

## High-Resolution Measurements of the Bands of Carbonyl Sulfide between 2510 and 3150 $\text{cm}^{-1}$

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The four strongest absorption bands of OCS in the region from 2500 to 3150  $\text{cm}^{-1}$  have been measured with FTS spectrometers with effective resolutions of about 0.010  $\text{cm}^{-1}$  or better. A total of 25 different vibrational transitions have been identified in the spectrum and have been analyzed to obtain improved band centers and rovibrational constants. Included in the bands identified are a few transitions due to the less abundant isotopomers,  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ ,  $^{16}\text{O}^{12}\text{C}^{33}\text{S}$ ,  $^{16}\text{O}^{13}\text{C}^{32}\text{S}$ , and  $^{18}\text{O}^{12}\text{C}^{32}\text{S}$ . Relative values are given for the transition moments of some of the overlapping bands.

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### INTRODUCTION

In two fairly recent papers Fayt and co-workers (1, 2) have given the rovibrational constants for a great many vibrational states of the four most abundant isotopes of OCS. Many of those constants were based on recent laser-Stark, heterodyne, and FTS measurements. In the higher-frequency regions, however, the rovibrational constants were based on old data (3). The last published rovibrational analysis of the bands between 2700 and 3200  $\text{cm}^{-1}$  seem to be those of Maki *et al.* (4) reported in 1962. Quite recently, Dang-Nhu and Guelachvili (5) have reported the analysis of the  $\nu_1 + \nu_2$  band<sup>2</sup> near 2575  $\text{cm}^{-1}$ .

For the  $^{16}\text{O}^{13}\text{C}^{32}\text{S}$  species Lahaye *et al.* (2) refer to more recent unpublished measurements. Measurements in this region are also given for the isotopomers  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$  and  $^{18}\text{O}^{12}\text{C}^{32}\text{S}$  by Blanquet *et al.* (7) and by Fayt and Vandenhoute (8), respectively.

In this paper we report the measurement and analysis of the four strongest absorption

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<sup>2</sup> The vibrational numbering system adopted by the IAU–IUPAP joint commission on spectroscopy (6) is used throughout this paper. Some papers use a notation that interchanges  $\nu_1$  and  $\nu_3$ .

bands of OCS in the region from 2500 to 3150  $\text{cm}^{-1}$ . Actually, this region encompasses six transitions from the ground vibrational state,  $00^03-00^00$ ,  $11^10-00^00$ ,  $02^02-00^00$ ,  $10^01-00^00$ ,  $04^01-00^00$ , and  $12^00-00^00$ . Three other vibrational transitions from the ground state fall in this region but have transition moments that are too small to give observable absorption lines in our spectra.

Only three papers have reported measurements of the intensities of the bands covered in this paper. The two earliest papers, (9, 10) only give integrated intensities measured with spectrometers having resolution too poor to allow the measurement of individual line intensities. The most recent paper (5) gives line intensities for the  $11^10-00^00$  band near 2575  $\text{cm}^{-1}$ .

#### EXPERIMENTAL DETAILS

Two FTS spectrometers were used to make the measurements reported here. The bands between 2500 and 2970  $\text{cm}^{-1}$  were measured on the BOMEM<sup>3</sup> DA.002 at NIST in Gaithersburg, Maryland. These measurements all had an effective resolution (full width at half-height of weak lines) of 0.010  $\text{cm}^{-1}$ . The bands between 2850 and 3150  $\text{cm}^{-1}$  were measured on a similar FTS spectrometer at NOAA in Boulder, Colorado. The NOAA measurements had an effective resolution of 0.004  $\text{cm}^{-1}$ .

The NIST measurements used a single-pass absorption cell 0.75 m in length. A pressure of 1.3 kPa (9.9 Torr) was used for the measurements below 2800  $\text{cm}^{-1}$  and a pressure of .66 kPa (5.0 Torr) was used for the NIST measurements between 2850 and 2970  $\text{cm}^{-1}$ . For the NOAA measurements a multipass absorption cell with a path length of 60 m was used with a pressure of 6 Pa (0.046 Torr) of OCS for measurements above 3000  $\text{cm}^{-1}$  and of 9 Pa (0.07 Torr) below 3000  $\text{cm}^{-1}$ .

