A SUGGESTED NEW INTERPRETATION OF THE STRUCTURE OF BAND-SPECTRA.

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1. Introduction.*

IT is well known that in general an electronic band of the simplest type due either to the emission or absorption by a diatomic molecule can be regarded as consisting of a series of lines all of which can be represented, to a first approximation, by a formula of the type $\nu = \nu_0 + BM + CM^2$, where M assumes in succession the values ± 1, ± 2, ± 3, ... etc. In the above formula $C = \dfrac{h}{8\pi^2 CI'} - \dfrac{h}{8\pi^2 CI''}$ where I' and I'' refer to the two electronic states causing the band in question. It is easily shown that such a formula gives rise to two different types of bands according as the constant C is positive (I' < I'') or negative (I' > I''). In the former case the band appears *degraded towards the violet* whereas in the latter it appears *degraded towards the red*. These general characters persist even in complicated types of bands and imply that absorption of energy by molecules can in some cases (*band degraded towards the violet*) result in a diminution of the equilibrium distance between the nuclei whereas in some others (*band degraded towards the red*) it can result in an increase. Closely connected with the change in the equilibrium nuclear distance of a molecule on being raised to a higher electronic state is the well-known fact that the binding strength between the two nuclei

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* The notation employed in this paper is as follows:—

h	= Planck's constant.
c	= Velocity of light.
U	= Potential energy of the molecule.
μ	= Reduced mass; $x_e w_e$ = Anharmonic constant.
ν_e	= Spacing of the two electronic levels involved.
μ_1, μ_2	= Electric moments induced in each of the two atoms.
I', I''	= Moments of inertia in the upper and lower electronic states respectively.
r_e', r_e''	= Equilibrium distances between the nuclei for the upper and lower electronic states respectively.
w_e', w_e''	= Vibration frequencies for the upper and lower electronic states respectively.

and with it the vibrational frequency also undergo marked changes. As is well known there is a striking relationship between the two phenomena ; if on being raised to a higher electronic state, the equilibrium distance between the nuclei of a molecule increases, the vibrational frequency is diminished, whereas if the equilibrium distance between the nuclei diminishes, the vibrational frequency is increased. These statements, to which there are only a few minor exceptions, are solely based on experimental facts and are to a large extent empirical. The existing ideas relating to the mechanism of light absorption by molecules provide no clue whatsoever as to either the direction or magnitude of the changes in the nuclear distances and the vibration frequencies to be expected when a molecule absorbs energy and passes over into a higher electronic state. It is the purpose of the present paper to suggest a new line of thought in this direction, which it is hoped will form the basis of a satisfactory interpretation of the experimental facts.

2. *The Potential Energy Function and Molecular Properties.*

Several equations[1,2,3] have been proposed which express the potential energy due to nuclear motion of a diatomic molecule as a function of the nuclear distance. These equations which are of fundamental significance in connection with problems relating to molecule formation involve constants such as the equilibrium nuclear distance, the vibration frequency and the anharmonic correction characterising the molecule in each one of its electronic states. It is possible to evaluate the potential energy function for the different electronic states of a molecule if the constants that enter into the equations are known and these constants (r_e, w_e and $x_e w_e$) for the different states of the molecule can at present be determined only experimentally if the band spectrum is completely analysed. Further, a theoretical computation and hence a prediction of the molecular properties in the different electronic states should also be possible. Mathematical difficulties have however prevented such calculations being successfully made except for two very simple cases of diatomic molecules, *viz.*, the hydrogen molecular ion and the hydrogen molecule, the potential energy curves for the various electronic states of which have been computed by Burrau, Morse and Stueckelberg, Heitler and London and others using different wave mechanical methods. No calculations of this type however are available for more complex systems.

