

BAND SPECTRA AND THE STRUCTURE OF MOLECULES.

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By the application of the quantum theory to the study of their characteristic band or fluted spectra, we have gleaned much valuable information as to the size, the stability, and the general behavior of certain diatomic molecules. According to our current ideas the molecule is considered to be a rotator, an approximately harmonic oscillator, and to have an electronic structure much the same as that of the atom. Both the rotational and vibrational energy are *quantized*; that is, they exist only as integral or half-integral multiples of fixed minimum values. And according to the Bohr postulate, when the molecule changes from one stationary state to another, the difference between the values of the energy in the two states is either radiated or absorbed as the case may be. Space does not permit here a discussion of the details of this theory⁽¹⁾ and so we must content ourselves with a mere enumeration of the resulting formulas which contain the molecular constants in which we are interested. Furthermore, we shall limit ourselves to electronic band spectra, which lie in the visible and ultra violet regions.

In the emission of the frequencies constituting the band systems in the visible region there is coupled with the radiated energy due to rotational and vibrational changes in the molecule that due to the falling in of a valence electron from an orbit of larger energy to one of smaller energy. The frequency ν of any band line is then given by:

$$\nu = \nu_e + \nu_n + \frac{\text{(Change in rotational energy)}}{h} \quad (1)$$

where ν_e is the electronic part of the frequency, and ν_n is that part of the frequency due to the change in the

¹The reader is referred for details to Chap. 9 of A. Sommerfeld's "Atombau und Spektrallinien" (4th Edition) and to the Bulletin of the National Research Council on Band Spectra scheduled to appear soon. (1926.)

vibrational state of the molecule. The ν_n is given by:

$$\nu_n = n' \omega_0' (1 - x' n') - n'' \omega_0'' (1 - x'' n'') \quad (2)$$

where the primes and double primes refer to the initial and final states of the molecule respectively. Here n is the vibrational quantum number, ω_0 is the vibrational frequency for infinitesimal amplitude of the oscillator, and x is a small constant introduced because the binding is in reality anharmonic. According to Kramers and Pauli⁽²⁾ the formula for the energy contribution due to molecular rotation or precession is

$$F_m = Bm^2 + Dm^4 + \dots = B(\sqrt{j^2 - \sigma^2} \pm \epsilon)^2 + D(\sqrt{j^2 - \sigma^2} \pm \epsilon)^4 + \dots \quad (3)$$

where

$$B = \frac{h^2}{8\pi^2 I} \quad \left(\begin{array}{l} h = \text{Planck's constant} \\ I = \text{moment of inertia of molecule} \end{array} \right)$$

m = nuclear angular momentum vector
 j = resultant " " "
 σ = component of the vector electronic angular momentum along the figure axis of the molecule
 ϵ = " of the vector electronic angular momentum perpendicular to the figure axis (parallel to m)

Changes in j are limited by the correspondence principle to changes ± 1 , which give the P and R branches of the bands, and to 0 which gives the Q branches. We cannot find this rotational energy function directly from the band spectrum analysis, but only the values

$$\Delta F(j) = F(j+1) - F(j) = R(m) - Q(m+1) \dots \text{final state} \\ = R(m) - Q(m) \dots \text{initial state, etc.}^3$$

From equation (3) we see that

$$\Delta F(j) = 2B(j + \frac{1}{2} \pm \epsilon) \pm \frac{B\epsilon\sigma^2}{j(j+1)} + \dots \quad (4)$$

and finally, Kemble has shown⁽⁴⁾ that the vibrational and rotational coefficients are related by the formula

$$\omega_0 = \sqrt{\frac{-4B^3}{D}} \quad (5)$$

² Zeit. für Physik, 13, 351, 1923.

³ For a more detailed account, see R. Mulliken, Proc. Nat. Acad. of Sciences, 12, 144, 1926.

⁴ E. C. Kemble, Jrl. Opt. Soc. Amer. 12, 1, 1926.

indicating a mutual action between rotation and vibration.

Let us now proceed to apply these relations to the measurements of particular band spectra, with a view to determining facts about the structure of the emitting molecules. Table 1 gives the values of the distance between the two nuclei in a number of diatomic hydrides of the elements in the first two rows of the periodic table. These distances have been computed from the moments of inertia given by the values of B as found from the

TABLE 1.
Internuclear Distances of Diatomic Hydride Molecules From Band
Spectra Measurements.
Angstrom Units.

