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A Search for Spectral Absorption in Active Nitrogen

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The problem of absorption through active nitrogen has been re-attacked, using a 13-meter path, at pressures of a few millimeters. A supplementary observation of the O_2 "atmospheric" bands indicated that an *allowed* transition would have been detected at a concentration of 10^{10} molecules/cm³ in the initial vibrational level. Absence of the $0-0$ band of N_2^+ implies that the (unexcited) ion is not a primary carrier of the energy, as was proposed by Mitra. Failure to observe first positive bands (N_2 , $B\ ^3\Pi \leftarrow A\ ^3\Sigma$) is discussed. A speculation is advanced concerning the activated molecules.

INTRODUCTION

SEVERAL unsuccessful attempts have been made to detect metastable atoms or molecules in active nitrogen by observing the absorption spectrum.^{1,2} Theories of active nitrogen have usually postulated such particles as the active centers or energy carriers, although a recent suggestion proposes the molecular ion.³ Inasmuch as a positive result in absorption should provide some direct evidence concerning the mechanism of excitation and afterglow, it was felt that a reinvestigation, using a substantially longer optical path than has been previously reported, would be worth while. Specifically, the experiments were designed to test for: (1) absorption by the small fraction of metastable molecules known to arrive in the $A\ ^3\Sigma$ state as a result of the afterglow; (2) absorption by ions in the $X\ ^2\Sigma$ state (Mitra's ion theory); (3) unsuspected absorption in the ranges studied, *viz.* $\lambda\lambda 3600-4200$; $\lambda\lambda 4550-10950$.

The negative result obtained in every case is believed to emphasize again a view made plausible by the more recent studies of Rayleigh,⁴ *viz.*

that ions, and *low lying* metastable molecules (or atoms) play only a secondary or indicative role in the phenomena of active nitrogen. These matters will be reviewed after describing the experiment.

EXPERIMENTAL ARRANGEMENT

The absorption tube, diagrammed in Fig. 1, utilizes the mirror system of Smith and Marshall.⁵ M_0 is a concave mirror of 130-cm focus; M_1 , M_2 are plane mirrors. All three were of glass, coated with an aluminum alloy (95 percent Al, 5 percent Mg), and held in adjustable mounts of nickel-plated brass.⁶ The optical path was 13 meters (ten traversals, 14 reflections).

A vertical-ribbon tungsten projection lamp, operated at 20 percent current overload, provided the continuum in the visible and near infra-red. Jena filters (GG-2 or OG-2) passed only the first order in the region photographed. A hydrogen arc continuum was used in the second order of the grating to test for the $0-0$ band of N_2^+ at $\lambda 3914$. The spectrograms were made with a red-concentrating Wood's grating of 3-meter radius and theoretical resolving power 80,000; (1st-order dispersion, ~ 5.5 Å/mm). Care was taken to assure an accurate focus over the central portion of 18" plates.

Nitrogen was drawn from a cylinder of water-pumped gas (Linde) and passed over moist red phosphorus to remove residual oxygen; it was dried by passage through tubes of $CaCl_2$ and

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¹ Molecular absorption: K. F. Bonhoeffer and G. Kaminsky, *Zeits. f. phys. Chemie* **127**, 385 (1927); A. E. Ruark, P. D. Foote, P. Rudnick, and R. L. Chénault, *J. Opt. Soc. Am.* **14**, 17 (1927); see also A. A. Frost and O. Oldenberg, *Phys. Rev.* **48**, 66 (1935).

² Atomic absorption: W. S. Herbert, G. Herzberg, and G. A. Mills, *Can. J. Research* **15**, 35 (1937); B. M. Anand, P. N. Kalia, and Mela Ram, *Indian J. Phys.* **17**, II, 69 (1943).

³ S. K. Mitra, *Active Nitrogen—A New Theory* (Indian Press, Calcutta, 1945). It was a reading of this review that stimulated my interest in the absorption problem.

⁴ Lord Rayleigh, *Proc. Roy. Soc.* **151**, 567 (1935); **176**, 1, 16 (1940); **180**, 123, 140 (1942).

⁵ H. D. Smith and J. K. Marshall, *J. Opt. Soc. Am.* **30**, 338 (1940). The mirror assembly used was kindly loaned by Professor Harvey White.

⁶ Preliminary tests had shown that these surfaces did not noticeably impair the afterglow.

