Spectrum of DBr in the One-Millimeter Wave Region*

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From measurements on the 0→1 transition of DBr at 1.18-mm wavelength the following information has been obtained:

	DBr^{79}	DBr^{81}
eQq(Br)	533±3 Mc/sec	455±3 Mc/sec
B_0	127 358.2±0.3 Mc/sec	127 280.0±0.3 Mc/sec
B_e	1286_{15} Mc/sec	1285_{38} Mc/sec
r_0	1.42136_2A	1.42136_2A
r_e	1.414_{40}A	1.414_{39}A

Values of α obtained from infrared spectroscopy by Keller and Nielsen were employed in calculating the equilibrium values.

WITH the new mm-wave methods already described,[1] the $J=0\rightarrow1$ rotational transitions of DBr^{79} and DBr^{81} have been measured at 1.18-millimeter wavelength. Both Br^{79} and Br^{81} have a nuclear spin of $\frac{3}{2}$, and the Br nuclear quadrupole interactions split the transitions into triplet components having relative intensities of 1, 2, and 3. The lines were easily seen and measured on the cathode-ray scope with an amplifier of 6-kc/sec band width (see Fig. 1).

Table I gives the observed and calculated frequencies and Table II the molecular constants derived from them. We also employed the auxiliary constants, $D=2.8$, 2.8 Mc/sec and $\alpha=1257$, 1258 Mc/sec for DBr^{79} and DBr^{81}, respectively, taken from the infrared data of Keller and Nielsen.[2] No observable difference was found between the r_0's for DBr^{79} and DBr^{81}. The equilibrium values are limited to four-place accuracy by the infrared α values employed. Because of the small effects of centrifugal stretching on the 0→1 transition, the infrared D value does not limit the accuracy of B_0. The B values of Keller and Nielsen are in complete agreement with ours to the four significant figures which they quote.

The Br nuclear coupling, eQq, with the coupling per unbalanced p electron from atomic beam measurements,[3] yields the number of unbalanced p electrons of Br in DBr as

$$U_p=(eQq)_{\text{mol}}/2(eQq)_{\text{atom}}=0.69.$$

With hybridization and other small effects neglected, a bond ionic character of 31 percent is indicated. This U_p value is in good agreement with that of 0.65 predicted from the nuclear coupling-electronegativity relation,[4] $U_p=1-|x_A-x_B|/2$.

Deuterium bromide has the smallest moment of inertia of any molecule so far measured with microwave electronic methods. It should prove worthwhile for optical spectroscopists to measure the wavelength separation of its higher J transitions very precisely in order to obtain a check on the velocity of light. Rank,

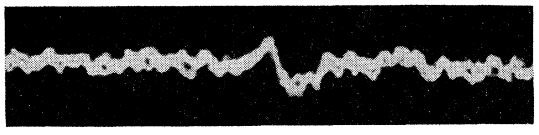

FIG. 1. Cathode-ray trace of the $F=\frac{3}{2}\rightarrow\frac{5}{2}$, $J=0\rightarrow1$, line of DBr^{81} at 1.18-mm wavelength.

TABLE I. $J=0\rightarrow1$ transitions of DBr^{79} and DBr^{81}.

$F\rightarrow F'$	Frequency in Mc/sec Calculated[a]	Observed
	DBr^{79}	
$\frac{3}{2}\rightarrow\frac{1}{2}$	254 572.0	254 572.2±0.5
$\frac{3}{2}\rightarrow\frac{3}{2}$	254 678.5	254 678.6±0.5
$\frac{3}{2}\rightarrow\frac{5}{2}$	254 811.8	254 812.9±1.0
	DBr^{81}	
$\frac{3}{2}\rightarrow\frac{1}{2}$	254 437.7	254 439.4±1.5
$\frac{3}{2}\rightarrow\frac{3}{2}$	254 526.8	254 526.7±0.5
$\frac{3}{2}\rightarrow\frac{5}{2}$	254 637.9	254 638.0±0.5

[a] Calculated with ν_0's and eQq's given in Table II.

TABLE II. Characteristic constants of deuterium bromide.[a]

	DBr^{79}	DBr^{81}
eQq(Br)	533±3 Mc/sec	455±3 Mc/sec
$\nu_0(0\rightarrow1)$[b]	254 705.2±0.5 Mc/sec	254 548.9±0.5 Mc/sec
B_0	127 358.2±0.3 Mc/sec	127 280.0±0.3 Mc/sec
B_e	1286_{15} Mc/sec	1285_{38} Mc/sec
r_0	1.42136_2A	1.42136_2A
r_e	1.414_{40}A	1.414_{39}A

[a] Atomic masses employed are those tabulated in reference 4.
[b] Rotational frequency corrected for nuclear quadrupole splitting.