From a study of the data available in a large number of cases, certain empirical rules have however been given which endeavour to correlate the

1 Fues, *Ann. der Phys.*, 1926, **80**, 367.

2 Morse, *Phys. Rev.*, 1929, **34**, 57.

3 Rydberg, *Z. f. Phys.*, 1931, **73**, 376.

different equilibrium nuclear distances and the vibration frequencies of a molecule in its various electronic states. Amongst these mention may be made here of the following due respectively to Mecke[4], Morse[5] and Badger[6]. $w_e r_e^2$ =Constant .. (1) ; $w_e r_e^3$ =Constant .. (2) ; $k_0(r_e - d)^3$ =Constant .. (3) Equation (1) applies to the different electronic states of a given molecule, equation (2) applies to the different electronic states not only of a given molecule but also of a group of different molecules and equation (3) applies to all molecules with varying values for d.

3. Theory of Induced Electric Doublets.

We shall now proceed to consider the mechanism of light absorption by a diatomic molecule. It will be assumed that the light wave, in the first instance, only affects the motion of the extra nuclear electrons. From an analogy with the classical theory of optical polarisation, we may regard the atoms as centres of temporary electrical doublets formed under the influence of the electric field in the incident light wave and all changes in the nuclear constants which occur when the molecule passes over into a higher electronic state are regarded as consequential on the formation of such electric doublets. As has already been remarked, there are two types of transitions one in which the equilibrium nuclear distance increases and the other in which it diminishes by light absorption. Various possibilities arise regarding the direction of the axes of the two doublets in the molecules, both with reference to one another, and with reference to the nuclear axis. For simplicity[5] we make what appears to be the most reasonable assumption, namely, that they are parallel to each other and lie either along the nuclear axis or transverse to it. In the former case, the doublets attract each other with a force equal to $\dfrac{6\mu_1 \mu_2}{r^4}$

and in the latter case repel each other with a force equal to $\dfrac{3\mu_1 \mu_2}{r^4}$ where μ_1 and μ_2 are the electric moments acquired by each of the two atoms. μ_1 and μ_2 will be regarded as equal to one another if the two atoms are identical. Under these conditions a new equilibrium will be established and the equilibrium distance will be less or more than the initial value according as the doublets are of the former or of the latter type. If we take the initial potential energy curve to be represented by the well-known Morse function, the potential energy after formation of the above doublets may respectively be written in the two cases as

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4 Z. f. Phys., 1925, 32, 823.

5 Phys. Rev., 1929, 34, 57.

6 Jour. Chem. Phys.

$$U_r = -2De^{-a(r-r_e)} + De^{-2a(r-r_e)} - \frac{2\mu_1\mu_2}{r^3} \qquad .. \qquad .. \quad (1)$$

$$U_r = -2De^{-a(r-r_e)} + De^{-2a(r-r_e)} + \frac{\mu_1\mu_2}{r^3} \qquad .. \qquad .. \quad (2)$$

In these equations $D = \frac{w_e^2 hc}{4x_e w_e}$ and $a = \sqrt{8\pi^2 c\, x_e w_e\, \mu/h}$ and the various letters have the usual significance.* Equations (1) and (2) may be expanded and rewritten as (3) and (4) respectively after neglecting higher powers.

$$U_r = -D + a^2(r - r_e)^2 D \ldots - \frac{2\mu_1\mu_2}{r_e^3}\left[1 - \frac{3(r-r_e)}{r_e}\ldots\right] .. \quad (3)$$

$$U_r = -D + a^2(r - r_e)^2 D \ldots + \frac{\mu_1\mu_2}{r_e^3}\left[1 - \frac{3(r-r_e)}{r_e}\ldots\right] .. \quad (4)$$

In order to obtain the conditions for the new equilibrium positions, we differentiate (3) and (4) and equate the forces to zero and derive the following relations.

$$(r_e - r) = \frac{3\mu_1\mu_2}{r_e^4 a^2 D} \quad .. \quad (5) \qquad (r - r_e) = \frac{3\mu_1\mu_2}{2r_e^4 a^2 D} \qquad .. \quad (6)$$

