43

Potential Energy Curves and Structure of the Alkaline Earth Oxides

By

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ABSTRACT.

The potential energy curves for the different electronic states of the alkaline earth oxides have been drawn after Morse. The electronic configuration, dissociation energy and the products of dissociation in each state are discussed and the similarities in the spectra of the different members have been traced as far as possible.

In the ground state of the alkaline earth oxides, the metal atom has been supposed to be in an excited ^3P state with outermost electrons in a $s\ p$ configuration and the oxygen atom in its normal ^3P state with p^4-configuration, the linkage in the molecule being due to a $p\ p$-type of binding between the constituent atoms.

Introduction.

The data obtained from the analysis of the spectra of a diatomic molecule can be utilised to construct $U(r)$ curves for its various electronic states. A study of these curves supplies us with many interesting informations about the nature of the molecules in question. From the data so far accumulated in literature, one finds that molecules with the same number of electrons and not differing too much in their nuclear charges, the so-called iso-electronic molecules, are closely similar to one another, in the order of binding of different types of electrons as is evident from the nature of potential energy curves, and also in respect to the positions of their different electronic energy levels for $r = r_e$. Where the nuclear charges are very unequal, (as in hydrides), the order of binding and arrangement of electron levels are essentially those of the atom with the same number of electrons (*i.e.*, united atom) except for the λ and Λ subdivision.

Furthermore, certain diatomic molecules show homologous characteristics as are found to exist between atoms occurring in the same column of the periodic table. These features are manifested in the existence of marked similarities between the energy level diagrams of molecules, one of whose atoms varies from one element to another in the same column of the periodic table, while the other remains fixed; or else both vary, each within a given column of the table. As yet, the data on such series of molecules are not extensive enough to show how far these similarities can be followed. For homologous hydride molecules, the similarities between their energy level diagrams can be explained from the consideration of their homologous united-atoms. In the case of non-hydride homologous molecules, it has been found that in most cases their resemblance to the united-atom is not close enough to be of any direct interest except in only a few aspects. They have, however, a relationship to their separated atoms, which is rather interesting. The object of the present paper is, firstly to trace the relationships which exist between the energy levels of different alkaline earth oxides with those of their separated atoms, from a study of the energy level diagrams and $U(r)$ curves, and secondly to determine the nature of the electronic structure in the different states.

Construction of U(r) Curves.

For each electronic state of a diatomic molecule there is a function $U(r)$ representing the relation between the potential energy and the internuclear distance which has a single minimum corresponding to an equilibrium value, r_e, of the distance r between the nuclei. If $U(r)$ is taken as zero, then $U(r)$ represents the total potential energy of a molecule whose nuclei are momentarily at rest at distance r apart. The variation of $U(r)$ with r can be graphically represented by means of a curve, called the $U(r)$ curve for that electronic state. Thus each electronic state has its own $U(r)$ curve.

Kratzer[1] was the first to work out a potential energy function of an anharmonic oscillator composed of a dipole and showed that $U(r)$ curves of molecules can be constructed with the help of this function. He gave the following expansion of $U(r)$ in terms of $\rho = r/r_e$.

$$U(\rho) = -a^*[-\tfrac{1}{2} + 1/\rho - \tfrac{1}{2}\rho^2 + b^*(\rho-1)^3 + c^*(\rho-1)^4 +] \quad \ldots \quad (1)$$

which is convergent for values of r not for from r_e.

From the analysis of band spectra if ω_e, $x_e\omega_e$, B_e and α are known, one can compute r_e, a^*, b^*, and c^* from the following equations.

$B_e = \frac{27 \cdot 7 \times 10^{-40}}{\mu r_e^2}$, where μ is the effective mass of the molecule.

$$\omega_e = \frac{1}{2\pi c}\left(\frac{a^*}{\mu r_{2e}}\right)^{\frac{1}{2}},$$

$$\bar{\alpha} = (6B_{2e}/\omega_e)(2b^* + 1),$$

and

$$x_e\omega_e = 3B_e\{1 + 5b^* + c^* + \tfrac{5}{2}.b^{*2}\}$$

There are, however, several objections to the series form used by Kratzer. Firstly, the effect of all the terms in $(r-r_e)$ to the power three or higher can only be approximately calculated. Secondly, it is only applicable over a restricted range of r. Thirdly, it does not take into account the relative magnitudes of the anharmonic co-efficients.

