

layer increases the back resistance and decreases the capacity of the contact, improving the rectification efficiency. The quantitative results of these calculations have been used only to demonstrate the reasonableness of the assump-

tions and to illustrate the direction of the effects.

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On the Electronic Structure of the Nitrogen Molecule

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It is shown that the Lyman-Birge-Hopfield bands of nitrogen represent a forbidden ${}^1\Pi_g - {}^1\Sigma_g^+$ transition. A considerable difficulty in the interpretation of the electronic states of N_2 by electron configurations is thus removed. A revised electronic energy level diagram of N_2 is given.

THE Lyman-Birge-Hopfield ($a-X$) bands of nitrogen have been considered a ${}^1\Pi_u - {}^1\Sigma_g^+$ transition ever since it was established¹ that each band has a P , a Q , and an R branch. However, on this basis a serious difficulty arises in the interpretation of the upper state of the $a-X$ bands by means of electron configurations. The lower state (X) of these bands is the ground state of the N_2 molecule whose electron con-

figuration is

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2, \quad (1)$$

where KK stands for the two K shells. The two lowest unoccupied orbitals are $(\pi_g 2p)$ and $(\sigma_u 2p)$, in this order, both of which are antibonding. Since, as shown by the N_2^+ spectrum, the orbitals $(\pi_u 2p)$ and $(\sigma_g 2p)$ have nearly the same energy, the lowest excited states of N_2 would be expected to belong to the following configurations:

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)(\pi_g 2p); \quad {}^1\Pi_g, {}^3\Pi_g, \quad (2)$$

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^3(\sigma_g 2p)^2(\pi_g 2p); \quad {}^1\Sigma_u^+, {}^3\Sigma_u^+, {}^1\Delta_u, {}^3\Delta_u, {}^1\Sigma_u^-, {}^3\Sigma_u^-, \quad (3)$$

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)(\sigma_u 2p); \quad {}^1\Sigma_u^+, {}^3\Sigma_u^+, \quad (4)$$

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^3(\sigma_g 2p)^2(\sigma_u 2p); \quad {}^1\Pi_g, {}^3\Pi_g. \quad (5)$$

They give rise to the states indicated at the right. Two of these, ${}^3\Sigma_u^+$ and ${}^3\Pi_g$, account readily for the two lowest observed triplet states A ${}^3\Sigma_u^+$ and B ${}^3\Pi_g$ of N_2 (compare the energy level diagram in Fig. 1) but a ${}^1\Pi_u$ state cannot be accounted for in this way. An electron configuration of higher energy would be required, which contradicts the fact that a ${}^1\Pi$ is a low, if not the lowest, excited singlet state.^{1a}

¹ E. T. S. Appleyard, *Phys. Rev.* **41**, 254 (1932); W. W. Watson and P. G. Koontz, *Phys. Rev.* **46**, 32 (1934); J. W. T. Spinks, *Can. J. Research* **A20**, 1 (1942).

^{1a} Compare R. S. Mulliken [*Rev. Mod. Phys.* **4**, 1 (1932)] and A. Recknagel [*Zeits. f. Physik* **87**, 375 (1934)] who have calculated the energies of the predicted low lying states. Both authors have emphasized the importance of the above mentioned difficulty.

This difficulty can now be resolved by a new interpretation of the Lyman-Birge-Hopfield bands made necessary by recent findings of new singlet band systems of nitrogen by Herman,² Gaydon,³ and Worley.^{4,5}

As has been recognized by Herman, the upper state of the new singlet bands found by her is identical with the upper state of the ultraviolet emission bands $h-X$ found by Watson and Koontz¹ while their lower state is the upper

² R. Herman, *Comptes Rendus* **217**, 141 (1943).

³ A. G. Gaydon, *Proc. Roy. Soc.* **182**, 285 (1944).

⁴ R. E. Worley, *Phys. Rev.* **64**, 207 (1943); **65**, 249 (1944).

⁵ A. G. Gaydon and R. E. Worley, *Nature* **153**, 747 (1944).



The upper state of another new singlet system,

⁶ To be sure Worley (references 4, 5) assumes the 0-0 band of the $m-X$ system to be unobserved and to lie at considerably longer wave-lengths. However, the agreement