In these equations $a^2 D = 2\pi^2 c^2 w_e^2 \mu$. Equations (5) and (6) correspond respectively to the cases of attraction and repulsion. In the former, the final equilibrium value of the nuclear distance is less than the initial value r_e and vice versa in the latter. The value of $\mu_1\mu_2$ pertaining to an electronic transition in any one molecule, which represents the strength of the induced doublets that have to be postulated to account for the observed changes in the equilibrium nuclear distances, may be obtained by substituting the actual changes derived from the absorption spectrum data in equations (5) and (6). The electric moments for a large number of molecules calculated in this manner are contained in the eleventh column of Tables I and II.

If $\frac{\mu_1\mu_2}{r^3}$ is small in comparison with D, the important terms in equations (3) and (4) may be rewritten as

$$-D - \frac{2\mu_1\mu_2}{r_e^3} - \frac{9\mu_1^2\mu_2^2}{r_e^8 a^2 D} + a^2\left(D + \frac{2\mu_1\mu_2}{r_e^3} + \frac{9\mu_1\mu_2}{r_e^8 a^2 D}\right)$$

$$\left(r - r_e + \frac{3\mu_1\mu_2}{r_e^4 a^2 D}\right)^2 \quad .. \quad (7)$$

$$-D + \frac{\mu_1\mu_2}{r_e^3} - \frac{9\mu_1^2\mu_2^2}{4r_e^8 a^2 D} + a^2\left(D - \frac{\mu_1\mu_2}{r_e^3} + \frac{9\mu_1\mu_2}{4r_e^8 a^2 D}\right)$$

$$\left(r - r_e - \frac{3\mu_1\mu_2}{2r_e^4 a^2 D}\right)^2 \quad .. \quad (8)$$

* See Condon and Morse, *Quantum Mechanics,* page 163.

TABLE I.

Bands Degraded to the Violet.

Molecule	ν_e cm.$^{-1}$	r_e'' A.U.	r_e' A.U.	w_e'' cm.$^{-1}$	$x_e'' w_e''$ cm.$^{-1}$	$D_e'' \times 10^{11}$	$D_e' \times 10^{11}$ (calc.)	w_e' (calc.)	w_e' (obs.)	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. Band spectra	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. polarisability
BeH	20031	1·340	1·330	2058·5	35·50	0·586	0·596	2076	2088	0·348	··
CaH	14432	2·020	1·990	1316·7	19·20	0·443	0·464	1347	1333	0·911	··
CN	25798	1·169	1·148	2068·8	13·18	1·594	1·730	2155	2164	1·029	2·245
MgH	19271	1·730	1·680	1493·5	31·25	0·350	0·388	1572	1604	0·971	··
C_2	19379	1·308	1·261	1641·6	11·67	1·133	1·337	1783	1793	1·472	2·122
N_2^+	25566	1·113	1·071	2206·8	16·04	1·490	1·819	2438	2418	1·463	2·076
B˙O	19344	1·348	1·301	1259·1	10·60	0·734	0·869	1370	1280	1·251	··
N_2	29653	1·201	1·140	1732·8	14·44	1·021	1·344	1988	2045	1·613	2·236
NO	44193	1·146	1·060	1908·5	14·42	1·237	1·815	2310	2375	1·977	2·747
CO	22164	1·232	1·118	1516·7	17·24	0·655	1·145	2005	2182	2·005	2·021

These may again respectively be regarded as the first two terms of modified Morse functions (9) and (10).*

$$- 2D' e^{-a(r-r_e')} + D' e^{-2a(r-r_e')} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (9)$$

$$- 2D' e^{-a(r-r_e')} + D' e^{-2a(r-r_e')} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \quad (10)$$

