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THE HEAT OF DISSOCIATION OF DIATOMIC HYDRIDE MOLECULES

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ABSTRACT

The computation of the heats of dissociation for several diatomic hydride molecules from the vibrational data of their band spectra is given, as well as a brief discussion of an apparent discrepancy between these estimates and those deduced from the phenomenon of instability at high rotational speeds. This rotational distortion is attributed to an uncoupling action on the electronic angular momenta.

FOR many diatomic hydride molecular spectra it is difficult to apply the well-known method of Birge and Sponer for the determination of the heat of dissociation D because of the paucity of available data concerning the vibrational energy levels.[1] In some of these hydride spectra the anomalous behaviour of the rotational levels for the greatest speeds of nuclear rotation (examples; CaH, AlH bands) has been attributed to a high degree of molecular instability, and suggests the possibility of computing D from rotational data alone. Franck and Sponer,[2] in a recent discussion of several phenomena connected with the determination of heats of dissociation from band spectra, have considered this question, and have come to the conclusion that it is possible so to determine D from this maximum rotational energy in some cases where the excited electronic state is more unstable than the normal state.

There is evidence[3] that these diatomic hydrides are polar in character, thereby bringing somewhat into question the validity of the process of extrapolation of the known vibrational levels to zero separation in order to estimate D, a procedure which holds only for non-polar molecules. It is clear, however, that upon dissociation a neutral H atom results, since the excitation of the H atom involves much too large an energy. Therefore, even though the $\omega_n:n$ curve departs markedly from linearity, it should be possible to estimate the heat of dissociation, providing the data go to high enough n values to make evident the further course of the curve. It is of interest to note the accuracy of such calculations for some of the few hydride systems where the data are sufficient, and where a check on the findings exists. This check is to be found in the conservation of energy relation[4]

$$D''+E_a=E_m+D' \tag{1}$$

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[1] For a detailed discussion of diatomic hydride spectra, reference should be made to recent articles by R. S. Mulliken in this journal, particularly Phys. Rev. **33,** 730 (1929).

[2] J. Franck and H. Sponer, Göttingen Nachrichten 1928, page 241.

[3] R. S. Mulliken, Phys. Rev. **33,** 737 (1929). R. Mecke, Zeits. f. Physik **42,** 393 (1927).

[4] H. Sponer, Ergebnisse der Exakten Naturwissenschaften, **6,** 84 (1927).

where D'' and D' are the dissociation heats in the lower and upper states respectively, E_a is the energy of the excited atom or atoms (only the M atom in our examples) resulting from the dissociation of the upper molecular state, and E_m is the molecular electronic energy for the band system. The quantities D'', D', and E_m are determined from the band spectrum analysis, and the resulting E_a should equal that of a (low-lying) excited level of the M atom.

Recently G. Nakamura[5] has reported a band system in absorption for LiH which, judging from its structure, is undoubtedly the predicted ${}^1\Sigma \rightarrow {}^1\Sigma$ principal combination for this molecule. Nakamura reports that the $\omega_n:n$ curve is linear for the vibrational levels in the normal state, yielding 2.56 volts for D'', but that for the excited state the spacing of the vibrational levels first increases to a maximum at $n' \cong 7$, and then decreases in the usual fashion for higher values of n'. Such a spacing is unique among the recorded data for band systems but the necessary changes in the potential energy as a function of r, the internuclear distance, are comprehensible. The question of interest for us, however, is whether the area under this peculiar $\omega_n:n$ curve gives the correct value of D'. The extrapolation is not too long, for $n'_{\max}$ is but 30, whereas Nakamura has recorded the bands to $n'=18$. The area under this curve is 1.1 volts, while the zero-point of the system (E_m) is given as 3.2 volts. Placing these values in (1), we obtain 1.74 volts for E_a. Now the predicted state for the Li atom in this dissociation process is the 2^2P resonance level at 1.84 volts. The discrepancy is only 0.1 volt.

