + \alpha_1^B/2 + \alpha_2^B/2 + \alpha_3^B + \alpha_4^B, \tag{3}$$

$$C_e = C_0 + \alpha_1^C/2 + \alpha_2^C/2 + \alpha_3^C + \alpha_4^C, \tag{4}$$

For α_1 we inserted the calculated value [24], for α_2, α_3, and α_4 the experimental values [14, 15]. The equilibrium rotational constants determined with (3) and (4) fulfill with high accuracy the condition $B_e = 2C_e$. The resulting bond length (S–O) is $r_e = 1.4175$ Å.

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[1] J. K. G. Watson, J. Mol. Spectrosc. **40,** 536 (1971).

[2] M. R. Aliev and V. M. Mikhailov, Opt. Spectrosc. **35,** 147 (1973).

[3] C. W. Holt, M. C. L. Gerry, and I. Ozier, Phys. Rev. Lett. **31,** 1033 (1973).

[4] P. Wolf and W. Stahl, Z. Naturforsch. **44a,** 651 (1989).

[5] I. Ozier, R. M. Lees, and M. C. L. Gerry, Can. J. Phys. **54,** 1094 (1976).

[6] M. Oldani, A. Bauder, and J. Pierre, J. Mol. Spectrosc. **117,** 435 (1986).

[7] R. H. Kagann, I. Ozier, G. A. McRae, and M. C. L. Gerry, Can. J. Phys. **57,** 593 (1979).

[8] W. Stahl and H. Dreizler, Z. Naturforsch. **42a,** 1402 (1987).

[9] S. Yamamoto, K. Kuchitsu, T. Nakanaga, H. Takeo, C. Matsumura, and M. Takami, J. Chem. Phys. **84,** 6027 (1986).

[10] S. Yamamoto, T. Nakanaga, H. Takeo, C. Matsumura, M. Takami, and K. Kuchitsu, Chem. Phys. Lett. **122,** 9 (1985).

[11] M. Oldani and A. Bauder, J. Chem. Phys. **86,** 624 (1987).

[12] K. Vormann, Dissertation, Kiel (1991).

[13] A. Kaldor, A. G. Maki, A. J. Dorney, and I. M. Mills, J. Mol. Spectrosc. **45,** 247 (1973).

[14] N. F. Henfrey and B. A. Thrush, Chem. Phys. Lett. **102,** 135 (1983).

[15] J. Ortigoso, R. Escribano, and A. G. Maki, J. Mol. Spectrosc. **138,** 602 (1989).

[16] H. Köppel and C. A. Coulson, J. Mol. Spectrosc. **75,** 64 (1979).

[17] H. Dreizler, Mol. Phys. **59,** 1 (1986).

[18] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).

[19] Ch. Keussen, R. Schwarz, U. Andresen, and H. Dreizler, Z. Naturforsch. **45a,** 711 (1990).

[20] M. Krüger and H. Dreizler, Z. Naturforsch. **45a,** 724 (1990).

[21] J. Haekel and H. Mäder, Z. Naturforsch. **43a,** 203 (1988).

[22] F. J. Lovas, J. Phys. Chem. Ref. Data **14,** 395 (1985).

[23] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Interscience, New York 1984, p. 368.

[24] A. J. Dorney, A. R. Hoy, and I. M. Mills, J. Mol. Spectrosc. **45,** 253 (1973).

[25] loc. cit. [23], p. 672.