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ON A RESONANCE-FLUORESCENCE PHENOMENON IN THE CYANOGEN SPECTRUM

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ABSTRACT

In a study of the spectra of organic compounds excited by streaming active nitrogen, the intensification of certain pairs of lines in the violet CN bands was observed. This phenomenon was reported recently by Herzberg who likened this intensification to the resonance-fluorescence of iodine. The cause, according to Herzberg, is absorption of radiation of short wave-length from nitrogen bands in the far ultra-violet. Experiments were made to test this explanation. Radiation from the nitrogen discharge was found to have no effect on the appearance or non-appearance of these intensified doublets. Additional experiments were made to observe the effect of pressure on the appearance of the intensification, and it was found that such intensification depends upon the pressure under which the excitation of the CN spectrum occurs. It appears that the intensification results through collision with some higher-energy atomic or molecular species whose formation is suppressed at higher pressures.

HERZBERG,[1] in several recent papers reporting a spectrographic study of the nitrogen after-glow, makes note of a peculiar phenomenon in the cyanogen bands developed in the after-glow. His photographs show groups of pairs of lines which, on comparison with the violet cyanogen bands developed in the carbon arc burning in air, seem to coincide with certain lines of these bands. The bands are of such low intensity relative to these particular lines that the photographs show these abnormally intense lines but few if any of the other lines making up the bands.

In a study of the spectra of organic compounds excited by streaming active nitrogen, to be reported shortly, the writer noticed this same phenomenon in the λ4606(0,2), λ4216(0,1), and λ3883(0,0) bands of the violet cyanogen system. The intensified doublets appeared in these band-groups with all the compounds used in the study, the only difference being slight variations in intensity from compound to compound, due perhaps to the variation in pressure necessary to draw a sufficient amount of the compound into the stream of active nitrogen. With all the compounds used, the violet cyanogen system is well developed, and even in active nitrogen alone, traces of carbon compounds from stopcocks are sufficient for the development of these bands. The intensity distribution within the bands is that characteristic of bands developed at low temperatures such as exist in the active nitrogen. The lower quantum rotation-levels are favored and the structure of the band at its origin is plainly discernible. In the λ4216 CN band, the position of the missing line is clearly defined, and the rotation lines are plainly resolved, to $m=14$

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[1] Herzberg, Naturwissenschaften **8**, June, (1928) 464; Ann. d. Physik **86**, 189 (1928); Zeits. f. Physik **49**, 512 (1928); Zeits. f. Physik **52**, 815 (1929).

in the P branch, which has the head, and to $m=22$ in the R branch. This is in marked contrast to the appearance of the same bands in the carbon arc,[2] where the higher quantum levels are favored and the structure of the origin is obscured by the P branch lines corresponding to transitions between these higher levels.

Chloroform introduced into active nitrogen gives these bands especially strong. This spectrum was photographed first with a Hilger $E1$ quartz spectrograph and the intensification was so marked as to permit the use of higher dispersion. The glass train was substituted in the spectrograph, giving a dispersion of 4.5A at λ4200, and the λ4216 group was photographed. The accompanying enlargement (Fig. 2) shows this group to good advantage, the dots marking the intensified lines of the first band (0,1). The intensified lines correspond, as pointed out by Herzberg, to the initial rotational states m 4, 7, and 15. These levels give the lines $R(3)$, $R(6)$, $R(14)$, and $P(5)$, $P(8)$, and $P(16)$. The writer's plates indicate still another initial state $m=13$ giving the lines $R(12)$ and $P(14)$.

The objection that this additional initial state gives these intensified P and R lines only because there is an overlapping of lines from other bands can be met by considering several of the intensified lines. The $R(12)$ line is nearly coincident with the head of the (1, 2) band in this sequence, but this band is weakly developed in active nitrogen and would contribute little to the observed intensity of this line. The $R(14)$ line appears to be multiple, and an examimation of Jevons' measurements[2] shows that two P branch lines of the (1, 2) band lie 0.7 and 2.35 wave-numbers to either side of this intensified line. The P branch lines $P(14)$ and $P(16)$ companions to the intensified $R(12)$ and $R(14)$ lines are observed to be intensified however and are free from close-lying lines, whereas $R(13)$ which coincides exactly with a line in the (1, 2) band shows no intensification. This indicates that the intensification is due not simply to the overlapping of lines.

Herzberg states that such intensification of certain lines in the cyanogen bands is probably due to absorption of radiation of very short wave-length from nitrogen bands in the far ultra-violet— a resonance-fluorescence phenomenon similar to that in iodine. The intensification is present in all the writer's photographs, and several experiments were made to test Herzberg's explanation.

