V. MICROWAVE SPECTROSCOPY

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A. MICROWAVE SPECTRUM OF OXYGEN

The analysis of the spectrum of the oxygen molecule in field-free space and in a magnetic field is essentially complete and is being prepared for journal publication. The important new results are given in the following abstract:

A rather complete solution for the fine-structure problem of O_2 is given in the framework of the Born-Oppenheimer approximation. The reduction of the effect of the electronic state on the fine structure to an effective Hamiltonian, involving only the resultant electronic spin in addition to rotational and vibrational quantum numbers, is demonstrated. In this Hamiltonian, the parameters λ and μ measure the effective coupling of the spin to the figure axis and the rotational angular momentum, respectively. The contributions to these parameters which are diagonal in electronic quantum numbers, namely λ' and μ', are evaluated by using Meckler's expression for the electronic wave function as a superposition of configurations. In the calculation of λ', exchange effects, inclusion of ionic states, and the rapid change of configuration-mixing coefficients with internuclear distance R, play leading roles; μ' is relatively insensitive to details. It turns out that λ' gives almost all of λ, whereas μ' gives only 4 percent of μ. The second-order contributions of spin-orbit coupling to λ and μ and the electronic contribution to the effective moment of inertia are related to each other and to certain magnetic effects to be given later. This interrelation enables them all to be essentially evaluated experimentally.

The effective Hamiltonian is diagonalized through terms in $(B/\hbar\omega)^2$ and the eigenvalues compared with the experimental 5-mm spectra. The fitting establishes the constants

$$\mu = 252.67 \pm 0.05 \text{ Mc/sec} \qquad \lambda_1 = \left[R\, d\lambda/dR\right]_e = 16,896 \pm 150 \text{ Mc/sec}$$

$$\lambda_e = 59,386 \pm 20 \text{ Mc/sec} \qquad \lambda_2 = \left[(R^2/2)\, d^2\lambda/dR^2\right]_e = (5 \pm 2)\times 10^4 \text{ Mc/sec}$$

$$\lambda_{\text{eff}}(v=0) = 59,501.57 \pm 0.15 \text{ Mc/sec.}$$

The transformations which diagonalize the field-free Hamiltonian are given with respect to both Hund case (a) and case (b) bases. These transformations are applied to matrix elements of S_Z. The results are tabulated and applied to calculate the exact intensity factors for spectral lines. This calculation shows slight deviations from the usual case (b) results for allowed lines and predicts quite sizeable intensities for the "forbidden" ΔK = 2 lines.

The dominant interaction of O_2 with a magnetic field is, of course, through the electronic spin magnetic moment. However, a precise comparison with experiment of the results of calculating the magnetic spectrum, assuming only this interaction, shows a systematic discrepancy. This discrepancy is removed by introducing two corrections. The larger (approximately 0.1 percent or 7 gauss) is a correction for the second-order electronic orbital moment coupled in by the spin-orbit energy. Its magnitude is fixed by the second-order term μ'' in the spin-rotation coupling constant, which is found by subtracting the calculated μ' from the experimental value for μ. The smaller (approximately 1 gauss) is a correction for the rotation-induced magnetic moment of the molecule. Since the dependence of this contribution on quantum numbers is quite unique the coefficient is determined by fitting the magnetic spectrum.

These corrections have been made on 15 X-band lines. The mean residual error is ± 0.3 gauss or ± 0.5 Mc/sec. This excellent agreement confirms the anomalous electronic moment to 6 parts in 10^5 and also confirms the validity of this theory of the Zeeman effect.

A new result is the rotational magnetic moment of (-0.25 ± 0.05) nuclear magnetons per quantum of rotation. Knowledge of this moment allows that determination of the electronic contribution to the effective moment of inertia. Making this correction of 65 ppm and using the latest fitting of the universal atomic constants, the equilibrium internuclear distance is recomputed to be $R_e = 1.20741 \pm 0.00002$ A. If we use the rotational magnetic moment, we can also deduce that the magnitude of λ'', the second-order contribution to the coupling constant λ, is 465 ± 50 Mc/sec, or less than 1 percent of λ. This shows that our calculation of the diagonal term λ' was qualitatively correct, but quantitatively deficient. It is proposed that calculation of λ' serves as an additional criterion for the quality of an electronic wave function for O_2.

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B. SPECTRUM OF OCS

The high-sensitivity spectroscope has been used to search for the $J = 1 \rightarrow J = 2$ transition of the state $v_3 = 1$ of OCS. The line was, according to a calculation of Townes (1), predicted at 24,115 Mc/sec. This region has been studied and several lines of higher vibrational states of OCS_{33} have been identified. The rotation-vibration interaction constants α_1 and α_2 and the l-doubling coefficient q have been determined.

The $v_3 = 1$ line of OCS_{32}, however, was found only after infrared measurements of Thompson (2) had predicted it to be at 24,179.8 Mc/sec; it turned out that it was hidden by the nearby $v_1 = 2$ line whose intensity is similar to the intensity of the $v_3 = 1$ line in magnitude and temperature dependence. The equilibrium reciprocal moment of inertia, α_3 and B_e, has been calculated. We had to use α_3 (unperturbed), which was obtained by taking into account the strong Fermi interaction with the $v_2 = 4$ state. The frequency of the $v_2 = 4$ line is the one measured by Thompson (2), and the accuracy of this measurement at present limits the precision of the determination of B_e. A microwave measurement of the $v_2 = 4$ line is planned.