LiH	BeH	BH	CH	NH	OH	HF
NaH	MgH	AlH	SiH	PH	HS	CLH
1.80	1.74	1.66	1.27
	CaH					BrH
	2.00					1.41

ΔF values for the bands of each of these molecules. It is to be noted that these carriers are not always stable chemical compounds. Both the absolute values of these internuclear distances and their change as you go along the row are interesting and significant.

Table II contains the results of the application of equation (4) to the MgH and CH bands. It is seen that for one thing $\epsilon=1/2$ in both cases in both initial and final states, while there is a σ in the initial state for MgH and in the final state for CH. In other words, there is a contribution from the electrons to the resultant angular momentum of the molecule. And it is to be concluded that the electron transition is from a P state to an S state in MgH, but the reverse for CH.

Applying equation (2) to the "zero-points" (the v for $m=0$ in the Q branch) of the various bands in the MgH system and assuming half integral values for n (evidence from the magnitude of the isotope effect—see below) we obtain

$$v = \left. \begin{array}{l} 19217 \\ 19224 \end{array} \right\} + (1603.5n' - 34.75n'^2) - (1493.5n'' - 31.25n''^2)$$

We note that the vibration frequency for the initial state is larger than that for the final state. And from the

TABLE II.
Rotational Energy Data.

MgH λ 5211 band			CH λ 4300 band		
j	$\Delta F'(j)$	$\Delta F''(j)$	j	$\Delta F'(j)$	$\Delta F''(j)$
1	14.38	11.81	1	—	—
2	25.33	23.01	2	—	55.4
3	37.07	34.28	3	87.4	84.4
4	48.89	45.96	4	116.32	112.93
5	61.00	57.08	5	145.02	141.13
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$B^1 =$	6.00	$B'' = 5.65$	$e'' = 0.39 (=1/2)$	$e'' = 0.48$	$e'' = 0.48$
$e' =$	0.43 ($=1/2$)	$e'' = 0.47$	$\sigma'^2 = \text{small}$	$\sigma'^2 = +1.4$	$\sigma'^2 = +1.4$
$\sigma'^2 =$	1.25	$\sigma'^2 = 0.1$	$\therefore \sigma' = 0$	$\therefore \sigma' = 0$	$\therefore \sigma' = 1$
$\therefore \sigma' =$	1	$\sigma'' = 0$			
electron transition $P_1 \longrightarrow S$			electron transition $S \longrightarrow P$		
first lines					
$(j' \longrightarrow j'') :$	$(1 \longrightarrow 2)$	$(1 \longrightarrow 2)$			
	$(1 \longrightarrow 1)$	$(1 \longrightarrow 1)$			
	$(2 \longrightarrow 1)$	$(2 \longrightarrow 1)$			

values of B we conclude that the distance between the two nuclei is greater in the final state. Therefore it is to be inferred that the stability of the molecules is greater in the initial more excited state. Just the reverse is true for the CH molecule. From these values of ω_0 and r_0 we have a means of gauging the relative stabilities of various molecules. In this same connection it should be mentioned that in some cases^{5, 6} the branches in a band stop sharply at a certain rotational quantum number. The explanation of this phenomenon is that at this point the centrifugal force becomes as great as the attractive force between the nuclei, with the consequent "blowing up" of the molecule.