Thus there are in N_2 two sets of three states $-X, a, h(\equiv l')$ and $X, a, m(\equiv q')$ —such that all three transitions in each set are observed (see Fig. 1). Such a situation is possible in a homonuclear molecule like N_2 only if one of the three transitions is a forbidden transition violating the (g, u) rule (i.e., the rule that even states combine only with odd). The question then arises which transition in each set is forbidden. Herman, who realized the necessity of a forbidden transition for the group X, a, h , assumed the $h-a$ transition to be forbidden. However, since the $h-X$ bands have a very high transition probability as shown by their occurrence in absorption with a path of only 0.2 mm at atmospheric pressure (see Worley⁴), it seems quite impossible that the $h-a$ bands could be observed in emission with moderate intensity if they represent a transition violating the (g, u) rule. An allowed transition to the ground state would take place long before the forbidden transition to the a level could occur. A corresponding difficulty arises for the assumption that the transition $m-a$ of the second set contradicts the (g, u) rule. These difficulties do not arise if it is assumed that the forbidden transition in either set is $a-X$, that is, that the *Lyman-Birge-Hopfield bands represent a ${}^1\Pi_g-{}^1\Sigma_g^+$ transition not ${}^1\Pi_u-{}^1\Sigma_g^+$ as hitherto assumed.* Unlike the previous cases there is here no other transition that competes with $a-X$ in depleting the number of molecules in the a state. The effect of collisions in reducing the number of molecules in the $a {}^1\Pi_g$ state probably accounts for the comparatively low intensity of the $a-X$ bands in emission particularly at high pressure.

There is possibly a third set of the type described above: The upper state c of one of the systems found by Birge and Hopfield⁷ in emission and by Worley⁴ in absorption may be identical with the upper state p' of one of Gaydon's systems whose lower state is $a {}^1\Pi_g$. While Gay-

don's p' state is fairly definitely a ${}^1\Sigma$ state, the c state is considered by Worley to be ${}^1\Pi$. However, it appears that the far ultraviolet data can also be accounted for on the assumption of a ${}^1\Sigma$ state so that p' and c could be identical. The B value of the c state which does agree with that of the p' state is somewhat in doubt since on its basis it is difficult to account for the great length of the v'' progression observed in emission.

The interpretation of the $a-X$ bands as a forbidden ${}^1\Pi_g-{}^1\Sigma_g^+$ transition is also in satisfactory agreement with the observed intensity of absorption. The absorption spectrogram published by Birge and Hopfield⁷ was obtained with an absorbing path of as much as 40 cm at atmospheric pressure and even at that the bands do not appear to be particularly strong. A ${}^1\Pi_g-{}^1\Sigma_g^+$ transition can occur as magnetic

TABLE I. Singlet states of the nitrogen molecule^a (revision of Gaydon and Worley's table, reference 6).

State	$A_0(\text{cm}^{-1})^b$ (excitation energy of lowest observed vibrational level)	$B_0(\text{cm}^{-1})$	$\Delta G_3(\text{cm}^{-1})$
$y^1\Pi_g$	$a'+46,420$	1.80	1705
$x^1\Sigma_g^-$	$a'+45,463$	1.73 ₅	1869
$w^1\Sigma_g^-$	$a'+40,914$	>1.47	1711?
$v^1\Sigma_u$	121,247 <i>H</i>	$\lesssim 1.9$	925
$u^1\Sigma_u^+$	120,584.6 <i>H</i>	1.07	533
$l^1\Sigma_u$	118,487.3 <i>H</i>	1.16	482
$s^1\Sigma_u$	116,683 <i>H</i>	1.11	522
$h \equiv l'^1\Sigma_u^+$	112,774.2	1.63	
$r^1\Sigma_u^+$	110,944.5 <i>H</i>	1.07	640
$s'^1\Sigma_u^+$	110,662.0	1.58 ₅	
$f^1\Sigma_u$	110,190 <i>H</i>	$\lesssim 1.9$	
$q^1\Pi_u$	109,832.8 <i>H</i>	1.11	697
$g^1\Sigma_u$	108,950 <i>H</i>	<1.99	
$p^1\Pi_u$	108,372.2 <i>H</i>	1.21	749
$o^1\Sigma_u$	107,657.0 <i>H</i> ^c	$\lesssim 1.8$	1918
$r'^1\Sigma_u^+$	106,373.5	1.67	
$m \equiv q'^1\Pi_u$	105,351.1	1.36 ₅	760
$\{p'^1\Sigma_u^+, c^1\Pi_u\}$	104,327.9	1.93	
$\{c^1\Pi_u, b'^1\Sigma_u^+\}$	104,316.1 <i>H</i>	1.92	2180
$b'^1\Sigma_u^+$	103,678 <i>H</i> ^d	1.44	741
$b^1\Pi_u$	101,456.0 <i>H</i>	1.41	698
$a'^1\Sigma_u^-$?	1.47	1504
$j^1\Sigma_u^+$	100,821.4?	1.45	
$i^1\Sigma_u$	98,486 <i>H</i>	$\sim 1.5?$	670
$a^1\Pi_g$	68,956.6	1.62	1666.7
$X^1\Sigma_g^+$	0	1.99 ₅	2330.7

^a Upper states of Rydberg series are not included.

^b An *H* indicates a value obtained from the measurement of band heads (Worley's Table IV). Gaydon has given band origins for his new bands and has based his energy values for the upper states on the value 68,956.6 for $a {}^1\Pi$. He does not state how this value was obtained. From Birge and Hopfield's value for ν_{00} of the $a-X$ bands which refers to band heads the writer obtains 68,954.3 cm^{-1} referred to band origins. The difference is probably within the accuracy of the ultraviolet measurements and no change from Gaydon's data was made in Table I.

