Microwave Spectroscopy in the Region from Two to Three Millimeters, Part II*

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Precise frequency measurements on rotational transitions occurring in the wavelength range from 2 to 3 mm for a number of molecules have been made. From these, centrifugal stretching effects have been determined and accurate values of the rotational constants obtained. A table including all frequencies so far measured in this region of the spectrum is given.

INTRODUCTION

THE present work is a continuation of a program[1] which has been underway in this laboratory for the past four years to extend the range of accurate radiofrequency methods of spectroscopy to wavelengths shorter than 5 mm (frequencies above 60,000 Mc/sec). This is the second of the papers to report precision measurements in the region from two to three millimeters. In the first paper, measurements on the rotational line of carbon monoxide at 115,270.56 Mc/sec were reported. The present work extends the measurements to a large number of other molecules and extends the range of precise frequency measurements to 130,000 Mc/sec—a frequency 26,000 times the 5 Mc/sec WWV frequency used as a monitoring standard. An accuracy of 3 parts in 10^6 is maintained in these measurements.

One of the advantages which the high frequency millimeter-wave spectroscopy has over that in the centimeter-wave region is the more accurate determination of centrifugal distortion effects of molecular rotation. For example, the third rotational line of ICN occurring at 1.5 cm wavelength is displaced only 0.095 Mc/sec, by centrifugal distortion, whereas the twentieth line at 2.3 mm wavelength is displaced 28 Mc/sec. The evaluation of these effects in some relatively simple molecules which will allow a critical testing of existing theories of molecular distortions and the establishment of secondary spectrum line frequency standards in this newly explored region are the primary purposes of the present investigation. Furthermore, when the rotational lines of a given molecule which occur in the region from 2 to 3 mm wavelength are accurately fitted to a formula, this formula can then be used to compute the positions of lines at still higher frequencies, even in the far infrared region, with sufficient accuracy for use as secondary frequency standards. For example, the centrifugal stretching constant, D_J, of N_2O is known from the present work to an accuracy of 0.05 kc/sec, and the B_0 value is known to an accuracy of 25 kc/sec. The rotational lines occurring at 100 microns (0.1 mm) wavelength can be computed to an accuracy of one part in 10^4. If microwave measurements were made only in the K-band region (1 cm), the centrifugal stretching effects could not be evaluated, and the rotational lines at 100 microns could be calculated to an accuracy of one part in 10^2 only. At one millimeter wavelength the N_2O rotational lines can be computed to an accuracy of three parts in 10^6, taking into account the centrifugal stretching information, or to one part in 10^4 without this information.

EXPERIMENTAL

Some descriptions of the methods and instruments are given in the earlier reports mentioned.[2] The principal difference in the present work is that fourth and fifth harmonic energy (third and fourth overtones) from silicon crystals driven by K-band klystrons was used almost exclusively, whereas in the previous measurements the second and third harmonics (first and second overtones) were employed. Because of the greater power output of the K-band tubes, approximately the same power in the region from 2 to 3 millimeters can be obtained from a higher harmonic of these tubes as from a lower harmonic of available millimeter wave tubes. Also, the use of K-band tubes as drivers for the multipliers considerably simplifies the problem of frequency measurement, since in the K-band region such strong markers are obtainable from the frequency standard that only a small fraction of the oscillator power need be used to "beat" with the markers. Thus, most of the power is reserved for driving the source multiplier.

RESULTS

Table I lists all spectral lines so far measured in the region from 2 to 3 mm wavelength. All except those for CO and O_2 are new measurements. For the sake of completeness those of the latter molecules are repeated from the previous papers.[1] In the same table are given molecular constants computed from the present data and those of lower transitions measured previously by others.

Linear Molecules

The rotational frequencies for linear molecules in the ground vibrational and ground electronic states are

[1] Smith, Gordy, Simmons, and Smith, Phys. Rev. **75**, 260 (1949); Gilliam, Johnson, and Gordy, Phys. Rev. **78**, 140 (1950); Anderson, Johnson, and Gordy, Phys. Rev. **83**, 1061 (1951).