In 1929 Morse[2] pointed out that the above objections can be met by a series form, which would satisfy the following requirements, *viz.*,

(1) It should come asymptotically to a finite value $r \longrightarrow \infty$
(2) It should have its only minimum point at $r=r_e$
(3) It should become infinity at $r=0$
(4) It should exactly give the allowed energy levels as the finite polynomial,

$$W(v)=h\omega_e[(v+\tfrac{1}{2})-x_e(v+\tfrac{1}{2})^2]$$

From the above considerations, he gave essentially the following function, *viz.*,

$$U(r)=D_e\left\{1-e^{-a(r-r_e)}\right\}^2 \qquad \dots \qquad \dots \quad (2)$$

where,

$$a=\left\{\frac{2\pi^2\mu\, c\omega_e{}^2}{h.D_e}\right\}^{\frac{1}{2}}$$

D_e may be determined independently or evaluated from the relation, $D_e=\frac{\omega_e{}^2}{4x_e\omega_e}$ cm^{-1}. This function has a minimum of 0 at $r=r_e$ and comes asymptotically to D_e at $r=\infty$. It does not, however, satisfy strictly the requirement (3). Morse's function permits, therefore, the construction of $U(r)$ curves, which are qualitatively correct, though not quantitatively, from $r=0$ to $r=\infty$ except in the region close to $r=0$, which is of no practical importance.

More recently Rydberg[3] has proposed for the $U(r)$ function an expression slightly different from that of Morse. This is given by,

$$U(r)=D_e\{a(r-r_e)+1\}e^{-a(r-r_e)} \qquad \dots \qquad \dots \quad (3)$$

where,

$$a=\left\{\frac{(0{\cdot}1735\ \ \omega_e)^2.\mu}{D_e}\right\}^{\frac{1}{2}}$$

He constructed the $U(r)$ curves for a few molecules on the basis of the above equation and found them to be in better agreement with the theoretically calculated curves than those drawn after Morse's function.

In the present paper the $U(r)$ curves for the different electronic states of the molecules have been drawn according to Morse's function, which is generally used by different investigators till now. Hence we are to know the values of r_e, ω_e and either $x_e\omega_e$ or D_e for each state. In many cases, however, r_e is not known owing to the lack of rotational analysis of the bands involving the given electronic level but the value of ω_e is known from their vibrational analysis. It may here be noted that when ω_e is known, the corresponding r_e can be estimated with fair accuracy by means of one of the two empirical relations, *viz.*, $\omega_e r_e^2 = \text{const.}$, or $\omega_e r_e^3 = \text{const.}$ as given by Birge[4] and Morse[2] respectively. Both relations, especially the first, hold fairly well for different states of a molecule if the value is known for one state. The second relation, with the constant as 3000×10^{-24} cm.^{2} is fairly applicable for a wide variety of states, even of different molecules, provided the masses of the two atoms are not too unequal. For our purpose the relation of Birge has been preferred since the value of the constant is known from at least two of the electronic states of each molecule under discussion.

BeO.

Excitation of the BeO molecule has so far been found to emit four band systems. Two of these have been analysed in detail and have been shown to be due to $^1\Sigma \longrightarrow {}^1\Sigma$ and $^1\pi \longrightarrow {}^1\Sigma$ transitions respectively, one lying in the blue-green[5] and the other in the near infra-red.[6] The other two band systems[7] lie in the near ultra-violet region and it has been suggested that both of them are due to $^1\pi \longrightarrow {}^1\pi$ transitions. The energy level diagram correlating the different electronic states of the molecule is given after Harvey and Bell in Fig. 1. The ultra-violet band system recently analysed by the above investigators has a peculiarity, *viz.*, that it consists of a strong 0-sequence with two very faint ones, *viz.*, $\triangle v = \pm 1$.

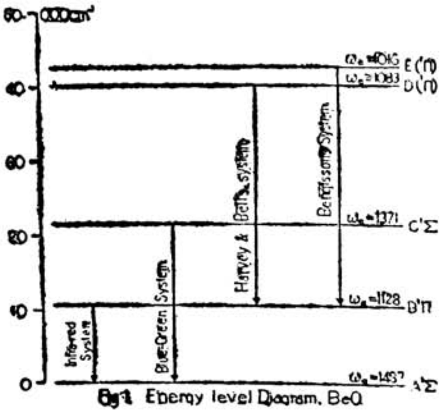

Fig. 1 Energy level Diagram, BeO

There have been of late interesting discussions by Mulliken,[8] G. Herzberg,[9] Lessheim and Samuel,[10] L. Herzberg,[6] and others on the electronic configurations and products of dissociation of BeO molecule corresponding to the two states of $C^1\Sigma \longrightarrow A^1\Sigma$ band system. According to Mulliken since BeO and C_2 are isoelectronic, it is expected that their spectra would be similar. Their r_e values also indicate that one is nearly as stable as the other. He is of opinion that the $C^1\Sigma \longrightarrow A^1\Sigma$ bands of BeO probably correspond to $\sigma\pi^4\sigma \longrightarrow \sigma^2\pi^4$, the energy interval between the two $^1\Sigma$ states being about the same as that predicted for the corresponding interval in C_2.

