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Active Nitrogen, Airglow*

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The theory of the "Lewis-Rayleigh afterglow" of nitrogen, originally given by Cario and Kaplan, is modified by taking into account recent work regarding resonance in collision processes and the value of the energy of dissociation of N_2, accepted in this paper as 9.76 ev. Kaplan's "auroral afterglow," in which the spectrum of N_2^+ is observed, is tentatively explained by ionization caused by collisions of two metastable molecules. The results are applied to the airglow.

I. INTRODUCTION

THE energy content of active nitrogen which is produced in an electric discharge at low pressures is dissipated so slowly that the resulting emission of light may be observed for minutes or even hours after the interruption of the discharge. At present there is general agreement that this energy is stored as energy of *dissociation* of the nitrogen molecules.[1] However, there is little agreement regarding the processes by which active nitrogen excites the observed emission.

The theory of active nitrogen was originally given by Cario and Kaplan[2] but because of conflicting results was later abandoned by one of the authors. We are concerned with the problem of modifying the theory by taking into consideration the following recent work. In a preceding paper it has been argued that Franck's principle of resonance in collisions has commonly been too loosely applied. In particular, this principle is not effective in the recombination of a pair of atoms disposing of their energy in a triple collision.[3] Another recent result is the measurement of the dissociation energy D of the nitrogen molecule by Kistiakowsky, Knight, and Malin.[4] Studying stationary detonation waves, these authors obtained a value of 225 kcal/mole $=9.76$ ev. The striking agreement between this result of an independent method and one of the spectroscopically determined values for D leads us to accept this value. Furthermore, it is supported by Douglas' recent extensive measurements of vibrational energy levels.[5] The same value had been advocated before by Gaydon.[6] However, we cannot find fault with Hagstrum's careful analysis which gives preference to the lower spectroscopic value of 7.37 ev.[7]

The experimental results to be interpreted are thoroughly reviewed by Mitra.[8]

II. LEWIS-RAYLEIGH AFTERGLOW

Kaplan distinguishes two types of nitrogen afterglow, the "Lewis-Rayleigh afterglow" and the "auroral afterglow," each of which depends on the degree of purity of the gas and the condition of the walls.

Rayleigh explored the most favorable conditions for the afterglow which bears his name and was able to detect it 5.5 hours after interrupting the discharge. This afterglow consists of that part of the spectrum which has the lowest excitation energy. The first positive bands appear with distinct maxima at $v'=6$ and

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[1] The alternative theory assuming *ionization* of N_2 molecules, which was advocated by Mitra, is made untenable by the recent measurement of the rate at which electrons and N_2^+ ions recombine. R. B. Holt and R. B. Bryan (to be published) measured the rate coefficient α for the disappearance of free electrons as 10^{-6} cm^3 sec^{-1}, which precludes a survival for hours or even minutes. For other arguments see L. Herman and R. Herman, Nature **161**, 1018 (1948).

[2] G. Cario and J. Kaplan, Z. Physik **58**, 769 (1929).

[3] O. Oldenberg, Phys. Rev. **87**, 786 (1952).

[4] Kistiakowsky, Knight, and Malin, J. Am. Chem. Soc. **73**, 2972 (1951).

[5] A. E. Douglas, Can. J. Phys. **30**, 302 (1952).

[6] N. Thomas and A. G. Gaydon, J. Chem. Phys. 20, 369 (1952); A. G. Gaydon, *Dissociation Energies* (John Wiley and Sons, Inc., New York, 1947), p. 159.

[7] H. D. Hagstrum, Revs. Modern Phys. **23**, 202 (1952).

[8] S. K. Mitra, *Active Nitrogen* (Indian Association for the Cultivation of Science, Calcutta, 1945).

$v'=11$ or 12 and are occasionally supplemented by the Vegard-Kaplan bands.

The theory of the excitation of this afterglow has been discussed by Cario and Stille[9] and is modified here. It is assumed that the recombination of two atoms in a triple collision in which the third body may be an atom or molecule makes the energy of 9.76 ev available. Since resonance is not effective in this process, excitation of atoms or molecules to any energy below 9.76 ev will occur. Some will be excited to metastable levels, and it is these metastable atoms and molecules which are considered to be important in producing the afterglow. It is further assumed that a metastable atom with an energy of 2.383 ev or 3.574 ev transfers its energy to a metastable molecule (in the $A^3\Sigma_u^+$ level) with an energy of 6.21 ev. In this process, in which electronic energy is transferred into electronic energy of another particle, resonance is expected to give a preferred probability.

