

SOME REMARKS ON THE BIRGE-SPONER METHOD OF VIBRATIONAL EXTRAPOLATION.

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THE correlation of molecular and atomic terms is of great importance for the determination of the electronic configuration of the diatomic molecule and therefore for any conclusion, derived therefrom. For such correlation, a knowledge of the excitation energy E of the dissociation products is essential. In most cases this is obtained by a linear extrapolation of the vibrational levels, which gives the dissociation energy D'' of the ground state and D' of the excited level. This procedure, as is well-known, more often than not, gives for the dissociation energy an absolute value, which is too high. The energy of excitation of the dissociation products, however, is related to the D values by the formula :

$$E = \nu_0 + D' - D'';$$

ν_0 being the energy of the origin of the band system. We intend to show that in many cases E is therefore determined to a higher degree of accuracy than either D'' or D' because it does not depend on their absolute values but on their difference only. In the present paper we shall compare the values of E obtained by such extrapolation with those derived from direct experimental observation. These examples comprise also ionised molecules for which the above formula reads :

$$J_A = J_M + D''(M^+) - D''(M),$$

where J_A is the ionisation potential of the constituent atom, J_M that of the molecule, and $D''(M^+)$ and $D''(M)$ are the dissociation energies of the ground levels of the molecule in the ionised and the neutral states respectively.

As a first example we take the molecules N_2 and N_2^+ . The energy of dissociation (D'') of N_2 in its ground state $X^1\Sigma$ is known from various considerations and particularly from predissociation data to be 7.35 e-volts. The ionisation potential (J) of the N_2 molecule¹ and of the N atom,² namely 15.65 and 14.48 e.v. respectively, being experimentally known $D''(N_2^+)$ can be calculated as follows :—

$$D''(N_2^+) = D''(N_2) + J(N) - J(N_2) = 6.18 \text{ e.v.}$$

From extrapolation of the vibrational levels, we get $D''(N_2 X^1\Sigma) = 11.75$ e.v. This value is obtained from the constants¹ $\omega''_e = 2359.60$ and $\omega''_e x''_e = 11.445$. The great discrepancy between the actual value of 7.35 and the extrapolated one of 11.75 e.v. is not due to inaccuracy in ω'' because this is directly confirmed by the Raman spectrum. The anharmonic constant, however, is by no means accurate, in spite of the wealth of experimental details from which it is deduced. If we arrange the observed bands of the Lyman-Birge-Hopfield system² into the usual Deslandres scheme, we obtain the following second differences:

$$2\omega''v'' = 39.4 \quad 22.5 \quad 37.1 \quad 16.0 \quad 37.1 \quad \dots$$

These are the means obtained from the seven v' progressions, in which nearly each vibrational level $v'' = 0$ to $v'' = 6$ is fixed by at least 4, but more often by 6 to 7 independent measurements. The deviation of these experimental values from the accepted values deduced for the whole system $2\omega''v'' = 28.89$ is, no doubt, due in some measure to the facts, that the measurements concern heads and not origins and that the bands lie in the Schumann region where on account of the obvious experimental difficulties relatively larger inaccuracies are to be expected, the more so since here a small error in λ brings about a large one in v .

In a similar way the extrapolation of $D''(N_2^+)$ by means of the constants¹ $\omega''_e = 2206.84$, $\omega''_e x''_e = 16.044$ yields the value 9.23 e.v. If in this case using the data of Merton and Pilley⁴ we obtain the following second differences as the mean values from the first seven v' progressions which again are the experimentally best known:—

$$2\omega''v'' = 32.4 \quad 33.3 \quad 32.8 \quad 29.9 \quad 31.6.$$

The divergence from the accepted value 32.09 is much less than in the above case, the bands lying in the visible and near ultra-violet spectrum. It is worthy of note that the discrepancy between the actual value of $D'' = 6.48$ and the extrapolated one of 9.23 is nearly as big as in the case of N_2 . Extrapolating $D''(N_2^+)$ with three constants given by Watson and Koontz⁵ we get 8.06 e.v., but for the sake of consistency $J(N)$ is calculated by means of the value obtained by two constants only as in N_2 .

