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An Attempt to Observe the Absorption Spectrum of Metastable Nitrogen Molecules

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Previous failures to observe the absorption spectrum of metastable N_2 might be explained on the basis of more recent information by the position of the spectrum in an infrared range in which plates are less sensitive and, therefore, the application of high resolving power is difficult. Since at this laboratory a special equipment for the investigation of very faint absorption spectra had been developed for another purpose the problem mentioned was reinvestigated under most favorable conditions with the newly developed plates, types *Q* and *Z*, of the Eastman Kodak Company. Again no absorption spectrum was observed.

THE mechanism of the light emission from active nitrogen has been interpreted in detail by Cario and Kaplan. The main source of energy, which maintains the afterglow through a considerable period of time, consists of the chemical energy of nitrogen *atoms*, most of them in the normal state.[1] Metastable molecules and indirectly metastable atoms are formed in this recombination process. Their concentrations are sufficiently high so that the excitation of the metastable molecules by impacts of the second kind with metastable atoms leads to a characteristic spectrum, observed as afterglow.

It has been reported[2] that active nitrogen, in spite of these metastable atoms and molecules present, does not show an *absorption* spectrum. On the other hand, very powerful absorption of light by metastable *mercury atoms* has been reported by Wood.[3] The absorption spectrum of the metastable N *atoms* is to be expected in the extreme ultraviolet; we are more interested, however, in the absorption spectrum of metastable N_2 *molecules* whose intensity distribution would give an opportunity to find out the details of the processes going on in active nitrogen. It is true that absorption of light is fainter by molecules than by atoms. But this difference might be compensated by higher pressure and a longer column.

At present we know that the absorption spectrum of metastable N_2 is to be expected in the infrared region which within the last years has become much more easily accessible. The high sensitivity of the new plates, types Q and Z, developed in the Research Laboratory of the Eastman Kodak Company[4] makes possible the application of a very high resolving power. This, in turn, is indispensable for the investigation of faint absorption lines.

A particularly sensitive apparatus was built at this laboratory for another investigation of faint absorption spectra of unstable molecules in electric discharges and their decay after interrupting the discharge.[5] It seemed promising to apply this apparatus to the search for the absorption spectrum of metastable N_2 molecules by using a pressure about 5000 times as high and an absorbing column about 10 times as long as the corresponding values in Wood's mercury experiment.

The result was negative. Nevertheless, it seems worth while to give a brief report since the experiment was carried through with a particularly good equipment.

The most favorable conditions for the absorption experiment can be predicted. From the energy level diagram[6] we expect absorption of the first positive group with the lower electronic level $A^3\Sigma$ and the lower vibrational quantum number $v''=0$.[7] Since this group shows a diagonal

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[1] G. Cario and J. Kaplan, Zeits. f. Physik **58**, 769 (1929); G. Cario, Zeits. f. Physik **89**, 523 (1934); J. Kaplan, Phys. Rev. **45**, 671 (1934); cf. J. Okubo and H. Hamada, Sci. Reps. Tohoku Imp. Univ. **23**, 281 (1934).

[2] K. F. Bonhoeffer und G. Kaminsky, Zeits. f. physik. Chemie **127**, 385 (1926); A. E. Ruark, P. D. Foote, P. Rudnik and R. L. Chenault, J. Opt. Soc. Am. **14**, 17 (1927). In Cario's papers no absorption spectrum is mentioned, contrary to a remark in a review (Ergebnisse der exakten Naturwissenschaften **8**, 247 (1929)).

[3] R. W. Wood, *Physical Optics*, 3rd ed., p. 606.

[4] C. E. K. Mees, J. Opt. Soc. Am. **25**, 80 (1935)

[5] O. Oldenberg, J. Chem. Phys. **3**, 266 (1935). The main purpose of this apparatus was the investigation of the kinetics of reactions in gases by measuring the concentration of radicals.

[6] G. Herzberg and H. Sponer, Zeits. f. physik. Chemie **B26**, 2 (1934).