Turning to the question of dissociation products, Mulliken has pointed out that since the two normal atoms Be $(1s^22s^2, {}^1S)$ $+O(^3P)$ give only a $^3\Sigma$ and a $^3\pi$ state, they must almost certainly be identified with the molecular states $\sigma^2\pi^3\sigma$, $^3\pi$ and $\sigma^2\pi^2\sigma^2$, $^3\Sigma$. But these states are of relatively higher energy content in BeO than in C_2 and are thus of low stability or possibly even repulsive. Hence $\sigma^2\pi^4$, $^1\Sigma$ the lower state of the $C^1\Sigma \longrightarrow A^1\Sigma$ system, is the normal state of BeO, and is derived from $Be(S) + O(^1D)$, which is the lowest energy pair of states capable of giving $^1\Sigma$ state.

On the other hand G. Herzberg was of opinion that the normal state, $\sigma^2\pi^4$, of BeO is obtained from Be(^{3}P)+O(^{3}P) while its excited state, $\sigma\pi^4\sigma$, from Be(^{3}S)+O(^{3}P).

Lessheim and Samuel have recently pointed out that if the normal state of BeO corresponding to the lower state of $C^1\Sigma \longrightarrow A^1\Sigma$ system, is taken to be derived from Be($2s^2$, ^{1}S)+O ($2s^2 2p^4$, ^{1}D) as suggested by Mulliken, one can then assume that in the excited state, the molecule dissociates either into an excited Be atom and a normal oxygen atom in the metastable ^{1}D state, or into a normal Be atom and an excited oxygen atom. With the first alternative, one finds that the energy interval between ($2s^2$) ^{1}S and the next higher term, *viz.*, ($2s2p$) ^{3}P, ^{1}P, ($2s3s$) ^{3}S of the Be atom, is 2·70, 5·25 and 6·43 volts respectively, while with the second alternative the energy interval between ($2s^2 2p^4$)^{1}D and the next higher terms, *viz.*, ($2s^2 2p^4$) ^{1}S, ($2s^2 2p^3 3s$)^{5}S of the oxygen atom, is 2·21 and 7·64 volts respectively. But the E_{atom} calculated from the data of the band system in question is 4·46 volts and is thus at large variance with any of the above values. They further point out that Be($1s^2 2s^2$, ^{1}S) as a dissociation product is to be excluded, since the closed shell of two *s*-electrons giving rise to a ^{1}S state may act similarly as in He-configuration such that the resulting molecular states would have either no minima in their potential curves or the curves would be very flat. Their internuclear distances would also be very large. These states would thus be repulsive or slightly attractive in nature. This view is substantiated from Hund's theory of crystal lattice for BeO.[11] The continuous absorption spectra[12] of a number of molecules which are known to be of this configuration also support the above view.

Furthermore if one assumes the nature of the dissociation products in the two states of BeO molecule to be that ascribed by Herzberg, the energy interval between ($2s3s$)^{3}S$-$($2s2p$)^{3}P of Be atom is 3·72 volts and it is not in agreement with the experimental data. It has also been remarked that in accordance with either of the above electronic configurations of BeO, one would expect the heat of dissociation in the excited state, $\sigma\pi^4\sigma$, to be lower than that of the normal state of completed shells with $\sigma^2\pi^4$ configuration. This is in contradiction to actual data, since the dissociation energy in the normal state is 5·66 volts and in the excited state 7·50 volts.

From the above considerations, Lessheim and Samuel were led to suggest that the ground level of BeO does not start with the configuration (s^2) of Be atom as assumed by Mulliken but probably starts from the first excited term of the metal atom with the configuration (sp) as proposed by Herzberg. Thus one may assume that the chemical linkage in BeO is due to a pp-binding between a p-electron of Be and a p-electron of oxygen atom. If the p-electron is excited we get a molecular state which has a decreased heat of dissociation and which dissociates adiabatically, yielding a metal atom in its ordinary excited state. The s-electron of the metal would not then take part in the linkage but would only disturb it. If on the other hand this electron is excited, the heat of dissociation would increase in the excited level and the molecule dissociates adiabatically yielding a metal atom in an anomalous excited state. The above authors were, therefore, led to suggest that in the lower $A^1\Sigma$ state of the band system, the electronic configuration of BeO corresponds to

$$k_1 k_2 2s\sigma^2(2s)2p\pi^4(2p)3p\sigma(2s)3d\sigma(2p),$$

dissociating into Be($k2s2p$, ^{3}P) and O($k2s^2 2p^4$, ^{3}P), *i.e.*, into an excited Be atom and a normal oxygen atom.

