

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Electronic Structure of the a-X Band System of N₂

By using a powerful discharge in pure nitrogen it has been found possible to photograph certain bands belonging to this system¹ in the first order of a twenty-one foot Rowland grating. The nitrogen was prepared from pre-baked sodium azide, and was allowed to stream through the discharge tube during the progress of a 48 hour exposure. Copper lines served as wave-length standards² and the very faint bands were measured using a cylindrical lens so as to eliminate the effect of plate grain. Every line was measured about twenty times in order to minimize error. The bands $\lambda\lambda 2006.01$ (3-11), 2023.48 (4-12), 2041.16 (5-13), 2059.04 (6-14), 2125.92 (5-14), 2143.95 (6-15), 2162.27 (7-16) were visible on the plates but only $\lambda 2041.16$ and $\lambda 2125.92$ were sufficiently developed to allow of measuring the branches.

The system is almost certainly a singlet transition to the ground state $^1\Sigma_g^+$ of nitrogen for it is the only strong system yet observed in absorption.³ Accepting this idea, the experimental results are to be explained by the assumption that it is a $^1\Pi_u - ^1\Sigma_g^+$ transition. All the bands show in addition to the head measured by Hopfield and Birge a faint second head displaced towards longer wave-lengths by about 13 cm^{-1} though only sharp and clear in the case of $\lambda 2125.92$ which is the best exposed band. In other bands it can however be made quite distinct by enlargement on contrasty film and subsequent superposition of the enlargements⁴ so as to enhance the photographic contrast. It is natural to account for this as a Q head. Unfortunately, the resolving power is too small to allow one to measure the branches in the neighborhood of the head, and where the series are resolved, (at about the twentieth member of the Q branch) the R branch is so faint that it occurs only as a few stray lines very difficult to

measure. A provisional analysis from the Q and P branches of (5-13) and (5-14) gives $B_5' = 1.5207 \pm 0.001\text{ cm}^{-1}$, $B_{13}'' = 1.7625 \pm 0.001\text{ cm}^{-1}$ and $B_{14}'' = 1.7424 \pm 0.003\text{ cm}^{-1}$, neglecting the contribution due to Λ -doubling which must be very small, since the stray R lines lie in their predicted positions as far as they can be measured. This assignment of constants accounts for the positions of all measured lines and heads to within experimental error, and, by using an estimated effective temperature, for their intensity also. One may say therefore with some confidence that this system is indeed a $^1\Pi_u - ^1\Sigma_g^+$ transition.

To account for the existence of a $^1\Pi_u$ level in this position seems very difficult, as Mulliken,⁵ has pointed out. If we assume with Hund⁶ that it has the electronic structure $\sigma_u^2 2s\pi_u^4 2p\sigma_g 2p\pi_u 3p$ then the $\pi_u 3p$ electron should be strongly bonding in character since it has descended from the high energy atomic orbit $3p$. This, experimentally, appears not to be the case.

Two other bands with heads at $\lambda 2033.6$ and $\lambda 2112.1$ also show on the plates. They are obscured by members of the a-X system but

¹ Birge and Hopfield, *Astrophys. J.* **68**, 257 (1928).

² Burns and Walters, *Allegheny Observatory Vol. 8*, No. 3. (Corrected by supplementary circular.)

³ Hopfield (*Phys. Rev.* **31**, 1131, (1928)) has reported a progression of bands in absorption whose upper level lies below the 'a' level. This might be the $^3\Pi_u$ level corresponding to the $^1\Pi_u$ of this system; but the spacings of the vibrational levels appear unfavourable to this interpretation.

⁴ Oldenberg, *Zeits. f. Physik* **58**, 722 (1929).

⁵ Mulliken, *Rev. Mod. Phys.* **4**, 53 (1932).

⁶ Hund, *Zeits. f. Physik* **63**, 749 (1930).

are strongly degraded to the violet; the best exposed shows strongly alternating intensities; hence it is certainly due to nitrogen or to ionized nitrogen. It has the appearance of a single branch whose spacing rapidly increases towards shorter wave-lengths. These bands appear not to have been observed before.

A more complete investigation of the a -X system is proposed in the near future using a large vacuum spectrograph.

E. T. S. APPELYARD

Ryerson Physical Laboratory,
University of Chicago,
June 26, 1932.

Deposition of Chromium on Glass

R. Ritschl¹ has perfected a simple apparatus with which a uniform half-silvering can be done on Fabry-Perot interferometer plates. The film is put on by evaporation of silver from a hot tungsten filament in a vacuum; the silver having been tied to the tungsten with platinum.

The writer has extended this process to chromium, with an idea to its use for astronomical reflectors. As is well known, the present silver-on-glass surfaces tarnish quickly, and do not reflect a usable fraction of incident light beyond 3350Å. To remedy this defect, other metals have been deposited by evaporation, but chromium seems to excel in reflectivity and permanence. The chromium

was electroplated about a millimeter thick on a tungsten filament and was evaporated *in vacuo* very quickly. The resultant surface is firm, and can be dissolved only by HCl. The reflectivity of a test surface has been determined as: 60 percent at 4200Å; 68 percent at 3450Å; and 62 percent at 2900Å. The adaptation of the process to large surfaces is now in progress.

ROBLEY C. WILLIAMS

Physical Laboratory
Cornell University,
June 27, 1932.

¹ *Half-Silvering Interferometer Plates*, Zeits. f. Physik **69**, 578–585 (1931).

Note on Molecular Structure

Hund¹ and Mulliken² in recent papers have considered the structure of polyatomic molecules, treating each electron as if it moved in a wave function which was a solution of a problem of many centers—a molecular orbital, as Mulliken happily names such a function. The writer³ and Pauling⁴ on the other hand have treated the same problem from a starting point in which each electron moves as in a single atom, or as Mulliken would say in an atomic orbital. It is the purpose of this note to point out the relation between the two methods. This has already been done to some extent in a paper on metallic cohesion;⁵ there the method used by Hund and Mulliken has an analogue in the treatment of Sommerfeld and Bloch, whereas the other method, used by Pauling, the present writer, Heitler and London, resembles more closely Heisenberg's treatment of ferromagnetism. In that paper, the connections between the two methods were brought out, and it was shown that if treated in the proper way both methods necessarily led to the same answer, so that a choice between them must be made on the basis of convenience rather than correctness. Essentially the same situation holds in the molecular case.

A first simple calculation by either method will be incorrect, and it is necessary to go to a considerable refinement to secure good results. First we shall describe these refinements necessary in the method of Pauling and the writer. One can start by assuming covalent bonds, and taking these bonds to be located between definite pairs of atoms. Then the writer has shown how to set up wave functions, correctly taking account of antisymmetry and of spin, describing this situation. But now to improve this we must (1) take account of other possible ways of drawing the valence bonds. This can be considered in one way as the correct perturbation treatment for spin degeneracy. Or it can be considered as taking account of *shared valence*, a common phenomenon, and the one which Mulliken

¹ F. Hund, Zeits. f. Physik **73**, 1 (1931); **73**, 565; **74**, 1 (1932).

² R. S. Mulliken, Phys. Rev. **41**, 49 (1932). I am indebted to Professor Mulliken for sending me a copy of the latter paper before publication.

³ J. C. Slater, Phys. Rev. **38**, 1109 (1931).

⁴ Linus Pauling, Journ. Am. Chem. Soc. **53**, 1367 (1931).

⁵ J. C. Slater, Phys. Rev. **35**, 509 (1930).