Equation (9) signifies that the creation of two attracting doublets of strength μ_1 and μ_2 may be regarded to a first approximation as causing an increase of the dissociation energy to D' equal to $D + \dfrac{2\mu_1\mu_2}{r_e^3} + \dfrac{9\mu_1^2\mu_2^2}{r_e^8 a^2 D}$ with a corresponding diminution of the equilibrium nuclear distance to r_e' equal to $r_e - \dfrac{3\mu_1\mu_2}{r_e^4 a^2 D}$. Similarly equation (10) signifies that two repelling doublets μ_1 and μ_2 cause a diminution of the dissociation energy to D' equal to $D - \dfrac{\mu_1\mu_2}{r_e^3} + \dfrac{9\mu_1^2\mu_2^2}{4 r_e^8 a^2 D}$ with a corresponding increase in the equilibrium nuclear distance to r_e' equal to $r_e + \dfrac{3\mu_1\mu_2}{2 r_e^4 a^2 D}$. In both cases D is equal to

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* This mode of representation is exactly similar to the one adopted in studying the effect of adding a small kinetic energy term due to the rotation of a molecule to its nuclear potential energy. For the details of calculation see Condon and Morse, *Quantum Mechanics*, page 164.

Table II.

Bands Degraded to the Red.

Molecule	ν_e cm.$^{-1}$	r_e'' A.U.	r_e' A.U.	w_e'' cm.$^{-1}$	$x_e'' w_e''$	$D_e'' \times 10^{12}$	$D_e' \times 10^{12}$ (calc.)	w_e' (calc.)	w_e' (obs.)	$\sqrt{\mu_1 \mu_2} \times 10^{18}$ calc. Band spectra	$\sqrt{\mu_1 \mu_2} \times 10^{18}$ calc. polarisability
AgH	29898	1·614	1·638	1760·0	34·05	4·465	4·237	1714	1664	0·991	··
O$_2$	13121	1·204	1·223	1568·0	11·65	10·350	9·493	1502	1433	1·237	1·415
BeF	33187	1·357	1·390	1265·6	9·12	8·612	7·790	1190	1173	1·460	··
BeO	21197	1·328	1·359	1487·5	11·87	9·154	8·166	1406	1371	1·549	··
AlO	20635	1·614	1·663	977·0	7·00	6·692	5·280	868	868	2·493	··
CuH	23311	1·460	1·568	1939·9	36·85	5·013	3·992	1731	1700	1·891	··
Li$_2$	20395	2·670	2·930	351·6	2·59	2·342	1·842	312	270	3·339	··
CO$^+$	45638	1·110	1·160	2212·0	15·17	15·830	12·440	1962	1722	2·229	2·900
HgH$^+$	44108	1·590	1·690	2016·0	40·80	4·889	3·744	1764	1647	2·254	··
CN	10900	1·169	1·236	2068·8	13·18	15·930	12·060	1800	1789	2·599	1·459
Na$_2$	20302	3·070	3·404	159·2	0·73	1·714	1·226	135	124	4·106	··
K$_2$	15369	3·910	4·220	92·6	0·35	1·190	0·841	78	75	4·863	··
AuH	27345	1·520	1·670	2302·0	42·00	6·193	4·181	1891	1690	2·879	··
ZnH$^+$	46432	1·510	1·710	1916·0	39·00	4·619	2·899	1518	1365	2·719	··
CdH$^+$	42680	1·660	1·860	1773·0	36·50	4·227	2·562	1380	1250	3·049	··
S$_2$	31673	1·603	1·806	727·4	2·75	9·441	5·080	534	435	4·709	4·306
PbO	30106	1·918	2·042	722·3	3·73	6·864	3·621	525	531	5·032	··
MgH$^+$	35629	1·649	2·008	1702·2	34·20	4·157	1·979	1174	1138	3·808	··
P$_2$	46802	1·880	2·120	779·3	2·72	10·960	4·258	486	471	7·423	··
SO	39109	1·489	1·769	1123·7	6·12	10·140	2·271	532	629	6·017	3·078

$\dfrac{hcw_e^2}{4x_e w_e}$ and as it is assumed that a and hence $x_e w_e$ does not change, the new value of w_e the vibration frequency, may easily be calculated. It may, however, be remarked even here that it follows very naturally from the equations that an increase in the equilibrium nuclear distance is always accompanied by a diminution of the vibration frequency and *vice versa*. This conclusion is in entire agreement with the observed facts.