In the upper $C^1\Sigma$ state of the band system, since the energy of dissociation is larger, leading evidently to stronger binding force, it may be assumed that this state is derived by the excitation of a s-electron in the molecule, so that a complete shell is formed in place of two incomplete ones in the ground state. Such an assumption leads to the following configuration, *viz.*,

$$k_1 k_2 2s\sigma^2(2s)2p\pi^4(2p)3d\sigma^2(2p).$$

This dissociates into $\mathrm{Be}(k2p^2, {}^3\mathrm{P})$ and $\mathrm{O}(k2s^2 2p^4, {}^3\mathrm{P})$, that is, into a Be atom in an anomalous excited state and a normal O-atom. The energy interval $(2p^2)^3\mathrm{P} - (2s2p)^3\mathrm{P}$ is 4·66 volts and is in fair agreement with the calculated value of $\mathrm{E}_{\mathrm{atom}} = 4{\cdot}46$ volts from the data of the band system.

The problem of the electronic configuration and the products of dissociation of BeO molecule has further been discussed by L. Herzberg. She has worked out the electronic configuration in each state after the "Aufbau" principle of Mulliken and Hund and has identified the different states of the infra-red, the blue-green and Bengtsson's ultra-violet band systems with the molecular states $\sigma^2\pi^4(\mathrm{A}^1\Sigma)$, $\sigma^2\pi^3\sigma(\mathrm{B}^1\pi)$, $\sigma\pi^4\sigma(\mathrm{C}^1\Sigma)$ and $\sigma\pi^3\sigma^2(\mathrm{E}^1\pi)$. She has also drawn the potential energy curves for each of these four states. From the course of these curves, L. Herzberg was led to infer that for large values of r, the curves for $\mathrm{A}^1\Sigma$ and $\mathrm{B}^1\pi$ and those for $\mathrm{C}^1\Sigma$ and $\mathrm{E}^1\pi$ merge into one another indicating that each pair dissociates into identical atoms. She was thus of opinion that while the molecular states of the former pair are derived from either $\mathrm{Be}({}^1\mathrm{S}) + \mathrm{O}({}^1\mathrm{D})$ or $\mathrm{Be}({}^3\mathrm{P}) + \mathrm{O}({}^3\mathrm{P})$, those of the latter are probably obtained from $\mathrm{Be}({}^3\mathrm{S}) + \mathrm{O}({}^3\mathrm{P})$ or $\mathrm{Be}^+({}^2\mathrm{S}) + \mathrm{O}^-({}^2\mathrm{P})$. This assumes that the excited $\mathrm{C}^1\Sigma$ state dissociates into $\mathrm{Be}^+({}^2\mathrm{S}) + \mathrm{O}^-({}^2\mathrm{P})$, which is an ionic binding, explaining the higher value for the heat of dissociation in this state than that in the normal $\mathrm{A}^1\Sigma$ state. The assumption of L. Herzberg of an ionic binding in the excited $\mathrm{C}^1\Sigma$ state does not seem justifiable as one finds that the value of electron affinity of oxygen calculated from the band analysis data is at wide variance with that directly measured by Mayer and Maltbie, while the value of $\mathrm{E}_{\mathrm{atom}}$ evaluated from the same data, is in fair agreement with the energy interval $(2p^2)^3\mathrm{P} - (2s2p)^3\mathrm{P}$ of Be atom as has already been pointed out.

It may further be noted that the assumption of an ionic binding, would lead one to expect a higher value of heat of dissociation in the $\mathrm{E}^1\pi$ state than that in the $\mathrm{B}^1\pi$ state of Bengtsson's ultra-violet band system. But the value calculated from band head data is lower. This means, therefore, that the products of dissociation in $C^1\Sigma$ and $E^1\pi$ states are not probably identical, so that their $U(r)$ curves would not merge into one another as shown by L. Herzberg in her paper. In fact she has herself noted that the $U(r)$ curve for the $E^1\pi$ state does not represent its actual course calculated from the available data. The $U(r)$ curve for the $D^1\pi$ state was not included as the analysis of the $D^1\pi \longrightarrow B^1\pi$ band system was not then published.

The potential energy curves for the different states of BeO have been drawn in Fig. 2(*a*) those of L. Herzberg being reproduced in Fig. 2(*b*) for a comparison. From both these figures, it is evident that allowing for small inaccuracy in the experimental data, the $U(r)$ curves for $A^1\Sigma$ and $B^1\pi$ states coalesce into one another for larger r values, indicating that their products of dissociation are identical as has been suggested by the above author. On the other hand, the $U(r)$ curve for $E^1\pi$ does not merge into that for $C^1\Sigma$ (Fig. 2*b*) but it runs together with the one for the $D^1\pi$ state (Fig. 2*a*). From this, one can reasonably suggest that $D^1\pi$ and $E^1\pi$ states would be derived from identical

