

V. MICROWAVE SPECTROSCOPY

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A. ZEEMAN EFFECT

The study of the interaction of a rotation-induced molecular magnetic moment with an external magnetic field is being studied for the case of an asymmetric $^1\Sigma$ -molecule. The molecules chosen for study are the isotopic modifications of water: H_2O , HDO , and D_2O .

It has been shown by Eshbach and Strandberg (1) that the matrix elements $\langle m_z \rangle$ for a general $^1\Sigma$ -molecule can be written in terms of a gyromagnetic tensor g_{ij} . After application of the Wang symmetrizing transformation, the only terms of importance in the first order are the diagonal terms $(J, K, M | m_z | J, K, M)$ and the terms $(J, K, M | m_z | J, K+2, M)$. The only elements of the gyromagnetic tensor g_{ij} which enter in the first-order perturbation are the diagonal elements g_{kk} , corresponding to rotations about the principal inertial axes in the molecule. Thus, the first-order perturbation energy can be expressed in the form $\Delta E = -\mu_0 g_{\text{eff}} M H$ where μ_0 is the nuclear magneton, M is the magnetic quantum number, and g_{eff} , the splitting factor, is a function of the rotational level and the diagonal elements of the gyromagnetic tensor.

Measurements of the Zeeman effect have been made on the $5_{23}-6_{16}$ line of H_2O , and the $2_{21}-2_{20}$, $7_{44}-7_{43}$, and $5_{33}-5_{32}$ lines of HDO , using a slow-sweep, high-resolution, microwave spectrograph, with both the π - and σ -transitions being observed. The splitting factors of the Q-branch transitions in HDO are nearly the same for both levels involved; and since the components form two symmetrical, though unresolved, systems of lines, the measured value is an arithmetic average of the g factors of the two levels. Furthermore, in the case of the 5-5 HDO line, measurement of the π -components demonstrated that these g_{eff} 's differ by less than 0.001.

In the case of the $5_{23}-6_{16}$ H_2O line, the σ -components are arranged in two asymmetrical patterns (though symmetrical about the center frequency). Since these patterns are unresolved, no precise information is obtained until the separations of the individual components are known. These separations were determined by means of a simultaneous Stark-Zeeman effect; an electric field was used to remove partially the M-degeneracy, so that the magnetic field was sufficient to resolve the $M = \pm 5$ components. By utilizing this information, it was possible to obtain a good fit of expected intensity pattern with experimentally observed data for both π - and σ -components, and hence the splitting factors for both rotational levels were determined.

Since g_{ij} is a tensor quantity, the g factors for all isotopic modifications of a molecule can be expressed in terms of the gyromagnetic tensor of any one. Hence, in all,

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only three parameters are involved. The experimental data so far have yielded average g values for two pairs of rotational levels and explicit g values for four levels, giving a total of six equations in three unknowns. A preliminary fit has been obtained which is well within experimental accuracy in all cases.

The absorption line at 26,880 Mc/sec observed by McAfee (2) and tentatively ascribed to D_2O has been examined and its splitting factor measured. No appreciable line broadening was observed when the guide was in the π -position; hence, the difference in g_{eff} 's for the two levels is small. For the same reason, only two σ -components were observed, for which the splitting factor was measured. The value of the splitting factor is not possible for D_2O but is of the proper magnitude for HDO. The only possible conclusion is that this absorption line is due to HDO.

Work is progressing on the remaining known absorption lines of the water molecule.

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References

1. J. R. Eshbach, M. W. P. Strandberg: Phys. Rev. 85, 24, 1952
2. K. B. McAfee: Doctoral Thesis, Harvard University, 1949

B. HIGH-TEMPERATURE MICROWAVE SPECTROSCOPY

A high-temperature waveguide system has been assembled. The waveguide is coaxial and of stainless steel. The center conductor also serves as the Stark electrode for the Stark-modulation system. A furnace has been built, using standard tube furnace heaters controlled by thermocouples and relays. The sample is contained in a Vycor cell designed to fit in the coaxial guide. A high-temperature valve has been provided in the pumping lead, so that the pumping rate may be controlled.

The system was tested by observing the 8577-Mc/sec, 10,278-Mc/sec, and 22,307-Mc/sec lines of HDO at temperatures up to 550°C. KCl lines, expected at 7680 Mc/sec and 15,376 Mc/sec, and a line observed by others at 23,066 Mc/sec were looked for but were not found.

P. A. Tate

C. WATER MOLECULE

A search of the absorption spectrum arising from the equilibrium mixture H_2O -HDO- D_2O has revealed two new lines at 10,920 Mc/sec and 10,947 Mc/sec. Work on the

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identification of these, and of the line at 26,880 Mc/sec, is proceeding.

Since P or R branch transitions appear to be involved, the energy calculations must be corrected for centrifugal distortion effects. Such effects are expected to be appreciable for these light molecules. An examination of the theory applicable for this type of molecule is being carried out.

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