Products of Dissociation in Nitrogen

By JOSEPH KAPLAN
University of California at Los Angeles

(Received August 17, 1932)

Use is made of four regions of predissociation in the triplet band systems of nitrogen in order to determine the products of dissociation from the known triplet states. Mulliken's proposal that the products of dissociation in the $^3\Sigma\mu^+$ level are two ^4S atoms does not agree with the evidence which is presented here. This evidence proves that the products are a ^4S and a ^2D atom. The bearing of these results on the heat of dissociation of nitrogen is briefly discussed.

IT IS the purpose of this note to present experimental evidence showing that the $^3\Sigma$ level of nitrogen (lower level of the well-known first-positive bands) dissociates into a ^4S atom and a ^2D atom. These products of dissociation are not in agreement with the ones recently proposed by Mulliken,[1] according to whom the products of dissociation are two ^4S atoms. We will also discuss the products of dissociation from the other triplet states of nitrogen.

Naudé's[2] recent analysis of the first-positive bands shows that the lower state of these bands must be a $^3\Sigma\mu^+$ state, and Mulliken has identified it as one of the states which can be obtained from two ^4S atoms. The vibrational levels of the $^3\Sigma\mu^+$ state have been followed to 2.1 volts above $v=0$, so that the heat of dissociation into two unexcited atoms must be equal to or greater than 2.1 volts plus the energy of $v=0$ of $^3\Sigma\mu^+$ to which we will sometimes refer as A_0. Recent experimental evidence has indicated that the heat of dissociation into normal atoms must be lower than the value of 9.1 volts, which has been proposed by Birge[3] and others,[4,5,6] probably as low as 8.2 volts. The $^3\Sigma\mu^+$ level must therefore be no higher than $9.1-2.1=7.0$ volts, and it may even be as low as $8.2-2.1=6.1$ volts, provided Mulliken's suggestion as to the products of dissociation is correct. The 6.1 volt value seems to be extremely low when compared with Sponer's 8.2 volt value for that energy.

We will now present the argument which will show that the products of dissociation of the $^3\Sigma\mu^+$ state are a ^2D and a ^4S atom. Elsewhere,[7] we have called attention to the phenomenon of missing heads in the first-positive bands in nitrogen, and this was ascribed to predissociation of the molecule. The effect is beautifully shown in bands which originate on $v=13$, 14, 15 of the

[1] Mulliken, Rev. Mod. Phys. **4,** 53 (1932).
[2] S. M. Naudé, Proc. Roy. Soc. **136,** 114 (1932).
[3] Birge, T. Faraday Soc. **25,** 713 (1929).
[4] Kaplan, Proc. Nat. Acad. **15,** 226 (1929).
[5] Tate and Lozier, Phys. Rev. **39,** 224 (1932).
[6] Sutton, Nature **130,** 132 (1932).
[7] Kaplan, Phys. Rev. **37,** 1406 (1931).

$^3\Pi g$ upper state of the first-positive bands. The one head, which does appear with any appreciable intensity, is very weak compared with the intensity of the corresponding head of the normal neighboring bands. Now the energy of $v=13$ is about 3.6 volts higher than the energy of $v=0$ of $^3\Sigma\mu^+$ and since strong predissociation occurs at this energy, it is certainly equal to or greater than the energy required to dissociate the molecule into two atoms. It is of course impossible to give the exact value of D in terms of the energy of $^3\Sigma\mu^+$ and this 3.6 volt value, because we cannot say definitely what the setting in of predissociation at $v=13$ means. The energy of $v=13$ may correspond very closely to the energy required to dissociate N_2 into two particles and again it may be somewhat larger.

There is another region of predissociation, however, similar to the one at $v=13$, and this region of single-headed bands begins at $v=20$. The difference between $v=20$ and $v=13$ is about 1.1 volts, and the difference between the $^2P(3.56)$ and $^2D(2.37)$ metastable states of atomic nitrogen is about 1.2 volts. The agreement between the two values suggests that the first region of predissociation involves a ^2D atom, and that the second region involves a ^2P atom. The only reasonable interpretation of the above results is that the first region corresponds to dissociation into a ^4S and a ^2D atom, and that the second region corresponds to dissociation into a ^4S and a ^2P atom. Hence, if A_0 is the energy of $v=0$ of $^3\Sigma\mu^+$, then $D \leqq A_0+3.6-2.37=A_0+1.2$ volts.

The predissociation at $v=13$ can also be compared with the predissociation at $v=4$ in the initial $^3\Pi$ state of the second-positive bands. The bands which arise in $v=4$ are the last ones of a sequence; there are no bands originating on $v=5$ or higher. This sudden curtailment of the band system is ascribed to predissociation. The energy of $v=4$ is 5.76 volts higher than the energy A_0, so that if $D \leqq A_0+1.2$, the energy $A_0+5.76$ volts must correspond to dissociation into two ^2D atoms, since that would require an energy of $D+2(2.37)$ or $A_0+5.94$ volts. The agreement between the calculation and the experiment is quite good since in order to compare with the previously discussed predissociation we should use the energy of $v=5$ rather than that of $v=4$. The energy of $v=5$ is about $A_0+5.95$ volts, so the agreement in this case is almost perfect.