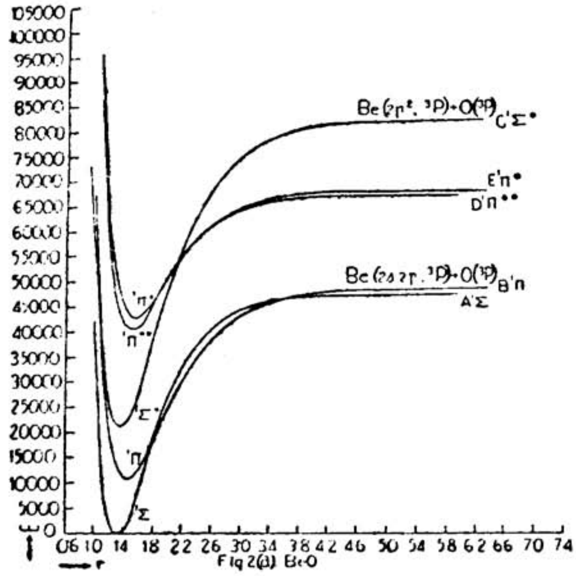

Fig 2(a) Be-O

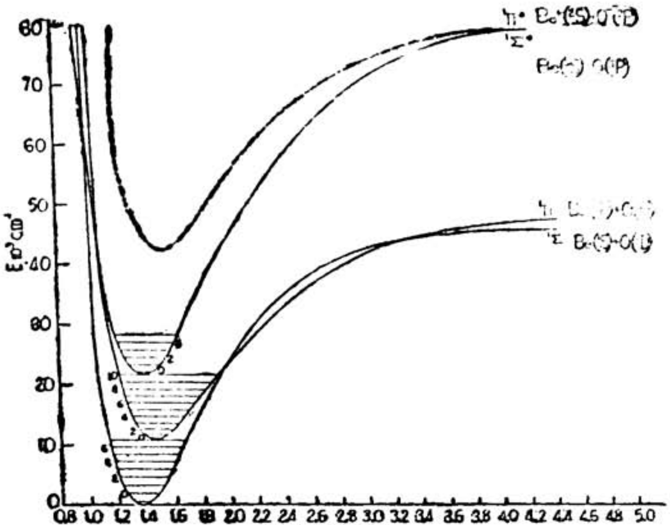

Fig 2(b)

atoms. Further definite information regarding the electronic configuration and products of dissociation of BeO in these two states can be had only when more accurate data on the analysis of the ultraviolet band systems will be available.

In our view we agree with Lessheim and Samuel in their assignment of electronic configuration and identification of the products of dissociation of the $A^1\Sigma$ and $C^1\Sigma$ states. The $B^1\pi$ state, whose $U(r)$ curve coalesces into that of the normal $A^1\Sigma$ state, dissociates also into Be ($k\ 2s\ 2p$, ^3P) and O ($k\ 2s^2 2p^4$, ^3P), *i.e.*, into a normal oxygen atom and an excited Be atom. Since the dissociation energy decreases in this state, one is to consider only those configurations of the excited molecule in which the excitation is due to a p-electron contributing to the linkage. This p-electron will, therefore, be excited to the next π-group, $3d\pi\ (2p)$. Hence the electronic configuration of BeO in this state would correspond to

$$k^1\ k_2\ 2s\sigma^2\ (2s)\ 2p\pi^4\ (2p)\ 3p\sigma\ (2s) 3d\pi\ (2p).$$

So it is different from what has been assigned by L. Herzberg.

MgE.

For MgO two band systems [13] are known, one lying in the green and the other in the red. The analysis [14] of the red system reveals that it is due to a $^1\Sigma \longrightarrow {}^1\Sigma$ transition. The green system is very similar in appearance to the ultra-violet system of Harvey and Bell for BeO, *viz.*, having a strong zero sequence with two faint sequences $\Delta v = \pm 1$ and has also ω_e' and ω_e'' value nearly equal in magnitude. From the high dispersion photopraphs of these bands, it appears that the higher members of the P and R series, are probably double, which may be attributed to Δ-type doubling. In view of the superposition of the higher members of the sequence and in the absence of a rotational analysis, this cannot be over-emphasised. One can, however, assume that these bands are analogues of ultra-violet bands of Harvey and Bell while the red systems are analogues to the blue-green system of BeO. The potential energy curves are given in Figs. 3 and 4.