[2] Further details will appear in the Proc. N. Y. Acad. Sci.

given by the theoretical formula,[3]

$$\nu = 2B_0(J+1) - 4D_J(J+1)^3, \qquad (1)$$

where $B_0 = h/8\pi^2 I_B{}^0$ and D_J is the constant which depends upon centrifugal stretching. By combining our results with the measurements on N_2O and OCS made at lower frequencies by others, one can check the accuracy of this formula. No higher order terms had to be included for present accuracy and range of frequencies. The values of B_0 and D_J determined from the observed frequencies are given in Table I.

For diatomic molecules or for symmetric, linear, XYZ triatomic molecules, D_J can be computed very accurately from Kratzer's formula[4]

$$D_J = 4B_0{}^3/\omega^2, \qquad (2)$$

where ω is the fundamental stretching vibrational frequency. If the linear triatomic molecule is of the form XYZ, there are two fundamental stretching frequencies, ω_1 and ω_3, and Kratzer's formula no longer applies. However, our results indicate that it can still be used to obtain the D_J to a first approximation if the lower of the two fundamental bond-stretching frequencies is used (see also Herzberg and Spinks[5]).

A. H. Nielsen has derived the expression,[6]

$$D_J = 4B_0{}^3(\xi^2{}_1/\omega_1{}^2 + \xi^2{}_3/\omega_3{}^2), \qquad (3)$$

which applies explicitly to the linear XYZ molecule, where ω_1 and ω_3 are the two fundamental vibrational frequencies which correspond to stretching of the molecule, and ξ_1 and ξ_3 are constants which weight each stretching frequency. The present experimental evaluation of D_J's with the known vibrational frequencies provides a test of Nielsen's equation. The results are shown in Table II along with values estimated with the simple approximation of Kratzer's formula and only the lower fundamental stretching frequency.

Symmetric-Top Molecules

The rotational frequencies of a symmetric-top molecule in the ground vibrational and the ground electronic state are given by the formula,[7]

$$\nu = 2B_0(J+1) - 2D_{JK}(J+1)K^2 - 4D_J(J+1)^3, \qquad (4)$$

where $B_0 = h/8\pi^2 I_B{}^0$ and D_{JK} and D_J are coefficients of distortion for the rotational motions described by the molecule. Like Eq. (1), this formula was found to hold within the accuracy of the measurements. Table I lists the values of the three constants, B_0, D_J, and D_{JK}, as determined from the observed frequencies.

[3] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 19.
[4] A. Kratzer, Z. Physik **3**, 289 (1920).
[5] G. Herzberg and J. W. T. Spinks, Proc. Roy. Soc. (London) **147**, 434 (1934).
[6] A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943); H. H. Nielsen, Phys. Rev. **78**, 296 (1950).
[7] See reference 2, p. 31.

TABLE I. Observed transitions and resulting values of B_0, D_J, and D_{JK} in the region from 2 to 3 mm wavelength.