^c Or 105,694.5 and $\Delta G_3 = 1962$.

^d This is Birge and Hopfield's value. Tschulanowsky (Bull. Acad. Sci. USSR, p. 1313 (1935)) gives a considerably higher value (103,767.06) which, though based on band origins, depends on a rather long extrapolation.

⁷ R. T. Birge and J. J. Hopfield, *Astrophys. J.* **68**, 257 (1928).

dipole radiation. As is well known, the atmospheric oxygen bands represent a magnetic dipole transition which is at the same time a singlet-triplet intercombination. They occur weakly in an absorbing path of 1000 cm. To obtain them with an intensity comparable to that of the $a-X$ bands of N_2 on Birge and Hopfield's spectrogram would require an absorbing path about 10,000 cm long. According to Van Vleck⁸ a magnetic dipole transition that is not an intercombination is expected to be about 10^4 times brighter than one that is an intercombination. Therefore about 1-cm absorbing path would be required for a non-intercombination magnetic dipole transition. The fact that the observed absorption intensity of the Lyman-Birge-Hopfield bands is even less than this theoretical estimate⁹ makes it rather certain, even apart from the previous argument, that they represent a forbidden (${}^1\Pi_g-{}^1\Sigma_g^+$) transition. The allowed transitions from the ground state found by Worley are observed to be about 2000 times stronger than the Lyman-Birge-Hopfield bands.

It should perhaps be pointed out that the rotational fine structure of a magnetic dipole ${}^1\Pi_g-{}^1\Sigma_g^+$ transition is the same (including the intensity alternation) as that of an ordinary dipole ${}^1\Pi_u-{}^1\Sigma_g^+$ transition except that the opposite Λ -doubling components form the upper states of Q and P , R branches. Since in none of the bands discussed here the Λ -type doubling has been resolved, the observed fine structure is equally compatible with either interpretation. If very precise data were available one would find that the combination differences of the lower state obtained from the P and R branches of the $h-a$ and $m-a$ bands would not agree exactly with those of the upper state obtained from the P and R branches of the $a-X$ bands.

From all these reasons the conclusion that the a state of nitrogen is ${}^1\Pi_g$ not ${}^1\Pi_u$ seems to be well established. At the same time the difficulty with the electron configuration mentioned at the beginning is removed. A low ${}^1\Pi_g$ is expected from

the electron configuration (2) above, the same electron configuration that accounts for the $B\ {}^3\Pi_g$ state. In agreement with expectation the ${}^3\Pi$ state is lower than the ${}^1\Pi$ of the same electron configuration. Also the two states have very similar ω_e and B_e values (1694.7 and 1.642 for $a\ {}^1\Pi$ and 1732.8 and 1.6430 for $B\ {}^3\Pi$) as expected if they have the same electron configuration. In this way one of the most unsatisfactory points in the interpretation of electronic states of diatomic molecules by electron configurations is cleared up.

On the basis of the above discussion the interpretation of the upper states of the new singlet bands found by Gaydon has of course to be changed. In particular the states q' and q'' of Gaydon (see above) are ${}^1\Sigma_u^+$ and ${}^1\Pi_u$, respectively, not ${}^1\Sigma_g^-$ and ${}^1\Pi_g$ as assumed by Gaydon. These are the term types indicated in Fig. 1. The revised types are indeed easier to account for on the basis of electron configurations than were Gaydon's types.

For the convenience of the reader, Table I lists the known data about the singlet states of nitrogen in the revised version. Unlike the similar table by Gaydon and Worley,⁵ Table I gives the energy of the lowest observed vibrational level rather than that of an extrapolated $v=0$ level since at least in the case of the m state such an extrapolation seems to lead to erroneous results.⁶ The states $a'\ {}^1\Sigma_u^-$ and $j\ {}^1\Sigma_u^+$ very probably belong to the same electron configuration [(3) above] as $A\ {}^3\Sigma_u^+$ thus accounting for three of the six states resulting from this configuration. Again the constants ω_e and B_e of these three states are very similar. The exact position of the a' state cannot be derived from the observations. In Fig. 1 it has been placed above $j\ {}^1\Sigma_u^+$ since theoretical calculations by Recknagel^{1a} indicate such an order. Gaydon^{3,5} has assumed it to be as low as 60,000 cm^{-1} .

I would like to express my appreciation to Professor R. S. Mulliken for a stimulating discussion of the subject of this paper.

Note added in proof: A more detailed paper by R. Herman-Montagne (Ann. de physique 20, 241, (1945)) has just been received here. In this paper a number of further band systems of N_2 are found and further energy levels established. Unfortunately these could not be included in Fig. 1 and Table I.

⁸ J. H. Van Vleck, *Astrophys. J.* 80, 161 (1934).

⁹ For a more accurate estimate the difference in frequency of the atmospheric oxygen bands and the $a-X$ nitrogen bands would have to be considered. It would increase the theoretical intensity of the latter by about a factor 5.