This modified theory is in agreement with a number of observations. It predicts that these impacts excite the levels $v'=6$ and $v'=12$ of the upper electronic level with preferred probability, in agreement with the observed intensity distribution in the first positive group. The emission of the Vegard-Kaplan bands belonging to the next lower step in the energy level diagram would be expected to follow every emission of the first positive group were it not for the fact that the upper level of the Vegard-Kaplan bands is metastable. This peculiarity causes these bands to appear only in particularly pure gases or at the very low pressures present in the upper atmosphere

The theory presented here is further confirmed by the following observations. When a stream of active nitrogen coming from a discharge tube flows through a glass tube which is locally heated, the heated section fails to show the afterglow. However, beyond the heated section the glow reappears, indicating that the heat does not destroy the activity but somehow impedes the processes by which the activity converts energy into light. This is called the dark modification of active nitrogen. Modifying the hypothesis of Cario and Kaplan, we assume that excitation of light is prevented in the heated section because the metastable levels of atoms or molecules are sensitive to intense thermal collisions. We refrain from speculating about the collision process reponsible. This assumption leads to the prediction that any atomic recombination *which does not rely on metastable levels* should occur as well in heated as in cold nitrogen. This is confirmed by the observation of Okubo and Hamada[10] who discovered that active nitrogen excites admixed mercury vapor to high energy levels (up to 9.51 ev) and that the ensuing emission is not quenched by heating. The present theory interprets this observation as the recombination of normal nitrogen atoms in triple collisions, the mercury atom acting as the receiver. Since there are no metastable levels involved, the process is not quenched by heating and the total energy of dissociation (9.76 ev) is available. Incidentally, this transfer does not show a preference for the highest levels of the mercury atom, in agreement with the argument against resonance presented in the preceding paper.[3]

Attention has been called by Dr. L. M. Branscomb to the following difficulty. The energy of recombination of 9.76 ev is sufficient to excite *directly* the level B of the N_2 molecule and thus the first positive bands without employing metastable levels in an elaborate mechanism as discussed above. This process may be expected to occur in heated as well as in cold nitrogen. It remains unexplained that in heated nitrogen, i.e., in the so-called dark modification, Hg may be excited but not N_2. One may assume that with N_2 as the third body, so much of the energy available goes into other degrees of freedom that the level B fails to receive a sufficient share. This difficulty is inherent in any theory based on the assumption of atomic recombination releasing the energy 9.76 ev.

We refrain from comparing the law of decay of intensity with the processes responsible for the emission of light since Rayleigh discovered that only an insignificant fraction of the total energy stored in active nitrogen is emitted as light.

III. ENERGY CONTENT

Rayleigh[11] measured the energy content of active nitrogen by flowing it over gold foil. The foil was heated to a high temperature first by active nitrogen and then by an electric current. The electrical energy required to heat the foil to the same temperature was assumed to be equal to the energy liberated by the active nitrogen. The energy content so measured was surprisingly large. Assuming optimistically that each individual molecule was activated and delivered its total energy to the foil, energy values as high as 12.9 ev per molecule resulted, that is, even considerably higher than the energy of dissociation. It is felt that this result, which has been of importance in theoretical interpretations, was affected by a source of error. In the first experiment, using active nitrogen, the red-hot gold foil was suspended at the center of a *spherical* bulb so that the energy radiated, which was largely in the infrared, was partly reflected back to the foil and helped to keep it hot. In the other experiment, however, the foil was suspended in a vessel of *different shape* so that the energy radiated from the foil did not return to the foil. This source of error would lead to an exaggerated energy content of the active nitrogen. Much smaller values (0.027 ev per molecule) were recently obtained in a different arrangement by Benson.[12]

[9] G. Cario and U. Stille, Z. Physik **102**, 326 (1936).
[10] J. Okubo and H. Hamada, Phil. Mag. **5**, 375 (1928).
[11] Lord Rayleigh, Proc. Roy. Soc. (London) **176**, 16 (1940).
[12] J. M. Benson, J. Appl. Phys. **23**, 757 (1952).

Closely connected with the energy content is the degree of dissociation. In the upper atmosphere nitrogen is supposed to be largely molecular, since even in the highest altitudes the molecular spectrum is observed. The Franck-Condon principle explains the persistence of the molecular state by the fact that nitrogen molecules, unlike oxygen molecules, do not change their internuclear distances in the process of excitation or ionization, so that these processes fail to produce dissociation. It remains to be explained why, in nitrogen activated by an electric discharge, a high degree of dissociation is readily obtained. One may well assume that absorption of sunlight and electron impact have different effects. In the upper atmosphere absorption of ultraviolet light generates a limited group of excited or ionized levels which may not dissociate. In the condensed discharge, however, which is most favorable for the Lewis-Rayleigh afterglow, fast electrons may cause other transitions which lead to dissociation. This distinction between the processes is confirmed by experiments which indicate that activation of nitrogen requires an electron energy as high as 20 ev,[13] exceeding the energy needed for dissociation, exitation, or ionization.

IV. KAPLAN'S AURORAL AFTERGLOW

Kaplan[14] found that the continuous operation of the electric discharge through several weeks removes the last traces of hydrogen lines from the spectrum and leads to a different type of afterglow with a spectrum resembling that of the aurora. The discoverer called this the auroral afterglow. Presumably it is identical with the short duration afterglow reported by Herman and Herman.[15] The spectrum, more complicated than that of the Lewis-Rayleigh afterglow, consists essentially of several systems of the neutral N_2 molecule, the two forbidden lines of atomic nitrogen and, surprisingly, the first negative bands of the molecular ion N_2^+.