Each band system was measured separately and was calibrated by means of OCS absorption frequencies that had been determined from earlier hot band measurements at lower frequencies. For the region from 2500 to 2600  $\text{cm}^{-1}$  the calibration was provided by both the  $00^03-00^00$  and  $11^10-00^00$  bands which had been measured by heterodyne techniques (11, 12). The regions 2695–2765  $\text{cm}^{-1}$  and 2859–2990  $\text{cm}^{-1}$  were calibrated by the  $02^02-00^00$  and  $04^01-00^00$  bands, respectively (13). The 3025–3120  $\text{cm}^{-1}$  region was calibrated by the  $12^00-00^00$  band as determined by the measurements of Hunt *et al.* (14) after correcting to agree with more recent heterodyne measurements in the 2060  $\text{cm}^{-1}$  region (12). The exact calibration frequencies used in this work were not taken from the references cited above but were determined from a more recent fit of OCS frequency measurements that included a slightly different data base such as the inclusion of the recent far-infrared measurements of Vanek *et al.* (15).

#### ANALYSIS OF THE WAVENUMBER MEASUREMENTS

The transitions were assigned in most cases by calculating the transition frequencies from the constants given by Fayt *et al.* (1). For the less abundant isotopomers the

<sup>3</sup> Brand names are used in this paper to identify experimental apparatus. Such use does not constitute an endorsement of products by NIST.

transitions were calculated or estimated from various other works of Fayt and co-workers (2, 7, 8).

With the exception of a few transitions as noted later, the measurements were analyzed by means of the equations given by Maki *et al.* (13). The analysis takes into account the effects of *l*-type resonance but does not include any specific allowance for Fermi resonance.

It is important to note that the band centers, given in Table I, are defined by the equations

$$E^0 = G + B_v J(J+1) - D_v [J(J+1) - l^2]^2 + H_v [J(J+1) - l^2]^3 + L_v [J(J+1) - l^2]^4 + \dots \quad (1)$$

and

$$\nu_0 = G' - G'' \quad (2)$$

Some authors use a somewhat different definition for the band centers,  $\nu_0$ . In Eq. (1)  $E^0$  denotes the energy level with the effect of *l*-type resonance removed, sometimes

TABLE I  
Band Centers Determined in This Analysis.

