

THE HEAT OF DISSOCIATION OF NITROGEN

BY JOSEPH KAPLAN

UNIVERSITY OF CALIFORNIA AT LOS ANGELES

Communicated December 16, 1928

In a recent letter in *Nature*, Gaviola¹ presented evidence for a value of the heat of dissociation of the nitrogen molecule considerably smaller than the heretofore accepted value of about 11.4 volts.² The purpose of this paper is to present arguments which show that the heat of dissociation is equal to about 9.0 volts. Recently, R. T. Birge and R. S. Mulliken,³ independently of each other, arrived at the conclusion that the heat of dissociation had a value of about 9.5 volts. These arguments have been presented in letters to *Nature* and before discussing the reasons for the 9.0 volt value, a brief résumé will be given of the methods by which Birge and Mulliken arrived at their conclusions.

Birge's arguments are based on the work of Herzberg⁴ on the negative nitrogen bands. Herzberg, by an extension of the negative bands was able to obtain a better curve for the variation of the frequency of vibration with the vibrational quantum number than that obtained by Birge and Sponer.⁵ From Herzberg's data Birge obtained a value of 7.1 volts for the heat of dissociation of the normal nitrogen molecule ion. This value was obtained by Birge in such a way that it was an upper limit, the most probable value being about 0.2 volt less. Using this upper limit for D' and a value of 16.9 volts for the ionization potential of the molecule, Birge calculated D , the heat of dissociation of N_2 , and obtained a value of 9.5 volts. This was done by solving the equation

$$I_m - D' = D - I_a,$$

where I_a is the ionization potential of the atom. Since the 7.1 value is an upper limit, the value of D found above is also an upper limit. It is certainly not surprising therefore to find that D is less than 9.5 volts.

Mulliken⁶ obtained his value of 9.5 volts for D from a consideration of the products of adiabatic dissociation from the X' and A' levels of the molecule ion. The best experimental values for the total energies in these levels are 26.0 and 24.0 volts, respectively. Assuming, as Herzberg suggested, that the products of dissociation from the X' level are a nitrogen atom in the 2D state and an unexcited atomic ion, Mulliken has shown that the value of D is 9.5 volts. This value agrees quite well with the 24.0 volt total energy for the A' level. It is not possible to reconcile the old value of D with the above facts relating to the A' and X' levels. It seems certain therefore that the heat of dissociation of N_2 is equal to about 9.5 volts.

In the October 6 number of *Nature*, Herzberg calculated D , using $D' = 6.9$, $I_m = 16.7$ and $I_a = 14.5$ volts and obtained a value of 9.1 volts.

The present method for determining D , which is based on ideas entirely different from those presented by the above authors, will now be discussed. Spomer's value for the energy of the nitrogen molecule in the D level is 14.8 volts. The only bands that have been observed in transitions between the D level and other levels of the molecule are the fourth positive bands. These bands all correspond to transitions between the D_0 level and the first seven B levels. The absence of transitions from higher D levels can be explained if it is assumed that the higher D levels do not exist, i.e., that the total energy of the nitrogen molecule in the D level is almost the same as the energy in the D_0 level. It would be difficult to explain the absence of the higher transitions in any other way. The value of ω_0 for the D_0 level is only slightly greater than that in the B_0 level. This statement is qualitative and it is made on the basis of the distribution of intensity among the seven fourth-positive bands.⁷ This intensity is such as to indicate a small relative shift in the two potential energy curves of the D and B level.

It is possible to obtain a fairly good estimate of the total energy in the D level if the truth of the above arguments is granted. The vibrational energy in centimeters⁻¹ of the level having n as its vibrational quantum number is

$$\nu_n = \omega_0 n(1 - xn).$$

If the number n of the vibrational level which corresponds to $\omega_n = 0$ is called n_0 , then the limiting vibrational energy D^v is equal to

$$D^v = \omega_0 n_0(1 - xn_0).$$

In the last paragraph the assumption was made that the total energy of the D level had a value very nearly equal to 14.8 volts because of the non-existence of the D_0 and higher D levels. Therefore if n_0 is taken to be equal to unity the value of D^v so calculated will be a fair estimate of the true value of D^v . Differentiating ν_n with respect to n we obtain

$$d\nu_n/dn = \omega_0 - 2\omega_0 nx.$$

When

$$d\nu_n/dn = 0, n = n_0$$

and

$$\omega_0 - 2\omega_0 n_0 x = 0$$

$$x = \frac{1}{2n_0}.$$

Consequently

$$D^p = \omega_0 n_0 \left(1 - \frac{n_0}{2n_0} \right) = \frac{\omega_0 n_0}{2}.$$

For the D level,

$$n_0 = 1 \text{ and } D^p = \frac{\omega_0}{2}$$

Reasons have already been given for thinking that the ω_0 for the D level is only slightly greater than ω_0 for the B level. It will be assumed here that the value of w_0 is about 2000 cm.⁻¹. Obviously, the value of ω_0 won't affect the discussion very greatly. If the value of 2000 cm.⁻¹ is used then $D^p = 1000 \text{ cm.}^{-1} = 0.1 \text{ volts}$, and the total energy in the D level is equal to $14.8 + 0.1 = 14.9 \text{ volts}$.