The earlier pictures were made using an apparatus similar to that of Mulliken[3] for producing the stream of active nitrogen. A modified apparatus shown in Fig. 1 was next constructed in which radiation, other than the after-glow, was isolated from the point of contact of the active nitrogen with the organic vapor. A number of right-angle T bends, painted black outside, were interposed between the discharge tube and this point of contact. The discharge tube itself was covered with asbestos. A second discharge tube, which could be independently operated, was attached, directly, without a window or other obstruction, to the after-glow tube at this same point of contact.

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[2] Jevons, Proc. Roy. Soc. **112A**, 407 (1926).

[3] Mulliken, Phys. Rev. **26**, 1 (1925).

In the one case, no radiation from any nitrogen discharge reached this point, while with the second tube operating in addition, such radiation must have been intensely concentrated at the CN emission area.

With acetylene in active nitrogen[4] duplicate exposures were made, first with the isolated discharge, then with both the isolated and the juxtaposed discharge tubes operating. If the intensification results from the absorption of radiation from the discharge, the first picture should show little or no effect, while the second picture should show a more marked effect. Actually the doublets appear with about equal intensity in both. This seems to disprove Herzberg's statement of the mechanism of such intensification.

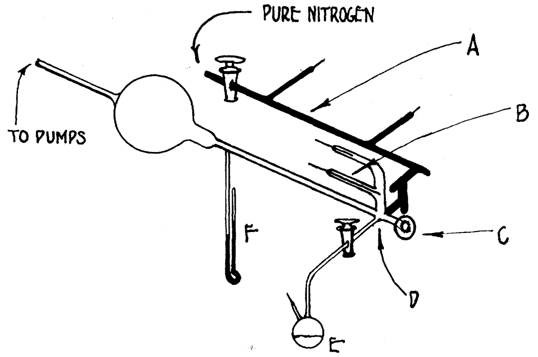

Fig. 1. Experimental arrangement: *A*, isolated discharge tube; *B*, secondary discharge tube; *C*, quartz window; *D*, point of contact—active nitrogen and organic vapor; *E*, reservoir with organic compound; *F*, manometer.

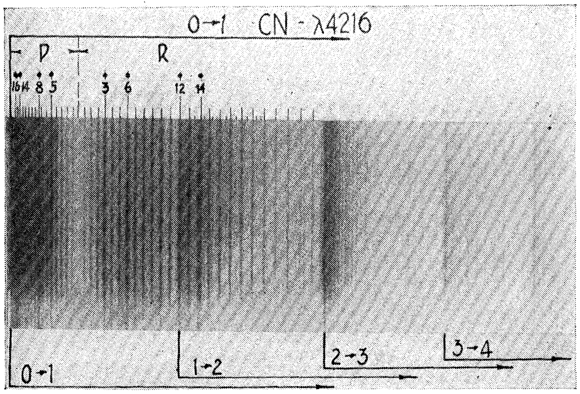

Fig. 2. Spectrum with chloroform in active nitrogen.

Next a series of such duplicate pictures was made in which the total nitrogen pressure in the system was varied for each pair of exposures. In the pictures taken with 5 mm, 8 mm and 10 mm pressure, the doublets appeared

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[4] In the work of Jenkins,[5] Jevons[2] and others, this doublet intensification did not occur when acetylene was used.

in both exposures, e.i. with single and double discharges. At 20–40 mm pressure the doublets were absent from both exposures. Thus there is some relation between the pressure under which excitation takes place, and the appearance or non-appearance of the intensified lines, but there is no influence due to radiation. This pressure relation would explain the non-appearance of the doublets in the work of Jevons,[2] Jenkins[5] and others, as well as the variation in intensity on some of the writer's plates.

The above experiments on the effect of radiation and pressure seem to indicate that the absorption of radiation, as suggested by Herzberg, is not the cause of this doublet intensification. The energy necessary to raise the cold CN molecules to those initial states, from which transitions give observed intensified doublets, probably is imparted through collision with certain high-energy molecular or atomic species. These higher-energy species are sensitive to pressure, their formation being suppressed at high pressures.

The writer wishes to express his appreciation and gratitude to Dr. R. S. Mulliken, under whom this work was carried out, for his advice and guidance.

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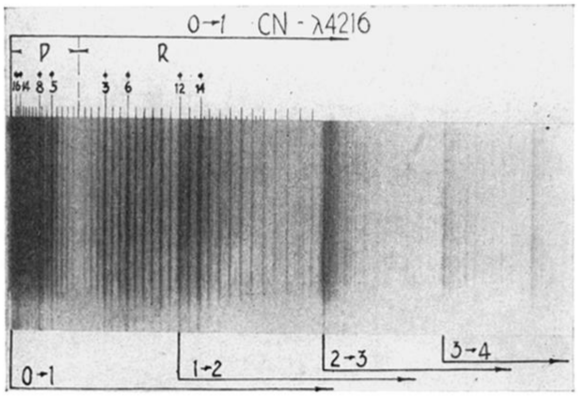
[5] Jenkins, Phys. Rev. **31,** 539 (1928).



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