Transition	$\nu_0$ this work (cm <sup>-1</sup> )	$\nu_0$ other work (cm <sup>-1</sup> )	[Ref]	rms dev. (cm <sup>-1</sup> )	J <sub>max</sub> <sup>a</sup>
<sup>16</sup> O <sup>12</sup> C <sup>32</sup> S					
00 <sup>0</sup> 3-00 <sup>0</sup> 0* <sup>b</sup>	2555.991 22(13) <sup>c</sup>	2555.990 91(66)	[1]	0.0004	75
01 <sup>1</sup> 3-01 <sup>1</sup> 0	2536.670 98(51)	2536.669 65(162)	[1]	0.0013	45
00 <sup>0</sup> 4-00 <sup>0</sup> 1	2535.002 20(59)	2535.001 96(212)	[1]	0.0011	44
11 <sup>1</sup> 0-00 <sup>0</sup> 0*	2575.307 59(18)	2575.307 74(23)	[1]	0.0005	74
02 <sup>0</sup> 2-00 <sup>0</sup> 0*	2731.399 12(24)	2731.399 08(56)	[1]	0.0006	77
03 <sup>1</sup> 2-01 <sup>1</sup> 0	2724.838 52(25)	2724.838 95(112)	[1]	0.0008	60
02 <sup>0</sup> 3-00 <sup>0</sup> 1	2705.512 88(97)	2705.519 52(159)	[1]	0.0017	40
10 <sup>0</sup> 1-00 <sup>0</sup> 0	2918.105 14(13)	2918.105 53(40)	[1]	0.0004	99
11 <sup>1</sup> 1-01 <sup>1</sup> 0	2903.717 64(21)	2903.718 11(31)	[1]	0.0003	78
10 <sup>0</sup> 2-00 <sup>0</sup> 1	2909.530 15(21)	2909.539 61(284)	[1]	0.0004	50
12 <sup>0</sup> 1-02 <sup>0</sup> 0	2890.385 31(33)	2890.384 41(125)	[1]	0.0004	57
12 <sup>2</sup> 1-02 <sup>2</sup> 0	2890.008 25(23)	2890.012 34(86)	[1]	0.0003	56
11 <sup>1</sup> 2-01 <sup>1</sup> 1	2893.865 89(52)	2893.868 31(229)	[1]	0.0007	48
04 <sup>0</sup> 1-00 <sup>0</sup> 0*	2937.146 85(21)	2937.148 24(33)	[1]	0.0005	82
04 <sup>0</sup> 2-00 <sup>0</sup> 1	2903.858 68(91)	2903.852 43(281)	[1]	0.0005	50
12 <sup>0</sup> 0-00 <sup>0</sup> 0	3095.554 42(11)	3095.554 71(42)	[1]	0.0003	68
13 <sup>1</sup> 0-01 <sup>1</sup> 0	3094.923 27(15)	3094.923 61(80)	[1]	0.0004	50
<sup>18</sup> O <sup>12</sup> C <sup>32</sup> S					
10 <sup>0</sup> 1-00 <sup>0</sup> 0	2860.687 37(70)	2860.685(16)	[8]	0.0007	50
<sup>16</sup> O <sup>12</sup> C <sup>33</sup> S					
10 <sup>0</sup> 1-00 <sup>0</sup> 0	2911.905 77(27)	---		0.0005	67
<sup>16</sup> O <sup>12</sup> C <sup>34</sup> S					
00 <sup>0</sup> 3-00 <sup>0</sup> 0	2523.003 11(83)	2523.000 76(190)	[2]	0.0012	39
02 <sup>0</sup> 2-00 <sup>0</sup> 0	2708.313 89(175)	---		0.0018	33
10 <sup>0</sup> 1-00 <sup>0</sup> 0	2906.045 61(17)	2906.054 7(48)	[7]	0.0003	75
11 <sup>1</sup> 1-01 <sup>1</sup> 0	2891.991 87(46)	---		0.0007	50
12 <sup>0</sup> 0-00 <sup>0</sup> 0	3092.797 37(70)	---		0.0007	36
<sup>16</sup> O <sup>15</sup> C <sup>32</sup> S					
10 <sup>0</sup> 1-00 <sup>0</sup> 0	2861.049 85(31)	2861.050(10)	[2]	0.0005	62

- a) J<sub>max</sub> refers to the highest value of J that contributes to the fit for the upper state energy levels. In some cases the present measurements may have terminated at lower values of J.  
 b) For transitions indicated by an asterisk (\*) the band center was determined from heterodyne measurements reported earlier.  
 c) The uncertainty (twice the standard error) in the last digits is given in parentheses.

called the deperturbed energy level. Our analysis treats the  $l$ -doubling as an effect of the  $l$ -type resonance. The  $l$ -doubling constant,  $q$ , has the form

$$q = q_v - q_{vJ}J(J + 1) + q_{vJJ}[J(J + 1)]^2. \quad (3)$$

Table I gives the band centers, the rms deviation of the fits, and the maximum  $J$  value included in the fit for each vibrational transition. Tables II and III give the rovibrational constants used or determined for each vibrational energy level involved in these measurements. The least-squares fits used in this analysis included a large body of infrared and microwave data to better define the constants. The uncertainties given in the tables are the statistical uncertainties given by the least-squares fit and do not include any allowance for systematic errors that may be hidden in the data. We believe that the main effect of such systematic errors will be an underestimate of the true error in the band centers. Probably a more realistic estimate of the accuracy of the band centers would be given by adding  $0.0006 \text{ cm}^{-1}$  to the uncertainties of the band centers given in Table I, except for those bands for which there are heterodyne measurements.

