

NOTE ON THE STRUCTURE OF N_2^+ AND ITS BEARING ON THE THEORY OF VALENCY.

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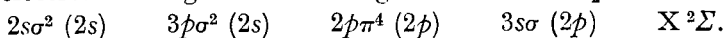
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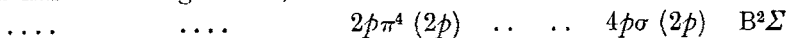
RECENTLY we have discussed relations between bond energies and electronic configurations in a number of diatomic molecules.¹ In the present paper we intend to apply the same ideas to the molecule (N_2^+) for which the actual value of D'' ($X^2\Sigma$) has been calculated in the preceding communication.²

The molecule N_2^+ has the same number of electrons as CN and is therefore of special interest. It may be recalled that Heitler and Herzberg³ tried to interpret the dissociation products of the ground level of CN as $C\ sp^3\ ^5S + N\ ^4S$, but this correlation was untenable because the excitation energy of $C\ ^5S$ is much larger than these authors supposed. Now-a-days it is generally assumed that the intersections of the potential curves indicated by the vibrational extrapolation are not real. The $C\ ^2\Sigma$ term of N_2^+ recently found by Watson and Koontz⁴ 6.67 e.v., above ($X^2\Sigma$) shows however, an energy of dissociation which is much bigger than that of the ground level. Vibrational extrapolation neglecting the cubic term with $\omega_e y_e$, gives for D ($X^2\Sigma$), 9.23, for D ($B^2\Sigma$), 8.46 using the accepted constants and D ($C^2\Sigma$), 13.84 e.v. with constants given by Watson and Koontz. The excitation energies of the dissociation products are therefore 2.58 e.v. for $B^2\Sigma$ and 11.28 for $C^2\Sigma$ (see Fig. 1).* ($B^2\Sigma$ lies 3.15 e.v. above the ground level of the molecule.

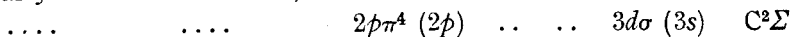
The electronic configuration of the ground level of N_2^+ is⁵ :—



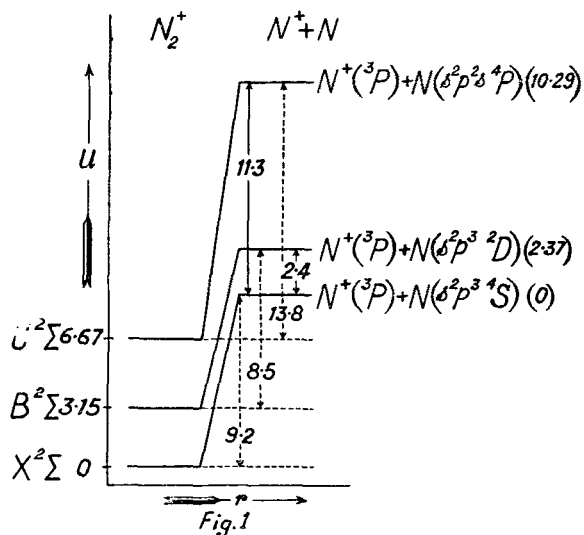
This is the energetically lowest possible configuration for the internuclear distance prevailing in N_2^+ . The excitation of the single $3s\sigma (2p)$ electron to the following π^* group produces a $^2\Pi$ term as actually observed in CN but not yet in N_2^+ . The groups next in order, are $\sigma^* (2p)$ and $\sigma (3s)$. Therefore the term $B^2\Sigma$ has the configuration,



and similarly the term $C^2\Sigma$ has,

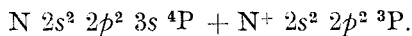


* The extrapolation taking into account the cubic terms in the equation given by Watson and Koontz yields D ($X^2\Sigma$) = 8.06 and D ($C^2\Sigma$) = 11.59 e. v. The excitation energy will then be $E = 10.20$ e. v., which is almost exactly the value of $N\ ^4P$ at 10.29 e.v.



These are the configurations in their energetical order. It follows that the dissociation products of $B^2\Sigma$ are still two atoms which together have five $2p$ electrons, whereas those of $C^2\Sigma$ are two atoms possessing four $2p$ and one $3s$ electrons. N^+ has only singlet terms near 2.38 e.v., but these do not yield in combination with N^4S a molecular doublet term. Therefore the dissociation products of $B^2\Sigma$ will be $N^+ s^2 p^2 {}^3P + N s^2 p^3 {}^2D$. The excitation energy of N^2D is indeed 2.37 e.v.⁶ This combination is the same as that which is accepted for the corresponding $B^2\Sigma$ term of CN .

The term $C^2\Sigma$ may dissociate either into $N 2s^2 2p^3 {}^4S + N^+ 2s^2 2p^2 3s$ or into $N 2s^2 2p^2 3s + N^+ 2s^2 2p^2 {}^3P$. But the lowest term of the former combination with excited N^+ , *i.e.*, $N^+ {}^3P$, lies at 18.37 e.v.⁶ and is therefore too high. On the other hand the lowest term of excited N , which possesses a $3s$ electron is the term 4P at 10.29 e.v.⁶ above the ground level. This is in very good agreement with the extrapolated difference of 11.28 e.v. within the error of this method, and shows that the products of dissociation of the $C^2\Sigma$ term are