The energy of the $v=5$ level of the initial state of the second-positive bands is about $A_0+5.95$ volts, and the energy in $v=13$ is $A_0+3.6$ volts. The difference between these two is 2.35 volts, and the energy of ^2D is 2.37 volts. This remarkable agreement certainly indicates that our arguments are consistent and probably correct.

The initial state of the fourth-positive group of nitrogen is the so-called D level, and only the $v=0$ level has ever been observed. The energy of the $v=1$ level is about $A_0+6.9$ volts, and the energy required for the production of a ^2D and a ^2P atom is equal to or less than $A_0+1.2+2.37+3.56$, i.e., $A_0+7.1$ volts. It seems reasonable once more to assign the non-appearance of higher vibrational levels to predissociation. It should be noted that we have made no use of an actual value for the energy of A_0, since this energy is known only by electron impact measurements. A strong point in the present argument lies in the fact that we have made no use of this value.

We concluded from the first example of predissociation, namely, the one at $v=13$ in $^3\Pi g$, that the heat of dissociation D was equal to or less than A_0 $+1.2$ volts. Since the $A^3\Sigma\mu^+$ level has been followed to at least 2.1 volts of vibrational energy, it must be concluded that the products of dissociation are not two ^4S atoms as Mulliken suggested, but that at least one excited atom is involved.

If we assume that D lies between 9.1 and 8.2 volts, then A_0 will lie between 7.9 and 7.0 volts, if the products of dissociation in $v=13$ are ^4S and ^2D. If we assume with Mulliken that the products of dissociation in $^3\Sigma\mu^+$ are two ^4S atoms, then D cannot be equal to $A_0+1.2$ volts, since the vibrational levels have been followed to $A_0+2.1$ volts. We must conclude then that the predissociation at $v=13$ corresponds to dissociation into two ^4S atoms, and D will be equal to or less than $A_0+3.6$. This would yield values for A_0 lying between 5.5 and 4.6 volts, and it is obvious that not even excitation potential measurements would account for the enormous difference between these values and the 8.2 volt value of Sponer. We must conclude that the products of dissociation from the $^3\Sigma\mu^+$ level are ^4S and an excited atom, probably ^2D. The triplet level due to two ^4S atoms is therefore not known, and it will be an interesting problem to try to obtain evidence for its existence.

The predissociation phenomena which have been discussed in this note, enable us to suggest the identity of the products of dissociation from the several triplet states of N_2. We have proved that the $^3\Sigma\mu^+$ level dissociates into an excited atom and a normal atom, and if we say that, in general, a linear extrapolation of the vibrational levels yields a value of the total energy which is too high, then there is no choice for the excited atom but the ^2D metastable state. The linear extrapolation yields a value of 11.9 volts, and predissociation sets in at 11.8 volts, and this makes $D \leqq 9.4$ volts. For the B level the linear extrapolation yields 14.62 volts, and if we use the 9.4 volt value for D the energy required to produce two ^2D atoms is 14.2 volts, hence the identity of the products of dissociation as two ^2D atoms is quite reasonable. For the C level, the products cannot be two ^2D atoms because predissociation sets in at that energy in a manner which shows that higher vibrational levels exist. The linear extrapolation yields a value of 14.62 volts for the total energy, and 15.3 volts are required to produce one ^2D and one ^2P atom. This is therefore an exceptional case in which the linear extrapolation must be too low.

TABLE I.

Predissociating level	Energy based on $A_0=8.2$	Products of dissociation	Heat of dissociation
B_{13}	11.78	$^4S+^2D$	9.4 or less
B_{20}	12.87	$^4S+^2P$	9.3 " "
C_5	14.14	$^2D+^2D$	9.4 " "
D_1	About 15.05	$^2D+^2P$	9.1 " "

The results of this paper are summarized in Tables I and II. The derived values of D are obviously too high in most cases because predissociation sets in at an energy in general higher than that required to dissociate the molecule.

TABLE II.[8]

Birge	9.04 ± 0.2 volts
Kaplan	9.0 "
Tate and Lozier	8.4 ± 0.5 volts
(corrected by Sutton)	9.0 volts

This is in good agreement with Table II of recent values of D, taken from a letter by Sutton.[8] The evidence indicates that D is probably slightly less than 9.0 volts because the data of Table I are based on Sponer's 8.2 volt value for A_0, and all of these values will have to be lowered by the same amount as the 8.2 volt value is lowered. Even though no definite conclusion can be drawn regarding the value of the heat of dissociation of nitrogen it is clear from this paper that the upper limit is about 9.3 volts, and probably even lower, because the 8.2 value of Sponer is too high.

[8] Sutton, Nature **130**, 132 (1932).