In the tables the separation of the vibrational energy levels is not given for the levels that differ only in the value of  $l$ . Those separations have been given by Fayt *et al.* (1) with sufficient accuracy to calculate the effect of  $l$ -type resonance. Some of our earlier papers give small corrections to those separations (13, 15).

For the  $02^02-00^00$  and  $12^00-00^00$  transitions of  $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ , we had no accurate estimate of the location of the  $l = 2$  levels so it was not possible to include the effect of  $l$ -type resonance in the analysis. Instead, the transitions were fit to the usual power series in  $J(J + 1)$  as given in Eq. (1). This accounts for the unusually small values of  $D_v$  for the upper states involved in those transitions.

#### RELATIVE INTENSITY MEASUREMENTS

Although the current spectra were not intended to be used for intensity measurements, the nearly complete absence of intensity data for this region prompted us to measure the relative intensities of a few lines. The results of the present measurements are given in Table IV.

The relative intensity measurements are based on only crude estimates of the relative intensities of adjacent lines that are weak and of similar intensity. The relative intensities were verified by comparing calculated spectra with the measured spectrum. For those hot band and isotopic transitions that are given in Table I, but not included in Table IV, the calculated spectrum was in good agreement with the measured spectrum on the assumption that the transition moment is the same as the ground state transition for the most abundant isotopic species.

The values given in Table IV are based on the following equation for the integrated intensity,  $S$ , of individual rovibrational absorption lines:

$$S = \exp(-E''/kT)[1 - \exp(-\nu/0.69504T)] \times [N_i/Q_v Q_R] \nu C |\mu(v' - v'')|^2 S_v^2 S_R^2 F, \quad (4)$$

where  $C$  is a proportionality constant that includes  $8\pi^3/(3hc)$  and other factors,  $N_i$  is the concentration of the isotopic species under consideration,  $Q_v$  and  $Q_R$  are the vi-

TABLE II

Rotational Constants (in cm<sup>-1</sup>) Used to Fit the Present Measurements for <sup>16</sup>O<sup>12</sup>C<sup>32</sup>S