The writer[6] and also E. Bengtsson[7] have studied an ultra-violet beryllium hydride band system, which, because of its singlet P, R branch structure and its definitely different lower state than that of the ${}^2\Pi \rightarrow {}^2\Sigma$ green BeH bands, has been thought to be due to the BeH^+ molecular ion. A computation of the heats of dissociation involved gives additional evidence in support of this conclusion. Bengtsson gives a more accurate vibrational energy level formula, including measurements of new bands. This formula contains a very appreciable term in n'^3, which is to be expected if the emitter is indeed BeH^+, while for the lower state the $\omega_n:n$ curve is quite linear. The resulting heats of dissociation are $D'=2.52$ volts and $D''=3.66$ volts. Since the system origin, E_m, is at 4.87 volts, Eq. (1) gives $E_a=3.73$ volts. Be II has its 2^2P levels at 3.93 volts, whereas the two lowest excited levels of Be I, 2^3P and 2^1P, lie at 2.84 and 4.84 volts respectively, thus making it rather certain, in view also of the other evidence just mentioned, that a Be^+ ion results from the dissociation of this molecule. The rough calculation as follows is also corroborative of the evidence for BeH^+. The analysis of the green BeH bands shows that there is scarcely any difference in the internuclear distance for the lower and upper electronic states ($r_0'=1.34$, $r_0''=1.35$ A.U.), thereby indicating that ionized BeH is just about as stable as the neutral molecule.

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[5] G. Nakamura, Zeits. f. Physikal. Chemie **B3,** 80 (1929), and Physikertag Jena, May, 1929. Article in press.

[6] W. W. Watson, Phys. Rev. **32,** 600 (1928).

[7] E. Bengtsson, Nature, **123,** 529 (1929).

Since only the $\Delta n=0$ sequence is present in the green system, it is difficult to determine accurately D''. From the known [6,7] rotational constants of the $n''=0$ and 1 states, however, together with the formula $\omega_0^2=-4B_0^3/D_0$ and the empirical relation $2\cdot x\cdot B_0/\alpha=R\cong 1.4$ given by Birge, it is possible to estimate the coefficients ω_0'' and $\omega_0''\cdot x''$ of the n'' and n''^2 terms in the vibrational formula. One obtains in this way the values $\omega_0''=2025$ cm^{-1} and $\omega_0''\cdot x''=38.47$ cm^{-1}, from which, assuming that the $\omega_n:n$ curve is linear for this lower state (probably the normal $^2\Sigma$ state of BeH), it follows that $D''\cong 25{,}650$ cm^{-1} or approximately 3.3 volts. This value is roughly about the same as the D'' computed above for the ultra-violet bands.

The vibrational constants of the analogous $^2\Pi\rightarrow{}^2\Sigma$ MgH band system are better known,[8] and give directly $D''=2.12$ volts as the heat of dissociation for the low $^2\Sigma$ state, and $D'=2.18$ volts for the $^2\Pi$ state. These values placed in Eq. (1) give $E=2.44$ volts as against 2.70 volts for the ^3P state of the Mg atom. The agreement here would probably be better if the course of the vibrational levels were known as well as for the LiH and BeH$^+$ systems cited above. Since in the corresponding CaH bands[9] only the 0, 0 and 1, 1 bands are known, the same difficulty in estimating D'' as in the case of the green BeH system presents itself. Employing the same rather crude methods again, however, with Hulthén's rotational data for the $n''=0$ and 1 vibrational states, one obtains $D''=1.9$ volts. There is apparently a decreasing stability of the $^2\Sigma$ normal state in passing down the series BeH, MgH, CaH, . . . HgH.

There is a rather large discrepancy for some molecules between values such as these for the heats of dissociation and those estimated from the phenomena of rotational distortion, the latter estimates being very much lower (0.6 volt for the low $^2\Sigma$ CaH level). It appears possible to explain some of these rotational distortions, such as the reverse bending of the branches of a band—examples; CaH, BeH, CH λ3143,[10]—as due to changes in the couplings of the electronic angular momentum vectors brought about by the nuclear rotation. Due to this uncoupling action, the molecule is perhaps in a state of "predissociation,"[11] quite a different situation from that of the nonrotating molecule dissociating because of its vibrational energy content. It is proposed to discuss later in some detail this rotational uncoupling phenomenon.

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[8] W. W. Watson and P. Rudnick, Phys. Rev. **29**, 413 (1927). It is necessary to estimate the constants from the $n=0$, 1, and 2 vibrational levels only.

[9] E. Hulthén, Phys. Rev. **29**, 97 (1927).

[10] R. Fortrat, C. R. **178**, 1247 (1925). This band has P, Q, and R branches which are very narrow doublets at the origin. Since the order of intensity is apparently $Q>P>R$, the R branch being so weak as to be undetectable at the origin, this may be the possible $^2\Sigma\rightarrow{}^2\Pi$ transition from a higher $^2\Sigma$ state than that of the λ3900 CH band to the same lower electronic level. Cf. F. Hund, Zeits. f. Physik **51**, 779 (1928), and R. S. Mulliken, Phys. Rev. **33**, 733 (1929).

[11] Cf. J. Franck and H. Sponer, ref. 2, especially their note 3, page 249, concerning the work of Bonhoeffer and Farkas.