Using these extrapolated values for the energy of dissociation and replacing in the formula $E = r_0 + D' = D''$, r_0 by $J(N_2)$ and D' by $D''(N_2^+)$ we can now calculate $J(N)$.

$$\begin{aligned} J(N) &= J(N_2) + D''(N_2^+) - D''(N_2) \\ &= 15.65 + 9.23 - 11.75 \\ &= 13.13 \text{ e.v.} \end{aligned}$$

This value is very close to the actual value 14.48. Considering the term system of N_2^+ as an extension of that of N_2 and $J(N)$ as an energy of excitation of dissociation products we can say that its value derived from vibrational extrapolation is only incorrect by less than 10 per cent. whereas $D'' [= D''(N_2)]$ is incorrect by about 60 per cent. and $D' [= D''(N_2^+)]$ by about 50 per cent.

Similar results are obtained for CO and CO^+ . We have shown elsewhere⁵ that $D''(CO)$ lies between 10.5 and 9.6 e.v. and we use here the value 10.45 e.v.⁶ The ionisation potential of the CO molecule and of the constituent atoms are well known.^{1,2} It is generally assumed that the ground level of CO^+ is formed by combination of $C^+(^2P) + O(^3P)$. In this case $D''(CO^+)$ can be calculated as follows:—

$$\begin{aligned} D''(CO^+) &= D''(CO) + J(C) - J(CO) \\ &= 10.45 + 11.22 - 14.1 = 7.57 \text{ e.v.} \end{aligned}$$

If, however, $CO^+(X^2\Sigma)$ arises from $C(^3P) + O^+(^4S)$, the value $J(O) = 13.55$ e.v. yields 9.9 e.v. for $D''(CO^+)$.

The vibrational extrapolation for $D''(CO^+)$ using¹ $\omega_e'' = 2211.1$ and $\omega_e'' x_e'' = 15.12$ gives 9.84 e.v. Similarly the level $X^1\Sigma$ of CO gives on extrapolation $D''(CO) = 10.95$ e.v. with the constants⁷ $\omega_e'' = 2168.7$ and $\omega_e'' x_e'' = 13.1$.^{*} This is another case where we should expect the inaccuracy of extrapolation to be brought about by the uncertainty of the magnitude of the anharmonic constant, for ω_e'' is fixed by the agreement between the results from band spectra and Raman effect.

These considerations lead us to the following cycle:—

$$\begin{aligned} J(O) \text{ or } J(C) &= J(CO) + D''(CO^+) - D''(CO) \\ &= 14.1 + 9.8 - 10.95 = 13.0 \text{ e.v.} \end{aligned}$$

This value compares favourably as well with $J(C) = 11.22$ as with $J(O) = 13.55$. To our mind the latter interpretation is the nearer to reality because combination of $C^+ + O$ admits the possibility of only one bond in the pair-bond theory and the dissociation energy of such a molecule should be of the order of 5 e.v. On the other hand, the combination of $C + O^+$ gives a double bond, both the p -electrons of C remaining intact and $D''(CO^+)$ will be of the order of 10 e.v. The extrapolated value agrees with this conclusion. Furthermore, in this case the term $A^2\Pi$ would be the lowest of the combination $C^+ + O$ and its extrapolated energy of dissociation, 5.27 e.v., is of the right order of magnitude for a single link. The intersection

* The value 13.1 for ωx corresponds to Read's value 13.28 when the third power is neglected.

of the potential curves would then be real and the energy difference of the dissociation products which amounts to about 2 e.v. again agrees with

$$J(O) - J(C) = 2.3 \text{ e.v.}$$

As a third example we consider the molecules O_2 and O_2^+ . Using the values⁸ $D''(O_2) = 5.05$, obtained from direct observation of the convergence point, and the accepted values^{1,2} $J(O_2) = 12.5$ and $J(O) = 13.55$ e.v., we obtain for $D''(O_2^+)$ 6.10 e.v.