Vib. State	B <sub>v</sub>	D <sub>v</sub> ×10 <sup>8</sup>	H <sub>v</sub> ×10 <sup>14</sup>	q <sub>v</sub> ×10 <sup>4</sup>	q <sub>vJ</sub> ×10 <sup>10</sup>
00 <sup>0</sup> <sub>0</sub>	0.202 856 740 80(83) <sup>a</sup>	4.340 64(25)	-0.329(30)	---	---
01 <sup>1</sup> <sub>0</sub>	0.203 209 834 8(21)	4.411 48(31)	-0.260(38)	2.121 938 68(53)	1.424 13(102) <sup>b</sup>
00 <sup>1</sup> <sub>1</sub>	0.202 251 831 6(60)	4.433 50(36)	0.045(45)	---	---
02 <sup>2</sup> <sub>0</sub>	0.203 480 484 7(123)	4.419 64(63)	-0.712(73)	2.086 287(47)	0.659(35)
02 <sup>2</sup> <sub>0</sub>	0.203 559 482 1(89)	4.483 28(93)	-0.135(80)	---	---
01 <sup>1</sup> <sub>1</sub>	0.202 657 042(22)	4.542 71(63)	[0.1] <sup>c</sup>	2.285 20(29)	3.593(114)
00 <sup>3</sup> <sub>0</sub>	0.201 006 219(100)	4.647 59(514)	1.60(70)	---	---
11 <sup>1</sup> <sub>0</sub>	0.202 015 427(45)	4.473 80(210)	2.85(28)	2.155 33(27)	3.764(70)
02 <sup>2</sup> <sub>2</sub>	0.202 414 701(226)	4.707(108)	[-0.3]	2.365(100)	2.76(137)
02 <sup>2</sup> <sub>2</sub>	[0.202 523 2]	[4.804 7]	[0.1]	---	---
10 <sup>1</sup> <sub>1d</sub>	0.201 102 978(109)	5.071 26(684)	54.36(148)	---	---
04 <sup>4</sup> <sub>1e</sub>	0.203 436 473(356)	3.943 2(254)	-52.44(633)	2.127 48(95)	-1.168(169)
04 <sup>4</sup> <sub>1</sub>	0.203 569 074(81)	4.668 2(13)	[-0.3]	---	---
04 <sup>4</sup> <sub>1</sub>	[0.203 799 95]	[4.34]	[-0.3]	---	---
01 <sup>3</sup> <sub>0</sub>	0.201 510 88(143)	4.824(80)	[2.2]	2.596 1(160)	3.2(118)
12 <sup>2</sup> <sub>0</sub>	0.202 311 240(147)	4.500 9(56)	[2.2]	2.130 1(101)	6.6(28)
12 <sup>2</sup> <sub>0</sub>	0.202 382 585(146)	4.531 9(48)	[2.2]	---	---
03 <sup>2</sup> <sub>2</sub>	0.202 744 75(41)	4.771 1(127)	[-0.2416]	2.302 77(227)	2.93(89)
03 <sup>2</sup> <sub>2</sub>	[0.202 936 096]	[4.776 6]	[-0.2416]	---	---
00 <sup>4</sup> <sub>0</sub>	0.200 363 45(170)	4.792(94)	[2.5]	---	---
11 <sup>1</sup> <sub>1</sub>	0.201 515 903(248)	4.755 4(110)	8.57(130)	2.373 71(134)	8.55(32)
02 <sup>3</sup> <sub>0</sub>	0.201 863 71(330)	4.989(216)	[2.397]	[2.42]	[0.6587]
02 <sup>3</sup> <sub>0</sub>	[0.201 981 318]	[4.983 28]	[2.397]	---	---
13 <sup>1</sup> <sub>0</sub>	0.202 617 950(628)	4.569(66)	6.7(186)	2.100 35(152)	2.06(86)
13 <sup>1</sup> <sub>0</sub>	[0.202 745 521]	[4.41]	[-1.948]	---	---
04 <sup>0</sup> <sub>2f</sub>	0.202 601 23(986)	15.06(342)	-5459.(5096)	---	---
10 <sup>2</sup> <sub>2g</sub>	0.200 849 07(207)	-10.236(610)	3965.(687)	---	---
12 <sup>1</sup> <sub>1</sub>	0.201 835 303(531)	4.745 3(178)	[6.00]	[2.255 63]	[3.7]
12 <sup>1</sup> <sub>1</sub>	0.201 923 654(434)	4.782 4(151)	[6.00]	---	---
11 <sup>2</sup> <sub>2</sub>	0.201 069 28(118)	6.539 7(543)	[240.0]	2.709 1(142)	47.6(84)

- a) The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.
- b) Also included in the fit was  $q_{vJJ}=0.574(44)\times 10^{-14}$ .
- c) The values enclosed in square brackets were fixed during the analysis.
- d) An additional term,  $L=-1.985(95)\times 10^{-17}$ , was needed in the analysis.
- e) An additional term,  $L=1.71(50)\times 10^{-17}$ , was needed in the analysis.
- f) Additional terms needed in the analysis were:  $L=0.16(366)\times 10^{-14}$ ,  $M=-1.03(125)\times 10^{-17}$ , and  $N=4.26(161)\times 10^{-21}$ .
- g) Additional terms needed in the analysis were:  $L=2.901(326)\times 10^{-14}$  and  $M=-8.41(54)\times 10^{-18}$ . See text for discussion of analysis beyond  $J=50$ .

brational and rotational partition functions, respectively,  $T$  is the temperature,  $E''$  is the lower state energy, and  $\nu$  is the wavenumber of the transition (in cm<sup>-1</sup>).

When ratios of line intensities are compared, as in this work, most of the terms in Eq. (4) cancel or are easily calculated. The principal terms that do not cancel are  $|\mu(v' - v'')|$ , the transition moment or dipole derivative,  $S_R$ , the rotational strength factor or direction cosine matrix element for rotation,  $S_V$ , the vibrational strength factor, and  $F$ , the Herman-Wallis factor.