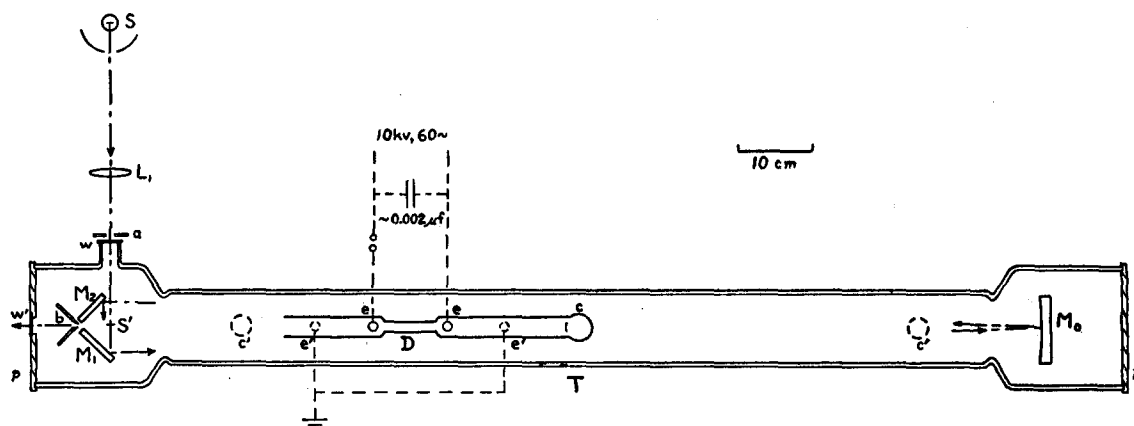


FIG. 1. Absorption tube and optical system (viewed from above). The tube T was of heavy-walled Pyrex, closed by nickel-plated brass end plates p, p fitted with Neoprene gaskets. Purified nitrogen was activated by a condensed discharge in side tube D , mounted just above T . e, e are the high tension electrodes of tungsten rod, with tantalum skirts; e', e' are grounded electrodes used to confine the discharge. The activated gas entered T through a right-angle bend at c (~ 30 -cm path), and was withdrawn at c', c' ; it was deactivated before reaching the pumps by a plug of oxidized copper screen.

Light from S , focused to S' by lens L_1 , traversed the tube ten times by reflections at mirrors M_1, M_0, M_2 , and was imaged at the exit aperture b . It then passed through a filter, and a lens L_2 (not shown), to the spectrograph slit ~ 80 cm from b . w, w' were quartz windows. External shields and apertures a, b , served to reduce stray light.

P_2O_5 . A fritted-glass filter, preceding the drying tubes, cushioned the flow and removed a fine yellow dust evidently carried over from the phosphorus. A slant-arm mercury manometer in the inlet, calibrated *in situ*, gave the pressure. Although a mercury circulating pump was used in preliminary work, it was found convenient simply to draw the nitrogen out by means of a Megavac mechanical pump. Usually the gas passed through a single trap in liquid nitrogen just before entering the (continuously operated) activating discharge shown at D , Fig. 1. The precautions for purification were *not* sufficient to eliminate spectroscopic traces of mercury vapor, nor of oxygen, during the work at large dispersion.⁷

Success in filling the absorption tube with glowing gas depended, in order of importance, on the pressure, the wall coating, and the rate of pumping. A metaphosphoric acid coating was applied for most of the work, and a good filling was usually obtained at pressures from 2 to 6 mm.⁸ Within reasonable limits, the pumping rate was not critical.

⁷ Initial low dispersion spectrograms showed only CN bands in the ultraviolet, with weak Hg 2536, but at the conclusion of the experiments, NO β bands were prominent.

⁸ The intensity in the exhaust tubes was, however, much less than at the inlet. It is believed that the acid wall coating passed partially to ordinary phosphoric acid, as it yielded only a moderate improvement of the afterglow.

A striking phenomena was observed when the inlet cock was opened suddenly, with the pressure in D and T comparatively low. With the momentary pressure blast, the characteristic orange glow was displaced downstream, and was first visible some 20 cm beyond the discharge (near c , Fig. 1), corresponding to a time lag of about 10^{-2} sec.⁹ The glow quickly returned to the discharge ($e-e$, Fig. 1) as the velocity of the gas fell off. This phenomenon clearly supports a secondary-reaction theory, for the afterglow.

RESULTS

Table I shows the four spectral ranges studied, and lists the experimental details for each. It will be seen that exposures in the visible and red were short. The slowness of Z plates made longer exposures necessary in the infra-red. In the ultraviolet, weakness of the 2nd-order hydrogen continuum, and diminished reflectance of the mirrors,¹⁰ made for long exposures, even on sensitive Ila-O plates. A sensibly constant pressure was maintained during these long exposures.

⁹ The gas velocity was taken as 10 times the final, steady value of 1 or 2 meters/sec.

¹⁰ The ultraviolet limit of 3600Å was presumably set by the decrease in reflectance. In preliminary low dispersion work, the range extended to 2900Å, but no absorption, such as might occur at the heads of strong bands, was found. Further work in the Schumann region is desirable in order to test for molecules in the metastable $a^1\Pi_g$ state (G. Herzberg, Phys. Rev. 69, 362 (1946)).