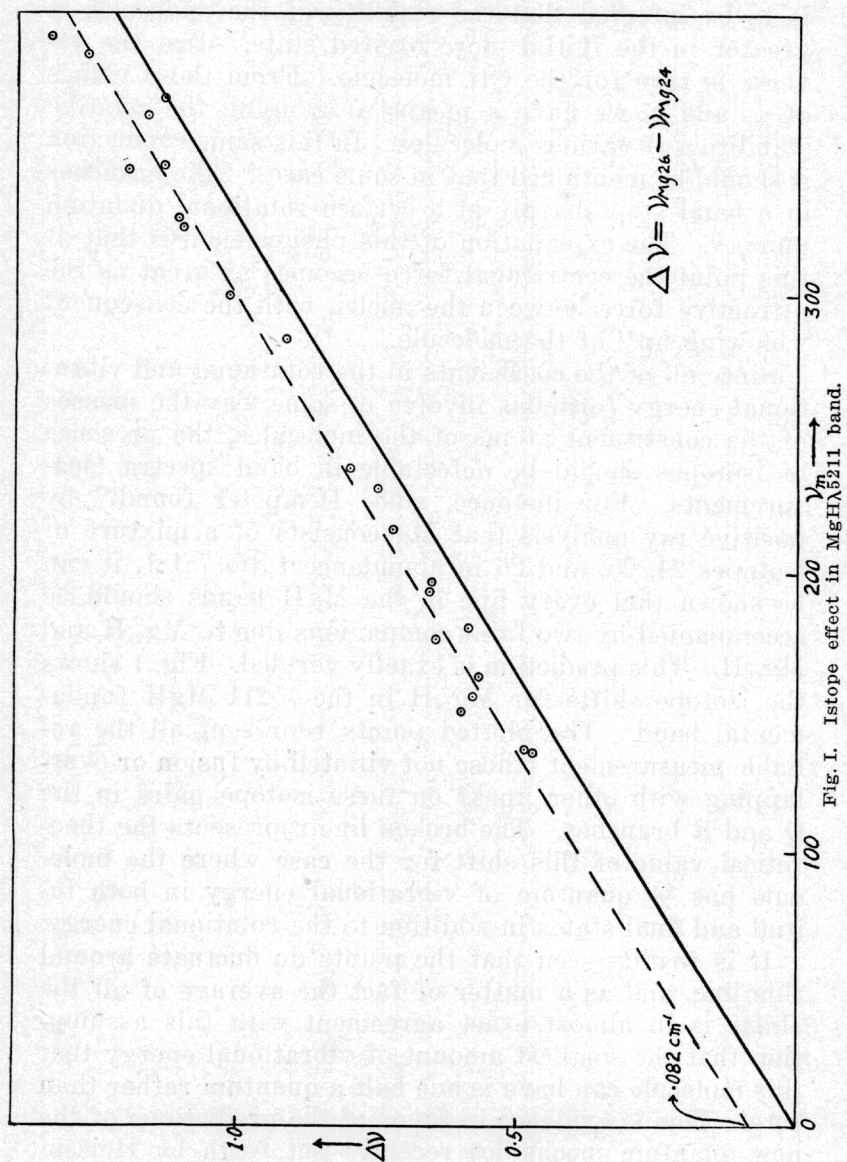
Since all of the coefficients in the rotational and vibrational energy formulas involve in some way the masses of the constituent atoms of the molecules, the presence of isotopes should be detectable in band spectra measurements. For instance, since Dempster found⁽⁷⁾ by positive ray analysis that Mg consists of a mixture of isotopes 24, 25, and 26 in abundance ratio 7:1:1, it can be shown that every line in the MgH bands should be accompanied by two faint companions due to Mg_{25}H and Mg_{26}H . This prediction is exactly verified. Fig. 1 shows the isotope shifts for Mg_{26}H in the $\lambda 5211$ MgH fundamental band. The plotted points represent all the reliable measurement (those not vitiated by fusion or overlapping with other lines) on these isotope pairs in the Q and R branches. The broken line represents the theoretical value of this shift for the case where the molecule has $\frac{1}{2}$ quantum of vibrational energy in both initial and final states in addition to the rotational energy.

It is readily seen that the points do fluctuate around this line, and as a matter of fact the average of all the shifts is in almost exact agreement with this assumption that the smallest amount of vibrational energy that this molecule can have is one half a quantum rather than zero. This is evidence in favor of the predictions of the new quantum mechanics recently put forth by Heisenberg and Born. It is also possible that new isotopes may

⁵ R. S. Milliken, *Physical Review*, 25, 509, 1925.

⁶ Eriksson and Hulthén, *Zeit. für Physik*, 34, 775, 1925.

⁷ A. J. Dempster, *Physical Review*, 18, 415, 1921.

Fig. I. Isotope effect in MgH_{5211} band.

be detected by band spectra measurements. We are at present trying to discover isotopes of sulfur by this means. The mass spectrograph has failed to reveal any isotopes of S, but there are reasons for believing that such do exist.

As a verification of the validity of equation (5) it is found that in the case of the MgH bands for instance, the values of ω_0 given in the empirical equation for the "zero-points" above are obtained to within the experimental error of the measurements when the rotation coefficients B and D are inserted. Other verifications of this relation have also been made recently.

From these few examples of the many which might be cited, one can conclude that in the application of the quantum mechanics to the fine structure of band spectra, we have a powerful method of obtaining information about the structure and behavior of certain molecules. And the work has scarcely been begun. It is to be predicted then, that many interesting results will follow from these investigations in the near future.