In this paper we have used a Herman-Wallis factor that has the form

$$F = 1 + a_1 m + a_2 J'(J' + 1), \quad (5)$$

where  $m$  has the usual meaning of  $J'$  for R-branch transitions and  $-J''$  for P-branch transitions. For the transitions involving  $\Delta v_2 = 1$ , a nonzero value for  $a_1$  is usually required, as found by Dang-Nhu and Guelachvili (5). For the 10<sup>02</sup>-00<sup>01</sup> and 04<sup>02</sup>-00<sup>01</sup> transitions a resonance perturbation requires that we use a nonzero value for the  $a_2$  term.

The rotational strength factors,  $S_R$ , were given by the usual equations. For  $\Delta l = 0$ , the  $\Delta J = 0$  transitions have

$$S_R = [(2J + 1)l^2/J(J + 1)]^{1/2}, \quad (6)$$

and the  $\Delta J = \pm 1$  transitions have

$$S_R = [(|m|^2 - l^2)/|m|]^{1/2}. \quad (7)$$

For  $\Delta l = \pm 1$  and  $\Delta J = 0$

$$S_R^2 = \frac{1}{2}(2J+1)(J+l+1)(J-l)/J(J+1). \quad (8)$$

For  $\Delta l = +1$  and  $\Delta J = +1$

$$S_R^2 = \frac{1}{2}(J+l)(J+l+1)/J \quad (9)$$

while for  $\Delta l = +1$  and  $\Delta J = -1$

$$S_R^2 = \frac{1}{2}(J-l)(J-l-1)/J, \quad (10)$$

where  $J$  is the larger of  $J'$  and  $J''$  but  $l$  is always  $l''$ .

The vibrational strength factors were slightly different for even and odd values of  $\Delta v_2$ . For simplicity the strength factor was broken into two factors such that

$$S_v^2 = S_{13}^2 S_2^2$$

with

$$S_{13}^2 = (v_1 + \Delta v_1)!(v_3 + \Delta v_3)!/(v_1!v_3!\Delta v_1!\Delta v_3!) \quad (11)$$

and for  $\Delta v_2$  even (or zero)

$$S_2^2 = [\frac{1}{2}(v_2 + l + \Delta v_2)]! [\frac{1}{2}(v_2 - l + \Delta v_2)]! / \{ [\frac{1}{2}(v_2 + l)]! [\frac{1}{2}(v_2 - l)]! [(\frac{1}{2}\Delta v_2)!]^2 \}, \quad (12)$$

TABLE III

Rotational Constants (in  $\text{cm}^{-1}$ ) Used to Fit the Present Measurements for Different Isotopes of OCS

Vib. State	$B_v$	$D_v \times 10^8$	$H_v \times 10^{14}$
$^{18}\text{O}^{12}\text{C}^{32}\text{S}$			
00 <sup>0</sup> 0	[0.190 293 541 5] <sup>a</sup>	[3.778 18]	[-0.300]
10 <sup>0</sup> 1	0.188 619 16(148) <sup>b</sup>	4.041(60)	[30.0]
$^{16}\text{O}^{12}\text{C}^{33}\text{S}$			
00 <sup>0</sup> 0	0.200 302 432(17)	4.237 48(159)	-0.314(433)
10 <sup>0</sup> 1	0.198 574 71(66)	4.948(38)	36.7(60)
$^{16}\text{O}^{12}\text{C}^{34}\text{S}$			
00 <sup>0</sup> 0	0.197 898 035 1(67)	4.141 19(125)	-0.351(184)
01 <sup>1</sup> 0 <sup>c</sup>	0.198 242 548 7(107)	4.208 25(86)	-0.319(91)
00 <sup>0</sup> 3	0.196 093 46(293)	4.429(206)	[1.151]
02 <sup>0</sup> 2	0.197 464 68(760)	3.423(672)	[22.5]
10 <sup>0</sup> 1	0.196 196 851(318)	4.916 1(155)	41.78(204)
12 <sup>0</sup> 0	0.197 377 02(92)	[3.8]	[8.8]
11 <sup>1</sup> 1 <sup>d</sup>	0.196 588 43(99)	4.556(40)	[10.0]
$^{16}\text{O}^{13}\text{C}^{32}\text{S}$			
00 <sup>0</sup> 0	0.202 204 013 7(99)	4.328 8(21)	-0.269(379)
10 <sup>0</sup> 1	0.200 626 85(98)	7.161 4(697)	232.9(129)

a) The values enclosed in square brackets were fixed during the analysis.