For $D''(O_2)$ Birge and Sponer extrapolated the value 6.65 e.v. and Herzberg⁹ obtains 5.67 e.v. by means of a formula involving higher powers of v'' . For O_2^+ using¹ $\omega_e'' = 1876.4$ and $\omega_e'' x_e'' = 16.53$ we obtain 6.45 e.v. for $D''(X^2\Pi)$. Employing the same cycle with these extrapolated values we obtain $J(O) = 12.30$ [with $D''(O_2) = 6.65$] and 13.28 [with $D''(O_2) = 5.67$]. It will be seen, that here again the agreement between the calculated and the real $J(O)$ is better than that between the extrapolated and the actual energies of dissociation of the two ground states. The discrepancy between the actual and the extrapolated value is about 6 per cent. for $D''(O_2^+)$ and about 30 or 12 per cent. for $D''(O_2)$, whereas for $J(O)$ the discrepancy is about 9 or 2 per cent. according to the value employed for $D''(O_2)$.

The energy of dissociation of the ground level $X^2\Pi$ of the molecule NO formed by unexcited atoms can be calculated from its heat of formation⁸ (-21.6 K cal./mol.) by means of Born's cycle and is 5.3 e.v. The products of dissociation of the excited term $A^2\Sigma$ are unexcited O and N in the term ($2s^2 2p^2 3s, ^4P$), 10.29 e.v. above the ground term. There is little doubt about the correctness of this correlation, since it has been confirmed by the band spectra of PO, AsO and SbO. NO, therefore, is one of the few molecules for which the energy of dissociation both for the ground state and for the excited state are known to a high degree of accuracy quite independently of the extrapolation method. Thus we obtain,

$$\begin{aligned} D'(A^2\Sigma) &= \nu_0 + E - D''(^2\Pi) \\ &= 5.46 + 10.29 - 5.3 = 10.5 \text{ e.v.} \end{aligned}$$

From the extrapolation of the vibrational levels, $D''(X^2\Pi)$ and $D'(A^2\Sigma)$ have been calculated earlier¹⁰ as 6.70 and 10.67 e.v. respectively. Introducing these extrapolated values in the above cycle, we obtain $E(N^4P) = 9.43$ e.v. which is less than 10 per cent. incorrect whereas the extrapolated values of D' and D'' are out by 2 and 28 per cent. respectively.

The molecule Na_2 is another example where although the extrapolated values for the energies of dissociation D'' and D' are unusually too high, the excitation energy of the dissociation products is given correctly. The green

band system $C^1\Pi_u \rightleftharpoons A^1\Sigma_g$ of this molecule exhibits the v' levels almost to the point of convergence and since the correlation of the atomic levels to the molecular ones is certain, D' and D'' have been calculated by the above cycle as 0.35 and 0.76 e.v. respectively.¹ Extrapolation using the accepted constants yields 0.74 and 1.07 e.v. respectively. We obtain from these latter data $E(^2P - ^2S)$ of Na = 2.18 e.v. while the actual value is 2.09 e.v.² It will be seen that the error is less than 5 per cent. even though the individual errors in absolute values of D' and D'' are 110 and 40 per cent. respectively.

These examples make it clear that under certain conditions it is possible to use the extrapolated values of dissociation for purposes of correlation between atomic and molecular levels. For, such a procedure does not necessarily involve an accurate knowledge of the absolute values of D' and D'' but only their difference $D' - D''$, and in forming this difference the errors in D' and D'' , more or less cancel out in many cases. A correct description of the complete vibrational function of a molecule cannot be expected to be given by neglecting powers of v higher than 2. The deviation of the actual law of force prevailing in a molecule from that of the simple harmonic oscillator is greater than what can be accounted for by the second power only. In certain cases such a formula is found insufficient to fit even a small number of low vibrational levels. Hence the extrapolation of the linear formula always leads to too high values as well of D' as D'' . The errors therefore almost always run in the same direction. In a case in which both D' and D'' are extrapolated with vibrational functions of the same accuracy, the excitation energy E should be the more correct the more D' and D'' are roughly of the same order of magnitude. Such a condition is fulfilled in most of the known band spectra for which correlations have been proposed. That the errors cancel out almost completely as *e.g.* in Na_2 is of course more or less fortuitous.