[7] We are sure that the vibration of this level is not affected by an unexpected persistence of vibration (J. Franck and A. Eucken, Zeits. f. physik. Chemie **20**, 460 (1933)) since in active nitrogen the excitation process can be recognized by a certain resonance phenomenon building up on this level $v''=0$.

distribution of intensities in the v'/v'' diagram,[8] the vibrational transition $v'=0\rightarrow v''=0$ at 10,500A is expected with highest intensity. Since high resolving power is required for the most sensitive test for faint and sharp absorption lines a 21-foot grating was used in the first order. The high sensitivity of the Eastman plates, type Z, is available only for rather intense spectra since the failure of the reciprocity law seems to be much more pronounced for these than for ordinary plates. Therefore, the intensity of the spectrum was increased by a cylindrical lens in front of the plate. The wavelength range 10,370–10,470A was investigated with IV–Q plates and the range 10,440–10,540A with I–Z plates. The progress due to the new I–Z plates is demonstrated by the fact that the emission spectrum of the 0→0 band, excited by a current density of only 7.5 ma per cm^2, could well be photographed with the 21-foot grating in 7 hours (Fig. 1), while previously no measurement or photograph, resolving individual lines, had been published.

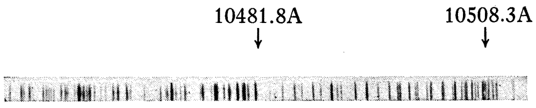

FIG. 1. Nitrogen, first positive group, 0→0 band.

The duration of the afterglow is determined by the lifetime of atoms (order of magnitude of many seconds), most of them in their normal state, while in the recombination process the metastable atoms and molecules (lifetime of the metastable states of the order 1/1000 sec. or less) represent only intermediate states which due to their shorter lifetimes have much smaller concentrations than the normal N atoms. For the absorption experiment the most abundant supply of metastable molecules formed per sec. is desirable. The *atoms of the active nitrogen* are a source of metastable molecules of less power than *a uniform electric discharge*. This can be estimated from energy considerations as well as from the comparison of intensities of emission.[9] Therefore it is obviously much better for the absorption experiment to observe the ordinary discharge in which *molecular* nitrogen is being excited directly to the metastable level by the current—instead of the condensed discharge forming *atomic* nitrogen which in turn more indirectly produces metastable molecules. In order to favor the lowest quantum transition of the molecules relatively high pressure was applied. The high intensity of the first positive group, which determines the bright color of the discharge, indicates a large supply of metastable molecules formed per sec. by the radiation process; possibly some more are produced by direct excitation from the normal electronic level. The absorption spectrum during the discharge running can be observed only with a source for the continuous background of predominant intensity. This is represented by a 500-watt bulb.

Active nitrogen is formed only in the presence of *impurities* whose function it probably is to form an adsorbed layer on the glass walls and so prevent the recombination of atoms on the wall. In the uncondensed discharge, however, in which we do not care for a high concentration of atomic nitrogen but instead try to excite directly and concentrate *metastable molecules*, very probably *pure* nitrogen is preferable since the impurities have hardly a chance to favor the production of metastable molecules but might very well partly destroy them by impacts of the second kind. Pure nitrogen was made by decomposition of NaN$_3$, several times recrystallized and baked out in vacuum.

Since metastable molecules probably have a lifetime smaller than 1/1000 sec., their concentration is expected to fluctuate with the 60 cycle a.c. Therefore a revolving sector in front of the slit was used, transmitting light of the continuous background for the absorption experiment during the periods of maximum current through the N$_2$ discharge tube, cutting out the intermissions.

In spite of the precautions described no trace

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[8] A. H. Poetker, Phys. Rev. **30**, 823 (1930); W. Weizel, *Handbuch der Exp. Phys. Ergangzungsband,* Bandenspektren, 1931, p. 356.