b) The uncertainty in the last digits (twice the estimated standard error) is given in parentheses.

c) The  $\ell$ -doubling terms were  $q_v = 2.024\ 338\ 01(78) \times 10^{-4}$  and  $q_{v,j} = 1.3084(74) \times 10^{-10}$ .

d) The  $\ell$ -doubling terms were  $q_v = 2.2610(130) \times 10^{-4}$  and  $q_{v,j} = 14.9(66) \times 10^{-10}$ .

TABLE IV  
Measurements of Relative Transition Moments

$\frac{ \mu(00^03-00^00) }{ \mu(11^10-00^00) }$	= 1.43 (14) <sup>a</sup>	$ \mu(11^10-00^00) $	= 0.00257 debye <sup>c</sup>
		$ \mu(00^03-00^00) $	= 0.00367 debye
$\frac{ \mu(00^03-00^00) }{ \mu(01^13-01^10) }$	= 1.29 (13)	$ \mu(01^13-01^10) $	= 0.00284 debye
$\frac{ \mu(02^02-00^00) }{ \mu(03^12-01^10) }$	= 1.026 (100)		
$\frac{ \mu(10^01-00^00) }{ \mu(04^01-00^00) }$	= 9.444 (944)		
$\frac{ \mu(04^01-00^00) }{ \mu(05^11-01^10) }$	= 1.44 (14) <sup>d</sup>		
$\frac{ \mu(10^01-00^00) }{ \mu(10^02-00^01) }$	= 1.097 (110) <sup>e</sup>		
$\frac{ \mu(10^01-00^00) }{ \mu(04^02-00^01) }$	= 2.33 (23) <sup>f</sup>		

- a) The uncertainty of these measurements is believed to be about 10% of the given values and is given in parentheses.  
 b) The transition moment for the 11<sup>1</sup>0-00<sup>0</sup>0 transition was adjusted to agree with the measurements of Dang-Nhu and Guelachvili (5), including the term  $a_1 = 0.00463$ .  
 c) 1 debye =  $3.336 \times 10^{-30}$  C m.  
 d) The transition moments for hot bands do not include the vibrational dependence terms that come from Eqs. (11, 12, and 13).  
 e) A Herman-Wallis term of  $a_2 = -0.00034$  is also needed for the line intensities of the 10<sup>0</sup>2-00<sup>0</sup>1 band.  
 f) A Herman-Wallis term of  $a_2 = 0.00105$  is also needed for the line intensities of the 04<sup>0</sup>2-00<sup>0</sup>1 band.

while for  $\Delta v_2$  odd

$$S_2^2 = [\frac{1}{2}(v_2 + l + \Delta v_2 - 1)]! [\frac{1}{2}(v_2 - l + \Delta v_2 - 1)]! (v_2 + \Delta l * l + \Delta v_2 + 1) / \{ [\frac{1}{2}(v_2 + l)]! [\frac{1}{2}(v_2 - l)]! \{ [\frac{1}{2}(\Delta v_2 - 1)]! \}^2 (\Delta v_2 + 1) \}. \quad (13)$$

Equations (12) and (13) only apply if  $|\Delta l| \leq 1$ , otherwise  $S_2 = 0$ . In Eqs. (11), (12), and (13) the smaller of  $v'$  and  $v''$  is used for  $v$ ,  $\Delta v = |v' - v''|$ ,  $l = l''$ , and  $\Delta l = l' - l''$ .

Equation (11) was derived from the properties of harmonic oscillator wave functions such as can be found, among other places, in Appendix III of Wilson *et al.* (16). Equations (12) and (13) were derived from the properties of the two-dimensional harmonic oscillator wave functions given by Moffitt and Liehr (17).