On the other hand, it is remarkable that a high accuracy in one of the dissociation energies coupled with the normal error of extrapolation in the other one always leads to entirely incorrect results in E . We take for instance the I_2 molecule. In this case, from the well-determined convergence point and the known energy of excitation of the iodine atom, the following energies of dissociation have been derived: $D''(X^1\Sigma_g) = 1.53$, $D'(A^1\Pi_u) = 0.08$, $D'(B^1O_u) = 0.55$ e.v. The linear extrapolation with the accepted constants gives for these 2.38, 0.06 and 0.60 e.v. respectively. Of these, the two excited levels A and B have vibrational levels which are traced almost to the limit of convergence and therefore the vibrational

functions are more accurately known, whereas only a few low levels are observed for the ground level whose vibrational function therefore is only roughly represented. The cycle $E = \nu_0 + D'(B) - D''(X) = 1.93 + 0.60 - 2.38 = 0.15$ therefore, gives only about 16 per cent. of the actual value 0.94, because the error of extrapolation of $D''(X)$ is not counter-balanced by that of $D'(B)$. If however $D''(X)$ in this cycle is replaced by $\nu_0(A)$ plus the extrapolated value of $D'(A)$ which level is known from the infra-red bands to a similar degree of accuracy as (B) O_u , we obtain $E = 1.93 + 0.60 - (1.45 + 0.06) = 1.02$ which is only 10 per cent. higher than the actual value. Similar circumstances occur in the other halogens and in O_2 , where on account of the observed convergence point in absorption, a large number of vibrational levels of the upper term are known while the ground state is known only with a few vibrational levels.

It has been recognised early that the accuracy of the dissociation energy is the greater, the shorter the extrapolation, *i.e.*, the greater the number of vibrational levels observed. Of the two constants on which D depends, ω is known experimentally with a fair degree of accuracy and its values can be checked in various ways. The true position of the origin of the band system and therefore the correct numbering of the vibrational levels can be accurately fixed by the isotope effect and by the origin of inter-combination systems, wherever available. Approximate check is moreover provided by the intensity distribution and by a number of empirical rules. Inaccuracies in D mainly arise therefore from inaccuracy in ω whose accurate determination as a second difference needs a larger number of observations. From this it follows that for a really accurate value of D we need to observe not only a large number of vibrational levels but that these levels should not show pronounced perturbations. Furthermore the accuracy of the spacing of these levels should be ensured by as many independent observations as possible. For instance, only two very long sequences enable us to observe a large number of vibrational levels but each of them only once. Such cases are by no means uncommon, *e.g.*, we get them in molecules of the type CaF . The correlation of the atomic and molecular levels in these molecules is so uniform that E in these cases is satisfactorily deduced from the linear extrapolation, evidently because the errors in the absolute values of the energies of dissociation in any one molecule are expected, as we have said above, to be in the same sense and of the same order of magnitude. The actual D values, however, are probably incorrect.

In order to bring about such a uniformity in error of D values it is obviously necessary that the terms in question should be comparable not only

as regards the number of vibrational levels but also with respect to the number of independent observations of each of them. If this condition does not obtain we sometimes come across very strange results. An example is afforded by SiCl. The band spectrum of this molecule has been measured several times, recently finally by Jevons.¹¹ Extrapolation for the ground level X and the excited level B gives $D'' = 4.0$ and $D' = 10.8$ e.v. The excited level B being 4.22 e.v. above X the excitation energy E of its dissociation products is 11.0 e.v. which is higher than the ionisation potential of Si, viz., 8.12 e.v. From comparison with the corresponding B level of SiF it can be seen¹² that the dissociation products will be unexcited Cl and Si in the term $3s^23p4p^1S$, with an energy of excitation of 6.16 e.v.² To our mind, this glaring discrepancy is undoubtedly due to the fact that the levels $v'' = 0$ to $v'' = 5$ of the ground level X are known from 4 to 8 independent observations, whereas though the levels $v' = 0$ and $v' = 1$ are known with a similar accuracy as the corresponding v'' levels, $v' = 2$ and 3 are represented by only one band each. Since ω' is calculated by the first difference of the observed frequencies and $\omega'x'$ by the second difference, these observations are sufficient for a fairly accurate determination of ω' but yield a value of $\omega'x'$ which is too low.