Molecule and transition	Measured frequency Mc/sec	D_J kc/sec	D_{JK} kc/sec	B_0 Mc/sec	Ref.
O_2 $J=0\to1$ $K=1$	118,745.5 ±0.3				(a)
$C^{12}O^{16}$ $J=0\to1$	115,270.56±0.25			57,635.66	(b)
$C^{13}O^{16}$ $J=0\to1$	110,201.1 ±0.4			55,100.90	(b)
$O^{16}C^{12}S^{34}$ $J=7\to8$ $J=9\to10$	97,301.31±0.20 121,624.79±0.25	1.27±0.05		6081.494	
$N_2{}^{14}O^{16}$ $J=3\to4$ $J=4\to5$	100,491.76±0.25 125,613.68±0.30	5.75±0.05		12,561.66	
$PO^{16}F_3$ $J=9\to10$ $K=0$ $K=3$ $K=5$ $K=6$ $K=7$ $K=8$ $K=9$	91,881.24±0.20 91,880.95±0.20 91,880.50±0.40 91,880.34±0.30 91,879.96±0.25 91,879.58±0.20 91,879.26±0.40				
$PO^{16}F_3$ $J=10\to11$ $K=0$ $K=3$ $K=5$ $K=6$ $K=7$ $K=8$ $K=9$	101,068.35±0.20 101,068.04±0.20 101,067.62±0.40 101,067.33±0.20 101,066.91±0.20 101,066.52±0.20 101,066.06±0.20	1.10±0.05	1.25±0.05	4594.282	
$J=12\to13$ unresolved $J=13\to14$ unresolved	119,441.32±0.45 128,626.60±0.20				
$C^{12}H_3F$ $J=1\to2$ $K=0$ $K=1$	102,142.62±0.20 102,140.85±0.20	32.5	443	25,535.91	
$C^{12}D_3F$ $J=2\to3$ $K=0$ $K=1$ $K=2$	122,695.50±0.30 122,694.20±0.30 122,690.02±0.30	32.5°	228±8	20,449.83°	
$N^{14}F_3$ $J=4\to5$ $K=0$ $K=2$ $K=3$	106,805.93±0.20 106,804.54±0.50 106,803.62±0.20	14.2	−25.7	10,681.072	
$PS^{32}F_3$ $J=22\to23$ $K=0$ $K=5$ or 6 $K=9$ $K=12$ $K=15$	122,237.90±0.30 122,235.80±0.30 122,231.30±0.30 122,225.50±0.30 122,219.00±0.30	0.30±0.05	1.8±0.07	2657.663	
$C^{12}H_3C^{12}C^{12}H$ $J=6\to7$ $K=0$ $K=1$ $K=2$ $K=3$ $K=4$ $K=5$ $K=6$	119,637.90±0.30 119,635.95±0.20 119,628.50±0.50 119,617.00±0.20 119,601.06±0.20 119,580.50±0.20 119,555.62±0.20	3.12	164±2	8545.87	
PF_3 $J=7\to8$ $K=0$ $K=3$ $K=4$ $K=5$ $K=6$	125,103.89±0.20 125,105.60±0.20 125,106.85+0.25 125,108.60±0.20 125,110.64±0.30	7.5±0.1	−11.7±0.1	7820.01	

a Anderson, Johnson, and Gordy (to be published).
b Gilliam, Johnson, and Gordy, Phys. Rev. **78**, 140 (1950).
c Obtained from these data and the $J=0\to1$ transition at 40,899.54 mc measured by one of us (R.F.T.).

TABLE II. Centrifugal distortion constants D_J for linear XYZ molecules.

| Molecule | D_J (kc/sec) | | |
| | Obs. | Calc.[a] | |
		Kratzer's approx.[b]	Nielsen's formula[c]
OCS	1.27 ± 0.05	1.35	1.32
N_2O	5.75 ± 0.05	5.21	4.83
$Br^{79}CN$	0.91 ± 0.09^d	0.92	0.85
$Br^{81}CN$	0.81 ± 0.09^d	0.91	0.83

[a] The fundamental frequencies and force constants used in these calculations were taken from G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 174, with the exception of those for N_2O which are given by W. S. Richardson and E. B. Wilson, Jr., J. Chem. Phys. 18, 694 (1950).
[b] See reference 3.
[c] See reference 5.
[d] J. W. Simmons and W. E. Anderson, Phys. Rev. 80, 338 (1950).