Since the identity of the D level is not certain, Mulliken⁸ has not discussed the products of adiabatic dissociation from it. According to the arguments of both Birge and Mulliken the heat of dissociation of N_2 is certainly not much different from 9.5 volts and it is therefore possible to predict definitely the products of dissociation from the D level. There can be only two possible products of dissociation from this level and they are an atom in the 2D state and one in the 2P level. The proof of this statement follows. The energy of the atom in the 2P state is given by Compton and Boyce⁹ as 3.56 volts and that in the 2D level has been shown to be 2.39 volts. If it were assumed that the products of dissociation are two 2D atoms then the total energy in the D level would have to equal $9.5 + 4.8 = 14.3 \text{ volts}$ and this is, of course, impossible. On the other hand, if the products are assumed to be two 2P atoms, then the total energy based on $D = 9.5 \text{ volts}$ would be $9.5 + 7.1 = 16.6 \text{ volts}$. This, in view of what has been said before, is obviously too high. It seems therefore absolutely necessary to say that the products are a 2D and a 2P atom.

It is possible therefore now to calculate the heat of dissociation D from this total energy in the D level, using the fact that adiabatic dissociation results in an atom in the 2D state and one in the 2P level. The value of D so found is $14.9 - 5.9 = 9.0 \text{ volts}$. The total energies in the other levels of the molecule will now be discussed in the light of this new value for D .

The total energy in the A level has been found by Birge and Sponer to be 11.9 volts.¹⁰ If we assume that the products of dissociation are a 4S and a 2D atom, the total energy should be 11.37 volts. The difference between this and the observed value is about the same as the error in most of the other cases that are to be discussed. On most of the levels the observed value for T. E. is larger than the predicted value. Only in the case of the C level, where the extrapolation is non-linear, does the experi-

mental value turn out to be lower than the theoretical one. Mulliken¹¹ notes that in this case the extrapolation should yield a low value.

The total energy in the "a" level is 14.24 volts and the products of dissociation according to Mulliken are two ²D atoms. The predicted total energy is $9.0 + 4.8 = 13.8$ volts. It should be noted that the energy in the "a" level is known absolutely from the study of the spectrum of nitrogen in the far ultra-violet¹² and is therefore not comparable with the energy in the other levels. The error in this case is 0.4 volt and measures the error of the linear extrapolation.

In the B level the total energy is 14.6 volts and the products of dissociation are two ²D atoms. The total energy should again be equal to 13.8 volts, the difference between the experimental and observed values being 0.8 volt.

In the C level the total energy was calculated by non-linear extrapolation and has been found to be equal to 14.6 volts. The products of dissociation are a ²D and a ²P atom and the calculated total energy is therefore 14.92 volts. The error in this case is 0.3 volt and is in the expected direction since the extrapolation was non-linear, the extrapolated value being probably too small.

In conclusion it may be mentioned that the data on which the new value of 9.0 volts has been calculated has been, as far as possible that determined by a single experimenter. It seems therefore that it is justifiable to draw the conclusion that the heat of dissociation of nitrogen is 9.0 volts within the same accuracy with which Miss Sponer's results have been observed.

¹ Gaviola, *Nature*, **122**, 313, 1928.

² Birge and Sponer, *Phys. Rev.*, **28**, 259, 1926.

³ R. T. Birge, *Nature*, in press; R. S. Mulliken, *Phys. Rev.*, **32**, 761, 1928.

⁴ Herzberg, *Ann. Physik*, **86**, 189, 1928.

⁵ Birge and Sponer, loc. cit.

⁶ Mulliken, loc. cit.

⁷ Strutt, *Proc. Roy. Soc.*, **A85**, 377, 1917.

⁸ Mulliken, *Phys. Rev.*, **32**, 186, 1928.

⁹ Compton and Boyce, *Bull. Am. Phys. Soc.*, Nov. 30, 1928.

¹⁰ Birge and Sponer, loc. cit. (2).

¹¹ Mulliken, loc. cit. (8).

¹² Sponer, *Proc. Nat. Acad. Sci.*, **13**, 100, 1927; Birge and Hopfield, *Phys. Rev.*, **29**, 356A, 1927.