The rotational and the electronic states also have a small mutual interaction (3), which was taken into account as an electronic correction to the B_e. An attempt will be made to make measurements analogous to the present ones on OCS_{34}, which should provide better values for the equilibrium bond distances and an estimate of the anharmonic force constants in OCS. New lines in the OCS spectrum and the resulting molecular constants are given in the following tables, along with the possible interfering absorptions.

Table 1

OCS_{32}

Vibrational State	Frequency	Intensity
$v_3 = 1$	24,180.47 ± 0.2 Mc/sec	2.5×10^{-9}

Derived Constants

α_3	36.36 ± 0.05 Mc/sec
α_3(unperturbed)	43.95 ± 0.3 Mc/sec
Electronic correction	0.08 Mc/sec
B_e	6103.25 ± 0.15 Mc/sec
I_e	$137.483 \pm 0.01 \times 10^{-40}$ gcm^2

Impurities

23,870 Mc/sec	NH_3
24,039 Mc/sec	O_2S
24,083 Mc/sec	O_2S
24,139 Mc/sec	NH_3

Table 2

Spectrum of OCS_{33}

The following lines have been identified in OCS, containing OCS_{33} in natural abundance:

Vibrational State	F_i F_f	Frequency (Mc/sec)	Intensity (cm^{-1})
$v_1 = 1$	1/2 1/2 3/2 5/2 5/2 7/2	23,947.4	5×10^{-9}
$v_2 = 1_1$	5/2 7/2	24,051.2	1.3×10^{-8}
	5/2 5/2 3/2 3/2	24,046.9	6×10^{-9}
	3/2 5/2	24,044.0	6×10^{-9}
$v_1 = 1_2$	5/2 7/2	24,075.7	1.3×10^{-8}
	5/2 5/2 3/2 3/2	24,072.0	6×10^{-9}
	3/2 5/2	24,069.2	6×10^{-9}
$v_2 = 2$	1/2 1/2 3/2 5/2 5/2 7/2	24,092.4	2×10^{-9}

$\alpha_1 = 18.2$ Mc/sec

$\alpha_2 = -10.52$ Mc/sec

$q = 6.3$ Mc/sec

M. Peter

References

1. C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. 74, 1113 (1948).
2. H. W. Thompson, St. John's College, Oxford (to be published).
3. M. W. P. Strandberg, Microwave spectroscopy (John Wiley, New York, 1953) p. 62.

C. EFFECT OF HINDERED INTERNAL ROTATION ON OVER-ALL ROTATIONS OF SYMMETRIC ROTORS: METHYL SILANE

An approximate theory of the interactions of internal rotation with over-all rotations of symmetric rotors has been worked out. This treatment considers the interdependence of hindered internal rotation and vibrations and their effect upon the rotational energy levels. The resulting expression for the frequencies of $\Delta K = 0$, $\Delta J = 1$ transitions is

$$\nu = 2J\left[B_v + F_v\,(m|1 - \cos 3\theta|m) + G_v\,(m|\vec{\Pi}_z^2|m) + L_v K\,(m|\vec{\Pi}_z|m)\right]$$

where B_v, F_v, G_v, and L_v are constants independent of the rotational quantum numbers, m represents the basis that diagonalizes the Hamiltonian corresponding to pure internal rotation, $\vec{\Pi}_z$ is the internal angular momentum operator, and θ is the angle of internal rotation. Procedures for evaluating $(m|1 - \cos 3\theta|m)$ and $(m|\vec{\Pi}_z^n|m)$ in terms of a parameter α have been described.

This theory has been applied to the $J = 0 \rightarrow 1$ transitions of methyl silane. The parameters B_v, F_v, G_v, and α were obtained empirically and were then used to calculate frequencies. The agreement between observed and calculated values was quite good. Furthermore, the anomalous ordering of the lines observed by Lide and Coles (1) is explained by these calculations. Assuming a cosine potential, the barrier height V_o is proportional to the parameter α. The value of V_o was set at 558 $\text{cm}^{-1} \pm 17\ \text{cm}^{-1}$. The constant B_v, which is the rotational constant in the ground torsional state for the limiting case of $V_o = 0$, is 10,985.79 Mc/sec and 9636.50 Mc/sec for CH_3SiH_3 and CH_3SiD_3, respectively.

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References

1. D. R. Lide and D. K. Coles, Phys. Rev. 80, 911 (1950).

D. HDO AND D_2O ROTATION LINES

Measurement and tentative identification of several new lines of HDO and D_2O in the millimeter wave region were recently reported by the Duke Microwave Laboratory (1). Using the theory of the Zeeman effect in asymmetric rotor molecules, we computed the effective g-factors corresponding to the assigned transitions. The computations showed good agreement with the observed data of the Duke report for the $\Delta J = 0$ transitions of HDO but not of D_2O. The difference between the observed and computed data for D_2O seems to indicate that the wrong transitions were assigned. The following table presents the compared data.

	Transition	g-factor(observed)	g-factor(computed)
HDO	$1_{1,1} - 1_{1,0}$	0.517	0.524
HDO	$6_{3,4} - 6_{3,3}$	0.482	0.462
HDO	$4_{2,3} - 4_{2,3}$	-	0.460
D_2O	$3_{3,0} - 4_{2,3}$	0.356	0.322 ± 0.012
D_2O	$5_{3,3} - 4_{4,0}$	0.350	0.319 ± 0.010

In view of the difference between observed and computed g-factors for the D_2O lines, a more accurate determination of the g-factors was not considered necessary.

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References

1. Report No. 3, August 1 - November 1, 1953, Duke Microwave Laboratory, Duke University.