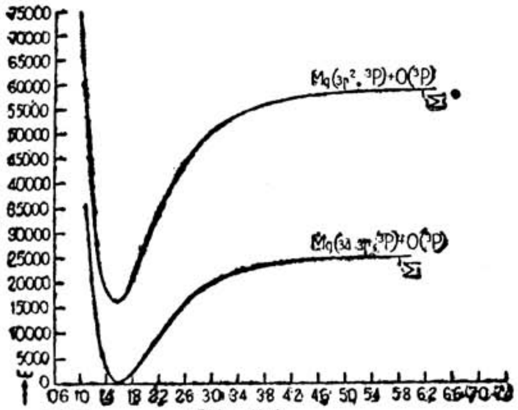

Fig 3 MgO
Red Bands

With a view to ascertain the atomic states from which the electronic levels corresponding to the two states of the red bands

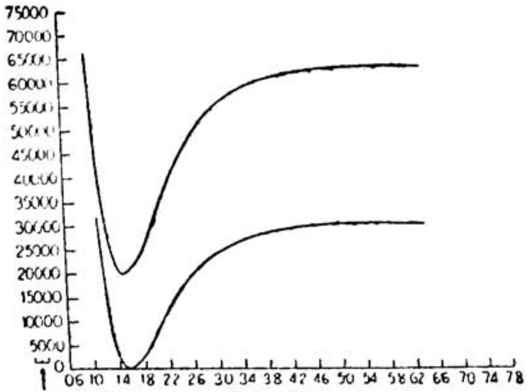

Fig4 MgO
Green Bands

of MgO are derived, E_{atom} was calculated. Since $E_{\text{mol.}}=2{\cdot}03$, $D'=5{\cdot}09$ and $D''=3{\cdot}06$ volts, we have

$$
\begin{aligned}
E_{\text{atom}} &= E_{\text{mol.}}+D'-D'' \\
&= 4{\cdot}06 \text{ volts.}
\end{aligned}
$$

From the line spectrum data of Mg, the energy interval between $(3s^2)\ {}^1S$ and $(3s3p)\ {}^1P$ is about 4·3 volts while that between $(3s3p)^3P$ and $(3p^2)^3P$ is nearly 4·4 volts. Both these values are in fair agreement with the value of E_{atom} calculated above from the band analysis data. We are thus presented with two possibilities.

If we adopt the view of Mulliken that the linkage in MgO starts also with the configuration (s^2) of the metal atom as in the case of BeO molecule, then the lower $A^1\Sigma$ state of the red system, which is probably the ground state of MgO, may be supposed to be derived from Mg $(3s^2, {}^1S)+O\ (2s^2\ 2p^4, {}^1D)$. Hence we are to identify the products of dissociation of the upper $C^1\Sigma$ state with Mg $(3s\ 3p, {}^1P)+O\ (2s^2\ 2p^4, {}^1D)$. One would, therefore, expect the heat of dissociation in the upper state, $\sigma\pi^4\sigma$, to be less than that of the lower, $\sigma^2\pi^4$, which consists of only completed shells. This is, however, in contradiction to the actual data. We may further exclude this possibility from the consideration which has already been made with reference to BeO that the helium-like configuration (s^2) usually gives rise only to repulsive or slightly attractive states of diatomic molecules.

On the other hand if we assume that the linkage in the ground level of the molecule is due to a *pp*-binding and thus starts from the first excited term of the metal atom with the configuration (*sp*) as has been suggested by G. Herzberg as well as by Lessheim and Samuel, then the lower ($A^1\Sigma$) and upper ($C^1\Sigma$) states of the red system may be taken to be derived from Mg ($3s\ 3p, {}^3P$)+O ($2s^2\ 2p^4$, ${}^3P$) and Mg ($3p^2$, ${}^3P$) + O ($2s^2\ 2p^4$, ${}^3P$) respectively. It is thus possible to explain the higher value of heat of dissociation in the excited $C^1\Sigma$ state. As in the case of BeO, we may here suppose that the *p*-electron of magnesium together with a *p*-electron of oxygen are responsible for the chemical linkage in the molecule in its ground state and that the upper $C^1\Sigma$ state has been derived by the excitation of the *s*-electron in the molecule. Hence the heat of dissociation increases in the excited level.

From analogy with BeO, one obtains the following configuration for the ground and excited levels of MgO according to Weizel's correlation scheme.[15]

$$\pi^2\sigma\sigma,\ A^1E : k_1k_2\ 2s\sigma^2(2s)\ 3p\sigma^2\ (2s)\ 3d\sigma^2\ (2p)\ 4f\sigma^2\ (2p)\ 2p\pi^4(2p)$$
$$3d\pi^2\ (2p)\ 3s\sigma\ (3s)\ 4d\sigma\ (3p).$$

$$\pi^2,\ C^1E : k_1\ k_2\ 2s\sigma^2\ (2s)\ 3p\sigma^2(2s)\ 3d\sigma^2\ (2p)\ 4f\sigma^2(2p) 2p\pi^4(2p)$$
$$3d\pi^2\ (2p)\ 4d\sigma^2\ (3p).$$