[9] In nitrogen of 2 mm with 10 percent dissociation, the partial pressure of metastable molecules is estimated to be only 10^{-4} mm on the following basis: each combination process of two atoms, taking place by a triple collision, leads to one metastable molecule; the rate of combination is derived from Kneser's measurement of the decay of the afterglow (Ann. d. Physik **87**, 725 (1928); the comparison of these rates in nitrogen and hydrogen indicates that in nitrogen only a small fraction of all triple collisions of two atoms with a third particle leads to the formation of a molecule); the lifetime of metastable molecules is assumed to be 1/1000 sec., presumably a too optimistic assumption.

of an absorption spectrum could be detected. The length of the absorbing column of gas was 152 cm. The pressure was varied from 2 to 10 mm, the current increased to 150 ma. The wavelength range around 10,500A, given by Birge's formula for the heads of the first positive group, was investigated as well as the range about 10,420A, given by Poetker's observation, made with small resolving power.[10] The 0→1 absorption band at 8911 did not appear in absorption either.

The failure to observe the absorption spectrum of metastable N_2 might be due to the fact that in the discharge the metastable molecules have no chance for a very long life, since they can be destroyed by the current itself, raising the molecules from the metastable to a higher level from which they go down to the normal level by radiation.[11] *A priori*, we did not expect a very pronounced destruction of metastable molecules by this process. The reason is that the next higher level ($B^3\Pi_g$) which is most probably reached does not readily combine with the normal level so that the radiation process probably leads back to the metastable level.[12]

The experiment, however, proves that the concentration actually is too small although the apparatus is particularly sensitive. In the electric discharge the metastable molecules, although amply produced, presumably have no chance to live long enough for building an appreciable concentration. On the other hand, in the afterglow, the total number of metastable molecules to be produced—one for each pair of atoms combining—is limited by the degree of dissociation caused by the disruptive discharge. Therefore, the slowness of the decay, the very same peculiarity that makes the afterglow conspicuous, indicates that the production of metastable molecules is spread over so long a period that their concentration never reaches the limit required for an absorption experiment.

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[10] R. T. Birge, Int. Crit. Tab. **5**, 409 (1929); A. H. Poetker, Phys. Rev. **30**, 812 (1927).

[11] An objection against the search for metastable N_2 in the uncondensed discharge might be raised on the following basis: In order to explain the observed quenching of the afterglow by a weak current, it has been suggested that metastable N_2 molecules are reduced to the normal state at a particularly high rate by an electric current (J. Kaplan, Phys. Rev. **33**, 191 (1929)). This assumption, however, turns out not to be adequate for the explanation of the observed facts, considering in particular the more recent results of Wrede (Zeits. f. Physik **54**, 69 (1929)). The destruction of metastable molecules would explain only a *temporary* inability of the active nitrogen to emit light, caused by the destruction of one of the *intermediate* states, but not of the *main source* of energy. It is true that this explanation well applies to the observed *temporary* quenching of the afterglow by heating; in this experiment the active nitrogen, flowing through glass tubes, is dark in the heated zone but starts radiating again beyond this zone, indicating a persistence of the main source of energy, the atoms. On the other hand, the quenching by an electric current is *permanent* (R. J. Strutt, Proc. Roy. Soc. **A92**, 444 (1916)); correspondingly Wrede observed a strong decrease of the concentration of nitrogen atoms by the effect of a current, observed by the effusion method. He concluded that the current creates a modification (for example, ions) which permits molecular formation in a rapid, bimolecular reaction (or possibly wall reaction), without the slow process of triple collisions. It is to be concluded that the observed quenching of the afterglow by a weak current does not indicate a particularly rapid destruction of metastable N_2 by the effect of the current.

[12] The process just considered—destruction of metastables by the current—does not lead to the result that metastables have a maximum concentration for a small current. Assuming that metastable molecules are *formed* by electron impact and *destroyed* either by electron impact or by another independent process (impact of the second kind or radiation), it can be shown by a simple analysis that the concentration of metastables is not decreasing with increasing current but instead increasing with the current according to a power less than the first. Hence strong current was applied in the experiments described.

FIG. 1. Nitrogen, first positive group, 0→0 band.