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[2] F. L. Keller and A. H. Nielsen, Phys. Rev. **91**, 235 (1953).
[3] J. G. King and V. Jaccarino, Phys. Rev. **91**, 209 (1953).
[4] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 284.

Ruth, and Vander Sluis[5] have attempted to check the velocity of light by comparing microwave and optical constants of HCN; but the results do not agree well with the accurate, recent values[6] from other sources. Better results might be obtained with DBr. The separations of the rotational lines of DBr (in a sample with one Br isotope concentrated) are three times those of HCN. Effects of the nuclear hyperfine structure are easily calculable with the known coupling constants, and for relatively high J values they can be neglected entirely. There is hope that DCl (first rotational line near 0.9 mm) can be reached with the present mm-wave techniques. If so, it would provide a still more desirable link between optical and radiofrequency measurements.

We wish to thank Dr. Albert Jache for preparing the sample of DBr.

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Theory of Fine Structure Pressure Broadening of Spectral Lines*

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The difference of pressure broadenings and shifts of the doublet components of the principal series lines of alkalis is treated in an approximate manner. Applying the perturbation method and the Franck-Condon principle to the Michels, deBoer, and Bijl model of compressed atoms in the doublet P states, it is shown that the doublet separation becomes smaller with increasing pressure at rather low pressure. Consequently, the shift of the $^2P_{\frac{3}{2}}$ must be smaller than that of the $^2P_{\frac{1}{2}}$ component of the principal series. The attractive forces are recalculated with the inclusion of the quadrupole moment for the $^2P_{\frac{3}{2}}$ state. This consideration requires the splitting of the state according to the magnetic quantum numbers so that the $^2P_{\frac{3}{2}}$ component will be 1.12 times larger in half-width than $^2P_{\frac{1}{2}}$ in the approximation of the collision theory. This result is in good agreement with experimental values.

I. INTRODUCTION

NONE of the theoretical work on the theory of the pressure broadening of spectral lines has served to explain the well-established experimental fact[1] that under the influence of a foreign gas at high pressure the shifts and half-widths of the different components of a multiplet are different, i.e., the so-called fine structure pressure effect, although in the case of self-broadening good theoretical work has been reported.[2] The reason may be to the lack of knowledge of the intermolecular forces, repulsive and attractive, including excited states.

In this article alkali atoms are treated as perturbed by rare gases in a rather approximate manner. Without the formation of chemical bonds in this case, rare gases serve to compress the electron clouds of radiating or absorbing atoms. The ambiguity of the separation of two molecules coming from the thermal motion of molecules will be disregarded so that the Hamiltonian concerned is a definite function of separation.

II. OVERLAP EFFECT

A. Perturbation Method Applied to a Compressed Atom

The Michels, deBoer, and Bijl model[3] of a compressed molecule may be used for the repulsive forces. The Franck-Condon principle is assumed in the absorption process starting from a spherically symmetric ground state. Thus the model is comparable to the replacement of the compressing molecules by a spherical infinite potential wall, such that

$$V(r)=0 \quad \text{for } 0\leq r<r_0,$$
$$=\infty \quad \text{for } r_0\leq r. \tag{2.1}$$

Assuming that the energy change of the atomic state is small in comparison with the energy level separations, the perturbation method is applied. Using the Dirac δ function,[4] the perturbation energy may be written as follows:

$$V(r)=\lim_{\Delta r\to 0}\sum_{k=0}^{\infty}\delta(r-(r_0+k\Delta r)). \tag{2.2}$$

The expression (2.2) may be taken as the definition of our potential wall if the discontinuity of (2.1) at the boundary is neglected. Denoting the wave function of the unperturbed state n of the absorbing atom without relativistic correction by ψ_n, the new energy and new normalized wave function are

$$W=W_n+(n|V|n)+\sum_i{}'\frac{(n|V|j)(j|V|n)}{W_n-W_j}, \tag{2.3}$$

$$\psi=\psi_n+\sum_i{}'\frac{(j|V|n)}{W_n-W_j}\psi_j. \tag{2.4}$$

The primed summation implies the exclusion of the

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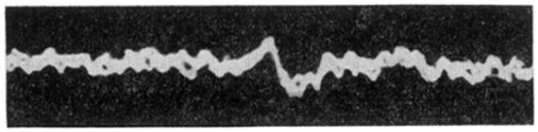

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