Note that  $S_v^2$  is normalized so that transitions from the ground state always have  $S_v^2 = 1$ . For some hot bands  $S_v$  may be 1, but for certain hot bands, such as 10<sup>0</sup>2-00<sup>0</sup>1,  $S_v^2 = 2$ , while for the hot band 00<sup>0</sup>4-00<sup>0</sup>1,  $S_v^2 = 4$ . Other authors sometimes

include  $S_v$  in the dipole derivative term,  $|\mu|$ , in which case the dipole derivative for certain hot bands will be very different from that for the ground state transitions.

THE  $\Delta v_1 = -1, \Delta v_2 = 4$  RESONANCE

For some of the transitions measured in this work there is a significant resonance coupling levels of the type  $(v_1, v_2, v_3, l)$  and  $(v_1 - 1, v_2 + 4, v_3, l)$ . This resonance has been recognized (1, 3, 14, 18) as contributing to unusually large values for the centrifugal distortion constants,  $D, H, L$ , etc., for levels with either  $v_1 \neq 0$  or  $v_2 \geq 4$ . The levels  $10^0_1, 04^0_1$ , and  $11^1_2$  are good examples of how this weak resonance affects the  $D_v$  and  $H_v$  terms.

Fayt (18) has shown that the  $10^0_2$  and  $04^0_2$  levels present a case where this resonance is particularly significant since the levels are only  $5.7 \text{ cm}^{-1}$  apart and the difference in their  $B$  values is such that their unperturbed energy manifolds would cross at  $\sim J = 39$ . Fayt has also found that the  $04^2_2$  level is only  $8.8 \text{ cm}^{-1}$  below the  $10^0_2$  level and, because of the difference in  $B$  values, their manifolds cross at  $\sim J = 55$ . Normally,  $l$ -type resonance couples the  $04^2_2$  and  $04^0_2$  levels. Consequently, it will couple the  $04^2_2$  and  $10^0_2$  levels because the  $\Delta v_1 = -1, \Delta v_2 = 4$  resonance mixes the wavefunctions of the  $10^0_2$  and  $04^0_2$  levels. This three level resonance has been carefully explained and analyzed by Fayt (3, 18) who had a more complete set of transitions from the ground state than we have from the  $00^0_1$  state.

In this work we have found transitions up to  $J = 55$  for the two highest-frequency rotational manifolds which we have labeled  $10^0_2-00^0_1$  and  $04^0_2-00^0_1$  according to the vibrational character of the lowest  $J$  levels. We have also found a fragment of the lowest energy levels of this triad between  $J = 54$  and  $70$  which at the highest  $J$  levels also becomes primarily a  $10^0_2-00^0_1$  transition. This latter fragment was not included in the fit that gave the constants in Tables I and II because the two avoided crossings make it impossible to fit both the high  $J$  and low  $J$  transitions to a single power series, such as Eq. (1).

The intensity of the observed transitions comes almost entirely from the transition moment of the  $10^0_2-00^0_1$  transition. For a quantitative description of the intensities of the transitions for the  $10^0_2-00^0_1$  and or  $04^0_2-00^0_1$  bands it would be necessary to take into account the mixing of the wavefunctions of the three levels involved in the interaction. An examination of the observed intensities and the mixing implied by the energy level diagram (Fig. 1 in Fayt (18)) leads us to believe that the intensities are in very good agreement with Fayt's analysis.

We have taken a more qualitative approach and have assigned transition moments to the low  $J$  transitions and given approximate values for effective Herman-Wallis-type constants. These are given in Table IV. The constants given in Tables I, II, and IV for these two interacting levels should *not* be applied to levels for  $J > 50$ .

One of the results of this resonance is the enhancement of the intensity of the  $04^0_2-00^0_1$  transitions beyond what one would expect from the intensity of the  $04^0_1-00^0_0$  transitions. The  $04^0_2-00^0_1$  and  $10^0_2-00^0_1$  transitions have nearly equal intensities because the wavefunctions of the upper states are so strongly mixed. The sum of the intensities of the two transitions is approximately equal to what the sum of the intensities would have been if there had been no coupling of the states.



## ACKNOWLEDGMENT

This work was supported in part by the NASA Office of Upper Atmospheric Research.

RECEIVED: December 19, 1990

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