We have restricted ourselves in this paper to those spectra and electronic levels of molecules for which the vibrational analysis is obviously essentially correct. It is clear that if such an analysis is itself open to objection, conclusions derived therefrom will have little meaning. We take as an example the molecule CaO. The spectrum of this molecule gives rise to bands in three regions, namely, the near infra-red, blue and the near ultra-violet.¹ These three groups of bands when analysed into three systems showed no relation among themselves and had no electronic term in common. A definite correlation is therefore not possible until the relative positions of these six terms are definitely fixed. Mahanti,¹³ however, has proposed certain correlations with a view to explain the structure of the molecule analogous to that of BeO and MgO. Recently Brodersen¹⁴ proposes a different structure on the basis of an analysis which splits these three systems into ten, most of them being of a fragmentary character. In a large number of given bands where on account of perturbations it is not always possible to give an analysis free from wide discrepancies in $\Delta G(v)$ values, it happens that a few bands which show more uniform differences can be picked out and the band systems split up into a number of independent systems. In view of our knowledge of such discrepancies in almost all extensive band systems, such a procedure is open to serious objection. Moreover, Brodersen's analysis does not avoid such discrepancies at all. For example, his systems

VI and VII should have the same final state as Mahanti's ultra-violet system. The latter system gives the following values of $\Delta G(v'')$ for the progressions $v' = 0$ and 1:—

| $\Delta G(v'')$ values. | | | | | |
|-------------------------|-------|-------|-------|-------|-------------|
| $v' = 0$ | 718.4 | 710.3 | 703.7 | 697.3 | 689.9 |
| $2\omega x$ | 8.1 | 6.6 | 6.4 | 7.4 | |
| $v' = 1$ | 718.3 | 710.4 | 703.8 | 696.9 | 690.7 682.8 |
| $2\omega x$ | 7.9 | 6.6 | 6.9 | 6.2 | 7.9 |

The corresponding values for the band systems VI and VII of Brodersen are given below:—

| | | | | | |
|------------|-------------|-----|-----|-----|-----|
| System VI | $v' = 0$ | 718 | 711 | 704 | 695 |
| | $2\omega x$ | 7 | 7 | 9 | |
| | $v' = 1$ | | 711 | 704 | 695 |
| | $2\omega x$ | | 7 | 9 | |
| System VII | $v' = 0$ | 721 | 711 | 704 | 697 |
| | $2\omega x$ | 10 | 7 | 11 | |
| | $v' = 1$ | 724 | 715 | 699 | |
| | $2\omega x$ | 9 | 16 | | |

The mean values for ω and $2\omega x$ obtained by Mahanti¹⁵ for all the observed ultra-violet bands are 718.3 and 7.12 respectively. The mean for $2\omega x$ derived from the values obtained from systems VI and VII together is 9.2. If we grant that the three levels are identical, it is obvious that no accurate value of ωx can be deduced for this level and therefore of the energy of dissociation. This alone is sufficient to show that correlation of molecular and atomic terms is not possible for this molecule at the present moment. Moreover, the relative positions of the electronic levels of the molecule are

by no means conclusively established. The conditions necessary for correlation discussed above are not fulfilled and this case cannot be compared to the previous ones described in this paper.

A correlation of molecular to atomic levels appears therefore possible, by the method of vibrational extrapolation, if the probable error in D'' and D' is in the same sense (equal, positive or negative curvature, for both $\omega : v$ curves), if D'' and D' are of comparable order of magnitude, and are known from observations of about equal accuracy. Under these conditions, it is always possible to have correct correlation, provided those atomic terms of the products of dissociation which by their L and S nature are at all possible, are not too numerous in the region in question.

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