The last column refers to positive tests for absorption in the visible, near infra-red, and red. These were: (1) the D -lines, from a small sodium flame placed just before either L_1 or L_2 (Fig. 1); (2) faint rotation-vibration lines of water vapor, near $\lambda\lambda 9400, 8200$, and 7200 , due to the external 7-meter air path;¹¹ (3) the forbidden A band of O_2 at $\lambda 7600$, due also to the air path. A similar check was not made in the ultraviolet, but there seems no reason to question the results for the range indicated. An over-all test of the absorption system was made at the end of the series by filling the tube first with dry air, then with dry oxygen at atmospheric pressure. Enhancement of the A band, above, was pronounced, and in the latter case the B band at $\lambda 6880$ appeared faintly.

Absorption due to active nitrogen was not observed in any of the regions photographed. The visible range is significant because it includes the (stronger) predicted first positive bands ($B^3\Pi \leftarrow A^3\Sigma$) that would originate on levels 6, 7, 8 of $A^3\Sigma$; these are the vibrational levels most favored by the afterglow transitions. It is shown that observable absorption would have implied a minimum (actual) life for state A of the order 10^{-3} sec.

If a molecule in $A^3\Sigma$ were to survive 10^{-3} sec., it would experience some 10^4 or 10^5 collisions at the pressures used. Hence, a vibrational redistribution, with lower energies favored, might occur. A test was accordingly made for the $0-0$ and $1-0$ first positive bands (heads at $\lambda\lambda 10491, 8912$)¹² but no clear indication of absorption was found.

The instrument focus for the 2nd-order ultraviolet was the same as for the first-order red (below). The best plate was a four-hour exposure at a nitrogen pressure of 6 mm, slit ~ 0.015 mm. The continuum was of only moderate intensity, but there was no confusion from emission bands near $\lambda 3900$. Hence there is believed to be no doubt as to the absence of the $0-0$ absorption band of N_2^+ at $\lambda 3914$.

No nitrogen absorption was found in the red region, but oxygen absorption due to the external

air path provided a reference for evaluating the sensitiveness of the tests. About one-fourth the actual concentration in the 7-meter air path would have sufficed for detecting the A band; this corresponds to $\sim 10^{18}$ molecules/cm³ for the 13-meter instrument path. The measurements of Childs and Mecke,¹³ and their interpretation by Van Vleck,¹⁴ show that the intercombination, magnetic dipole transition in O_2 (${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$) is some 10^{-8} as probable as an allowed dipole transition. Hence, one would expect to detect *allowed dipole* absorption from a given initial vibrational level, at a concentration in that level of $c_0 \sim 10^{10}$ molecules/cm³.¹⁵ Thus, the experimental method is seen to be quite sensitive.

Account must now be taken of the fact that only a small fraction of the N_2 molecules pass through the afterglow transition. In an arrangement rather similar to mine (internal electrodes, 6-mm pressure), Herbert, Herzberg, and Mills² measured about 5×10^{14} quanta/cm³/sec. from the visible afterglow. If this represented a region near the discharge tube, the *average* intensity for my absorption tube was considerably less. It may be assumed, however, that a mean of at least 10^{13} molecules/cm³/sec. reached state A .¹⁶ If now t is an effective mean life of state A for the prevailing experimental conditions, the concentration would be $10^{13}t$. To obtain the life *needed* for detectable absorption, this is equated

TABLE I.

Wave-length Range	Slit width	Plate type	Exposures required	Nitrogen pressures	Check test
Visible 4550-6800	0.01 mm	panchro. (18'') 103-F (10'')	10 min. 1 min.	2-6 mm	sodium flame
Near i. r. 8600-10950	0.02 mm	Z (18'') (hypersens.)	2-3 hrs.	3-6 mm	water vapor
Red 6500-8900	0.01 mm	I-N (18'')	2 min.	3-4 mm	O_2 band; water vapor
Near u. v. 3600-4200 (2nd order)	0.015 mm	IIa-O (10'')	3-4 hrs.	4-6 mm	—

¹³ W. H. J. Childs and R. Mecke, *Zeits. f. Physik* **68**, 344 (1931).

¹⁴ J. H. Van Vleck, *Astrophys. J.* **80**, 161 (1934).

¹⁵ The single-level restriction relates to the fact that in O_2 ~ 90 percent of the absorption occurs in one band.

¹⁶ A figure of 10^{13} is given also by Rayleigh's measurements at lower pressures, if the *ratios* of active to inert particles are assumed independent of pressure. (The molecules remained in the absorption tube several seconds, long enough for most to undergo transition.)

¹¹ The equivalent path for water vapor was ~ 100 mm-atmos. (hygrometric data kindly supplied by Professor John Leighly).