The products of dissociation in the two states of the green system can be fairly ascertained by calculating also the value of E_{atom} from the band analysis data. This is found to be 4·05 volts, since $E_{mol.} = 2{\cdot}46$, $D' = 5{\cdot}36$ and $D'' = 3{\cdot}77$ volts. Comparing this value with that evaluated from the red system, it seems likely that the products of dissociation of the lower states of the two systems are identical and so also of their upper states. But the values of ω_e and $x_e\omega_e$ in the band head equation of the green system are a bit uncertain as they have been evaluated only from $\Delta v=0$ and -1 sequences. This renders the values of D' and D'' also unreliable. Hence the above statement regarding the nature of the products of dissociation in the two states of the green system cannot be over-emphasised. In the absence of a rotational structure analysis of these bands, the electronic configuration of MgO in these states cannot also be ascertained with certainty. But it seems most likely that a transition between two similar states, probably $^{1}\pi$, is responsible for the emission of the band system. It may be noted that the molecular states derivable from combination of an unexcited O-atom (^{3}P) with a Mg-atom in ($3s\ 3p, ^{3}P$) or in ($3p^{2}$, ^{3}P) state are two quintets, triplets, singlets Σ and π-states and one quintet, triplet, and singlet Δ state in each case.

BaO.

Excitation of the BaO molecule has so far been found to give rise to a single extended band system[15] lying in the region λ 8000 – λ 4300. From its fine structure analysis it has been

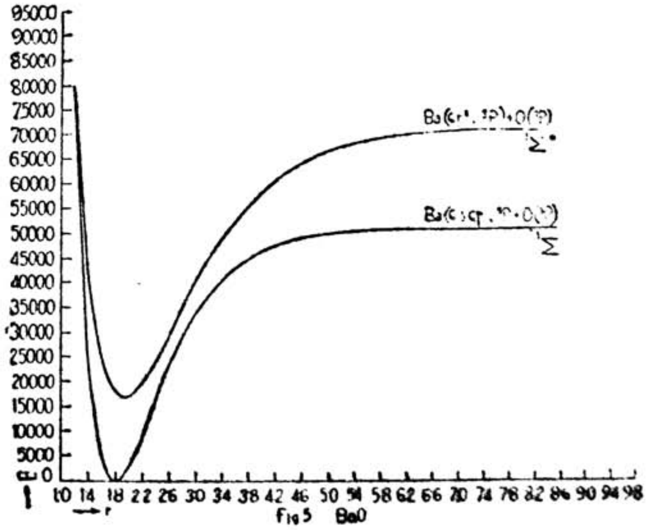

Fig 5 BaO

attributed to be due to a $^1\Sigma \longrightarrow {}^1\Sigma$ transition. $U(r)$ curves for the two states are given in Fig. 5. This system is in all probability analogous to the blue-green bands of BeO and the red bands of MgO, so that it is schematically represented as due to a transition between $C^1\Sigma$ and $A^1\Sigma$ states. It is further noticed that the heat of dissociation in its upper state is also greater than that in the lower, which is possibly the ground state of the molecule. Hence from considerations, similar to those of BeO and MgO, we can here also assume that the linkage in the ground state of BaO is due to a *pp*-binding which starts from the first excited term of Ba atom with the (*sp*) configuration, and that the *s*-electron is excited to give rise to the upper state of the band system. Thus the ground state $A^1\Sigma$ is derived from Ba $(6s\,6p,\, {}^3P) + O(2s^2 2p^4,\, {}^3P)$ while the upper state, $C^1\Sigma$, from Ba $(6p^2,\, {}^3p,\, P) + O(2s^2\, 2p^4,\, {}^3P)$. The energy interval between $(6p^2)^3P - (6s\,6p)^3P$ of Ba is 2·74 volts, which is in sufficiently close agreement with the value of E_{atom} 2·52 volts, calculated from band analysis data. It may here be pointed out that the interval between $(6s\,6p)^1P - (6s^2)^1S$ of Ba is 2·23 volts. Although this value may be considered to be in fair agreement with the calculated value of E_{atom}, we have excluded this possibility for reasons which have already been given in connection with BeO and MgO.

In this case, however, we cannot be certain of the quantum numbers of the molecule. But adopting Weizel's correlation scheme we can derive the configuration of BaO in each state analogous to that of BeO or MgO.

CaO and SrO.

Three band systems are known for each of these molecules. One of these lies in the near infra-red,[16] another in the blue and a third in the ultra-violet.[13] Comparing the co-efficients, ω_e and $x_e\,\omega_e$ in the band head equations of the different systems, it is found that there is no state in common amongst them.