Pyramidal XY_3 Molecules

Phosphorus trifluoride and nitrogen trifluoride are pyramidal oblate $(I_A > I_B)$ symmetric-top molecules. The moment of inertia I_B for an XY_3 pyramidal symmetric top is given by

$$I_B = \frac{3M_y d_{xy}^2}{2(1+3M_y/M_x)}[2-(1-3M_y/M_x)\sin^2\beta],$$

where M_y and M_x are the masses of the atoms Y and X and β is the angle between the XY internuclear axis and the figure axis. It is readily seen that I_B increases with an increase in β when $3M_y/M_x > 1$, and decreases with an increase in β when $3M_y/M_x < 1$. For both NF_3 and PF_3, I_B increases with an increase in β. An increase in the angular momentum $Kh/2\pi$ about the symmetry axis should increase β and should also stretch the XY bond, both of which would increase I_B. However, as K increases, the component of angular momentum N which is perpendicular to K must decrease for a given J. A decrease in N tends to decrease I_B. The observed lines of a given J transition fall to higher frequency with increasing K. (D_{JK} is negative.) Therefore the net effect of increasing K and decreasing N is to decrease I_B.

X_3YZ Symmetric-Top Molecules

From infrared spectral constants Slawsky and Dennison[8] predict negative values of D_{JK} for the methyl halides. Earlier microwave measurements[9] in this laboratory revealed that D_{JK} is positive in the methyl halides as well as in a large number of molecules such as CH_3F, CD_3F, POF_3, PSF_3, and CH_3CCH investigated here.

By a partial differentiation of the expression for the moment of inertia I_B with respect to β (the acute angle between the bond XY and the symmetry axis), it is seen that I_B decreases as β increases. In the methyl halides both an increase in K and the accompanying decrease in

[8] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. 7, 509 (1939).
[9] Gordy, Simmons, and Smith, Phys. Rev. 74, 243 (1948); J. Simmons and W. E. Anderson, Phys. Rev. 80, 338 (1950).

TABLE III. Comparison of calculated and observed centrifugal distortion constants, D_J for the methyl halides and methyl acetylene.

| Molecule | D_J (kc/sec) | |
	Obs.	Calc.[a] Kratzer's approx.[b]
CH_3F	32.5	67.0
CH_3Cl	26.4^c	19.5
CH_3Br	11.1^c	10.4
CH_3I	7.95^c	6.6
CH_3CCH	3.12	3.24

[a] The values of the stretching frequencies used for the calculations were taken from G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 315 and 338.
[b] See reference 3.
[c] J. W. Simmons and W. E. Anderson, Phys. Rev. 80, 338 (1950).

the component of momentum perpendicular to K tend to increase β and hence should decrease I_B. Since the opposite effect is observed, it is apparent that the change in bond lengths must also be considered. The surprising implication is that the stretching of the CH bonds more than compensates for the bond-bending effects. Simmons and Anderson[8] suggest that the unexpected sign of D_{JK} in the methyl halides indicates considerable lengthening of the CH bonds.

In POF_3 the center of gravity if between the plane of the F atoms and the P. In this case, the increase in K tends to increase β as before, but now the associated decrease in N lowers β, and the two effects on I_B are opposed. D_{JK} is small and positive. Hence, the two effects are almost balanced. In PSF_3 the center of gravity is near the central atom P, and again D_{JK} is small and positive.

No very satisfactory theory is available for calculating the stretching constant D_J from the vibrational frequencies of the symmetric-top molecule, as can be done for diatomic or linear triatomic molecules. It was shown by Simmons and Anderson that the D_J's calculated by Slawsky and Dennison for the methyl chloride, bromide, and iodide differ by a factor of about ten from the observed value, although they have the correct sign. The agreement in the value for methyl fluoride is much better but still differs by a factor of about 2.

We have applied the simple Kratzer formula (2) to the methyl halides with ω taken as the normal vibrational frequency ω_1 for which the nuclear displacement most nearly corresponds to those of centrifugal stretching for end-over-end motion. This is the mode which represents essentially the stretching of the C—Hal bond. The results are shown in Table III. The agreement with observation is fairly good except for the fluoride. Also included in this table is CH_3CCH, with ω taken as $\omega_5 = 926$ cm^{-1}, the normal frequency which most nearly approximates the motion for end-over-end centrifugal stretching.