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4. Comparison of Theory and Experiment.

The theory outlined in the foregoing section has been applied to almost all cases of bands for which complete data are available. The data contained in Tables I and II are taken from the International Critical Tables, Vol. 5, and "Report on Band Spectra of Diatomic Molecules" by W. Jevons. Unit of ν_e, w_e'' and w_e' is one cm.$^{-1}$ and of r_e'' and r_e' is 10^{-8} cm.

5. An Independent Method of Calculating the Electric Moments.

An alternative method is to regard the energy of electronic excitation as having been spent in creating an electric moment in the molecule. If it is assumed that the molecule is composed of uniformly polarisable matter of volume v, having a dielectric constant K and an optical polarisability P the energy of electrification is easily seen to be $\dfrac{E^2(K-1)v}{8\pi}$ where E represents the field strength. This may be rewritten as $\dfrac{E^2 P^2 v^2}{2Pv}$ after multiplying both the numerator and denominator by Pv since $K - 1 = 4\pi P$. The numerator represents the square of the total moment $\bar{\mu}$ induced in the molecule as a result of electronic excitation and the denominator is twice the polarisability $\bar{P}$ per single molecule. Equating this to the energy of electronic excitation we have

$$\frac{\bar{\mu}^2}{2\bar{P}} = h\nu c \text{ or } \bar{\mu}^2 = 2\bar{P}\,h\nu c$$

for a transition in which ν represents the spacing of the two electronic levels involved. $\bar{P}$ is the polarisability of the molecule in question and if it is known, the value of $\bar{\mu}$ may be calculated. In case of molecules having identical atoms, it is assumed that this moment is shared equally by them and in other cases, it is divided in the ratio of the optical polarisabilities of the constituent atoms, thus obtaining the values of μ_1 and μ_2 of the preceding section which together constitute $\bar{\mu}$ the total moment of the molecule. The quantity $\sqrt{\mu_1 \mu_2}$ calculated in this way for a few molecules for which data are available is given in the last column of Tables I and II which may be compared with a similar quantity in the adjoining column.

6. Discussion of Results.

The outstanding feature exhibited by the results in the eleventh column of Tables I and II is the close correspondence between their order of magnitude and the permanent electric moments that are frequently met with in molecules. This lends a strong support to the ideas contained in the present paper. The frequency in the lower state and the frequencies (calculated and observed) in the upper state have been printed in thick type to facilitate comparison.

made of the electric moments that are to be postulated in several cases and it is found that these are of the same order of magnitude as the permanent moments frequently met with in molecules.

By adding the mutual potential energy of the doublets to the nuclear potential energy function, it is shown that the creation of doublets may be regarded as equivalent to an increase in the vibrational frequency of the molecule if they are of an attracting type and a decrease of the vibrational frequency if they are of a repelling type. This explains in a very satisfactory manner the well-known experimental fact that increase in the nuclear distance on electronic excitation is always accompanied by a diminution in the vibrational frequency and *vice versa*. Quantitative calculations reveal good agreement between the theoretically deduced and the experimentally observed oscillation frequencies in the higher electronic states for molecules in which changes of nuclear distances are relatively small.

An independent method of calculating the strength of the induced electric moments is given by assuming that the energy of electronic excitation is all spent in polarising the atoms. Good agreement is observed between the values so calculated and the moments deduced from the known changes in the nuclear distances. It is found that large electric moments have to be postulated to account for the observed changes in the nuclear distances and vibration frequencies of highly polarisable molecules, thus indicating a fundamental relationship between the phenomenon of optical polarisability and electronic excitation.

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