The rotational analysis of the infra-red bands reveals that they are due to $^1\Sigma \longrightarrow {}^1\Sigma$ transitions, and are probably analogous to the $C^1\Sigma \longrightarrow A^1\Sigma$ band system of the oxides of the remaining alkaline earth metals. It is further noticed that the heat of dissociation in the upper state of the infra-red system is less than that of the lower which may be supposed to be the ground state of the molecule concerned. If we now assume that the linkage in each of these two molecules is also due to a *pp*-binding with the metal atom in the (*sp*) configuration and that the *p*-electron is excited to give rise to the upper state of the infra-red systems, we can explain the decreased heat of dissociation in the excited states of the molecules. Thus the ground state, $A^1\Sigma$, is derived from Ca $(4s\ 4p,\ ^3P) + O(2s^2\ 2p^4,\ ^3P)$ in the case of CaO and from Sr $(5s\ 5p,\ ^3P) + O(2s^2\ 2p^4,\ ^3P)$ in the case of SrO. The products of dissociation of their upper $C^1\Sigma$ states may then be associated with $Ca(4s\ 3d,\ ^3D) + O(2s^2\ 2p^4,\ ^3P)$ and Sr $(5s\ 4d,\ ^3D) + O\ (2s^2\ 2p^4,\ ^3P)$ respectively. The energy interval between $(4s\ 3d)\ ^3D - (4s\ 4p)\ ^3P$ of Ca is 0·64 volts while E_{atom} calculated from the data of Brodersen is 0·75 volts. In the case of strontium, the interval between $(5s\ 4d)^3D - (5s\ 5p)^3P$ is 0·47 volts. From Mahla's data one finds that E_{atom} gives a negative value, which may, however, be attributed to error in extrapolation.

The blue systems of calcium and strontium oxides consist of single headed bands and are probably analogous to the ultra-violet $D^1\pi \longrightarrow B^1\pi$ system of BeO. The heats of dissociation of their upper states are also less than those of their lower, which may be assumed to be derived from atoms, identical with the products of dissociation of the lower states of the infra-red bands of each molecule. It may here be noted that a ^3P term of the excited metal atom with *sp*-configuration and ^3P term of the normal oxygen atom combine to give a number of molecular states other than the $A^1\Sigma$ state of the red bands. These possible molecular terms have already been noted in the case of MgO molecule. As in the case of the infra-red bands, we may also assume that the *p*-electron is excited to give rise to the upper state of each of the blue systems. Hence the products of dissociation in these states may be identified with Ca ($4s\ 5s$, ^3s)+O ($2s^2\ 2p^4$, ^3P) and Sr($5s\ 6s$, O^3S) + ($2s^2\ 2p^4$, ^{3}P) for CaO and SrO respectively. In the case of Ca the interval between $(4s\ 5s)^3\ S-(4s\ 4p)^3P$ is 2·0 volts while the E_{atom} calculated from band analysis data is 1·3 volts, the discrepancy between the two values being attributed to an error in extrapolation. Similarly the interval between $(5s\ 6s)^3\ S-(5s\ 5p)^3P$ of Sr is 1·8 volts while the calculated value of E_{atom} is 2·1 volts and is thus in fair agreement.

Finally the ultra-violet systems of these two molecules may be assumed to be analogous to Bengtsson's ultra-violet system in the case of BeO molecule. In view of their uncertain vibrational analysis, it is preferable to postpone any further discussion on these bands.

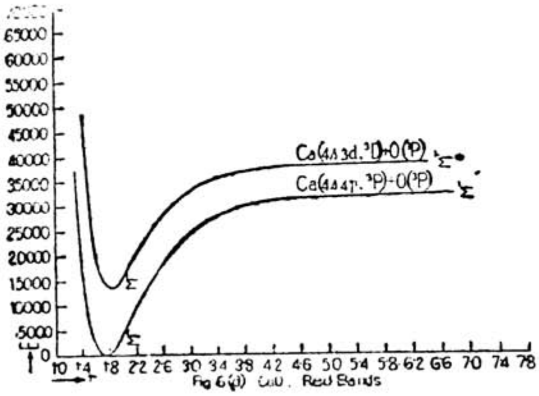

Fig 6(a) CaO. Red Bands

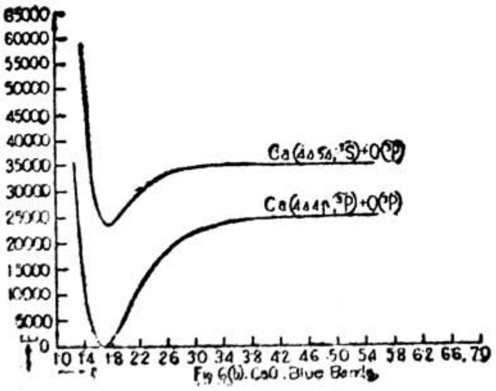

Fig 6(b). CaO. Blue Bands