This correlation shows that in the ground state N_2^+ possesses a double link which is to a certain extent disturbed by the odd p electron. On excitation of this electron to the next orbital as in $B^2\Sigma$, which process does not involve a change of the main quantum number but means only a rearrangement of the l and s vectors, the linkage is slightly

weakened by excitation. If, however, N^+ combines with a N atom in which this odd electron is removed to the next orbit, a molecular term results, *viz.*, $C \ ^2\Sigma$, in which the bond is considerably strengthened. Indeed if this electron would be entirely removed from the atom the molecule would resemble in respect of stability, the molecule CO in which the free valencies of the two atoms just match each other. The molecule N_2^+ therefore furnishes another example in support of the pair-bond theory of valency. A further significance attaches itself to this correlation of the new term $C \ ^2\Sigma$. The rôle of the disturbing electron has been pointed out⁷ in many earlier cases where, however, the odd electron always has been, a promoted one. The view of the pair-bond theory though more straightforward was not entirely conclusive, as far as the odd electron was concerned. The decision against the hypothesis of single bonding and anti-bonding electrons was based more on other considerations, *e.g.*, the nonbonding character of the s^2 group in the presence of an excess of bonding electrons, the course of the dissociation energies, etc. The odd electron of N_2^+ , *i.e.*, $3s \sigma (2p)$ furnishes the first example of a non-promoted electron (which should be bonding in the theory of molecular orbitals), whose excitation to an orbital of higher energy strengthens the bond. This is in direct contradiction with the hypothesis of bonding and anti-bonding electrons and shows that such classification of single electrons according to the orbitals is not possible. The behaviour of N_2^+ indicates that promotion has, on the linkage, only a secondary effect superimposed on the primary one produced essentially by the pairing of electrons.

In the preceding paper the actual value of $D'' (N_2^+ \ X \ ^2\Sigma)$ has been determined as 6.18 e.v. On the basis of the above correlations, *i.e.*, using the values of the excitation energies of $2p^3 \ ^1D$ and $2p^2 \ 3s \ ^4P$ of N (2.37 and 10.29 e.v. respectively⁶) the actual values of the energies of dissociation of the excited terms can now be calculated. In this way $D' (B \ ^2\Sigma)$ is 5.40 and $D' (C \ ^2\Sigma)$ 9.80 e.v. It will be seen that the former is only slightly lower than $D'' (X \ ^2\Sigma)$ whereas the latter is indeed very near to that of $D'' (CO)$. In this connection, attention should be directed to the fact, that the electron configurations determined for N_2^+ obviously hold good for CN also. From this it follows, that the spectroscopically known CN molecule possesses a double bond only and a free electron belonging essentially to the N atom. Its chemical formula therefore is $C = N -$, or in other words it is the radical of the isonitriles. Attempts which have been made to calculate its energy of dissociation from thermochemical data obtained from HCN which definitely contains the $-C \equiv N$ radical or from $(CN)_2$ which probably has it, are therefore not permissible. This radical constitutes a higher electronic term of $C = N -$

involving a C atom in which one of the 2s electrons has been excited to 2p, probably a C 5S atom.*

The disturbing rôle played by the odd electron can also be seen from the dissociation energies of the ground levels of a number of molecules in the neutral and ionised states, derived in the preceding paper. These figures are not obtained by extrapolation but from direct experimental data and represent within a very few tenths of a volt the actual values of D'' . They are as follows :—

Molecule	CO	CO ⁺	N ₂	N ₂ ⁺	NO	NO ⁺	O ₂	O ₂ ⁺	Cl ₂	Cl ₂ ⁺
D'' (e. v.)	10.45	7.57 or 9.9	7.35	6.18	5.3	9.4 or 13.3	5.05	6.10	2.47	2.2

The values for NO⁺ and Cl₂⁺ have been calculated in the same way and included for comparison. For CO⁺ two values are given, the first referring to C⁺ + O, the second to C + O⁺, their respective merits being discussed in the preceding paper. Again for D'' (NO⁺), 9.4 e.v., refers to N + O⁺, and 10.3 e.v., to N⁺ + O, which is more probable, the odd electron of NO belonging essentially to the N atom. It can be seen that in a molecule which does not possess odd electrons but has a $^1\Sigma$ ground level, like CO, N₂ or Cl₂, the bond is weakened if an electron is removed by ionisation, whereas it is strengthened in those molecules which possess free valencies as NO (X $^2\Pi$) or O₂ (X $^3\Sigma$). The small change for CO, and Cl₂ suggests that in these saturated molecules the ionisation refers to one of the p-electrons not taking part in the linkage, which in the separated system form a closed orbital in O and Cl respectively.

The results described in this paper are, to our mind, a further essential proof of the correctness of the pair-bond theory of valency and confirm the conclusions already reached in earlier papers.

* G. Nordheim (*Ann. D. Physics*, 1936, 26, 258, cf. W. Heitler and G. Poschl, *Nature*, 1934, 133, 833) suggests that the ground level $^2\Sigma$ of CN is brought about by resonance between terms involving N (4S) + C (3P) and N (4S) + C (5S). Indeed, otherwise according to the Heitler-London theory in which the terms of the separated atoms determine these of the molecule, the ground level of CN or N₂⁺ should be the same as that of NO, i.e., $^2\Pi$. It is therefore gratifying to see that the potential curve of $^2\Sigma$ lies, at small internuclear distances, lower than that of $^2\Pi$ on account of strong repulsion brought about by a higher $^2\Sigma$ term. There is, however, no experimental evidence that this involves, to any practical extent, also a hybridisation of the two forms C = N — and — C ≡ N. At least in the lower part of the potential curve of X $^2\Sigma$ which is under direct band spectroscopical observation, no strong perturbations, disturbing the positions of the vibrational levels occur, either in CN or N₂⁺ and the linear extrapolation for the excitation energy of the dissociation products leads directly to term differences of the separated atoms which are in no way modified.

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