¹² A. H. Poetker, *Phys. Rev.* **30**, 812 (1930).

to the required concentration c . Here $c=c_0$ (above), or $c\sim 10c_0$, according as the molecules are distributed chiefly in a single, or in several vibrational levels. One thus finds for t , 10^{-3} or 10^{-2} sec., respectively. A rough estimate of the spectroscopic life of state A (effect of collisions, neglected) gives 10^{-4} to 10^{-3} sec.¹⁷ Hence it appears that a 10-fold increase in optical path should yield detectable absorption.¹⁸ Shortening of the inlet tube between a and c (Fig. 1) might be nearly as effective. At the same time, attention should be given to the elimination of mercury vapor, as even small traces may reduce the effective mean life below the spectroscopic value.¹⁹

DISCUSSION

The studies by Rayleigh, referred to in the Introduction, reveal a phenomenally long life for the afterglow, and a much higher energy content for the gas as a whole than had previously been suspected. In fact, the average energy of ~ 10 ev per molecule of N_2 admitted²⁰ is evidently a lower limit to the energy of active centers, if the ionization associated with the afterglow is actually produced in the gas by single processes. However, the ionization and afterglow phenomena together accounted for only a small fraction of the molecules; hence the chief modes by which the active centers dissipate their energy, when wall reactions are avoided, still appear to be unknown.

It is, of course, just the small concentration of molecules in $A\ ^3\Sigma$, inherent in the afterglow process, that has prevented detection of this state by absorption. Even if a positive result were obtained by refinements in technique such

as those suggested above, the absorption would be intrinsically weak. Strong absorption from the populous active centers presumably occurs in some unexplored region of the spectrum.

The situation in respect to the N_2^+ ion is different. If one assumes these ions to be in fact the active centers, then one must expect them to be present in large concentration. Inasmuch as previous tests, and particularly the one reported here at high resolution, give no indication of the predicted absorption, it seems safe to assume that the ion in $X\ ^2\Sigma$ is *not* the carrier of the energy.²¹

In conclusion, I wish to mention a speculation concerning the mechanism of active nitrogen, which may lend itself to a test. In order to explain the recent evidence for a high concentration of active centers; apparently capable of producing volume ionization, one is led to think of stable, neutral molecules in states above the first ionization limit. The absorption spectrum does, in fact, reveal the existence of such states, for in addition to continuous absorption beyond the ionization limit, a number of narrow bands are found.²² These levels shown by absorption would hardly be long-lived, but others in the same range might be metastable. In particular, the upper levels of the Rydberg emission bands reported by Hopfield²³ and by Takamine, Suga, and Tanaka²⁴ were attributed by me to "hybrid" and presumably metastable states. An attempt to observe weak emission from these levels by means of a vacuum spectrograph, used with an active nitrogen source, is planned.

I appreciate the courtesy extended by Professor Birge, and the encouragement of Professor Jenkins to work on this problem in the physics department at Berkeley during parts of two summers. I wish to thank Dr. Kasha and Miss Gundelfinger at the chemistry department for the loan of equipment needed on short notice.

²¹ It may also be noted that Mitra's argument for the metastability of $X\ ^2\Sigma$, viz. that it combines but weakly with the ground state of N_2 , is not substantiated here. Thus the A band of O_2 whose upper state has a life of ~ 10 sec. appeared clearly at $\sim 10^4$ mm-atmos., while with comparable resolution the Rydberg absorption bands of N_2 that converge to $X\ ^2\Sigma$ were well developed at 0.2 mm-atmos. (reference 22).

²² R. E. Worley, Phys. Rev. **64**, 207 (1943).

²³ J. J. Hopfield, Phys. Rev. **36**, 789 (1930).

²⁴ T. Takamine, T. Suga, and Y. Tanaka, Sci. Pap. Inst. Phys. Chem. Research Tokyo **34**, 854 (1938).

¹⁷ I have used simply $\tau\sim(\nu/\Delta\nu)10^{-8}$ sec. For $\Delta\nu$ of $A\ ^3\Sigma$, see S. M. Naudé, Proc. Roy. Soc. **136**, 114 (1932).

¹⁸ In correspondence, Professor Herzberg has called my attention to the feasibility of such an increase in path, by use of the mirror system of J. U. White, J. Opt. Soc. Am. **32**, 285 (1942).

¹⁹ Compare J. Janin, Ann. de physique (Ser. 12) **1**, 570 (1946).

²⁰ In a more recent paper (Proc. Roy. Soc. **189**, 296 (1947)), Rayleigh reports energies as high as 230 ev/molecule. The new experimental arrangement was designed to avoid loss of energy between exciter and detector, but it seems probable that kinetic energy given electrons (and ions) by the ring discharge may have been passed on to the detector foil. The inverse dependence on pressure favors this explanation. There seems no reason however to question the previous results.