Since the removal of the last traces of hydrogen is an outstanding prerequisite for obtaining the auroral afterglow, one may assume that the various metastable levels which presumably are susceptible to destruction by H_2 or H survive for long periods in the absence of hydrogen and thus emit the forbidden radiation or perform impacts of the second kind.

In a recent paper, Cario and Stille[16] describe some detail of Kaplan's observations and state that the auroral afterglow can be traced through 9 seconds after the interruption of the discharge. Cario and Stille attribute this afterglow to the survival of N_2^+ ions and free electrons and the excitation of these ions by collisions with metastable atoms in the ^2P state. However, the survival of ions seems incompatible with recent measurements by Holt and Bryan (to be published) of the recombination of N_2^+ ions and electrons. The recombination coefficient α was found to be of the order 10^{-6} cm^3/sec, that is, 100 or more times higher than the value assumed by Cario and Stille. It seems difficult to reconcile the rapid recombination with the survival of an appreciable concentration of N_2^+ ions. It is unlikely that the high value of α obtained by Holt and Bryan is due to electron attachment to O or O_2, since attachment would lead to a different time dependence (exponential decrease of n instead of linear increase of $1/n$). Kaplan's auroral afterglow may instead be explained by assuming a regeneration of N_2^+ ions by collisions of two metastable molecules. More specifically, the recombination of two N atoms may excite molecules to the metastable level $a^1\Pi_g$ (initial state of the forbidden Lyman-Birge-Hopfield bands, excitation energy 8.55 ev). Two such metastable molecules may produce an ionized molecule. This part played by metastable molecules would explain the fact that the spectrum of the ions shows up only in extremely pure nitrogen. The recent work of Biondi[17] proves the occurrence of ionization by the collision of two metastable atoms in helium and neon. In both gases immediately after the interruption of the discharge an increase of ionization is observed. In the afterglow the conditions are more complicated, since we must assume a gradual regeneration of the metastables. An alternative is the ionization of metastable molecules (6.17 or 8.54 ev) in a triple collision with a pair of recombining atoms (9.76 ev).

V. THE AIRGLOW

What bearing has the theory of active nitrogen on the theory of the airglow? The airglow[18] is related to the Lewis-Rayleigh afterglow by the fact that its spectrum is limited to lines and bands of neutral molecules showing low excitation. Therefore, the energy released is due presumably to the same type of process, recombination of neutral atoms. In the upper atmosphere oxygen is completely dissociated above a limit of about 110 km, while nitrogen is certain to be at least partly molecular as indicated, for example, by the occurrence in the auroral spectrum of N_2 bands at altitudes as great as 1100 km. This difference in the behavior of O_2 and N_2 is well understood on the basis of the Franck-Condon principle.

S. Chapman suggested that the spectrum of the airglow might be explained by recombination of O atoms ($D=5.08$ ev) in triple collisions. It may be that we must supplement this hypothesis by assuming at least a partial dissociation of N_2. This is indicated by the predissociation discovered near 1400A by Herzberg and Herzberg.[19] However, this process may not be

[13] Z. Bay and W. Steiner, Z. Physik **B9**, 116 (1930).
[14] J. Kaplan, Phys. Rev. **42**, 807 (1932); **45**, 671 (1934); **48**, 800 (1935); **51**, 143 (1937); **54**, 176 (1938); **73**, 494 (1948).
[15] L. Herman and R. Herman, Nature **161**, 1018 (1948).
[16] G. Cario and U. Stille, Z. Physik **133**, 209 (1952).
[17] M. A. Biondi, Phys. Rev. **88**, 660 (1952).
[18] The observations are thoroughly reported by A. B. Meinel, Repts. Progr. Phys. **14**, 121 (1951).
[19] G. Herzberg and L. Herzberg, Nature **161**, 283 (1948).

probable enough to produce an appreciable concentration of N atoms by the action of sunlight.

To test for the occurrence of N atoms we must answer two questions. (1) Is the higher value of the energy of dissociation of N_2 required to explain the spectrum of the airglow, in particular the occurrence of the Vegard-Kaplan bands? Here one may question the rather uncertain observation which seems to show these bands with vibrational quantum numbers as high as $v'=9$. If this observation is correct the excitation energy would be sufficient to excite as well the first positive group ($v'=0$ or 1) which in laboratory experiments is the most prominent feature of the nitrogen spectrum but is absent in the airglow. (2) Do the observations indicate the absence of N atoms? That the spectrum of the aurora exhibits *molecular* nitrogen with predominant intensity does not contradict the occurrence of a large concentration of *atomic* nitrogen. This is illustrated by the low pressure discharge which, although emitting almost exclusively the molecular spectrum, produces a large concentration of atomic nitrogen which is evident as "active" nitrogen. At low excitation the spectrum of N atoms consists only of two forbidden lines which do appear in some low pressure discharges and the aurora but are absent from the airglow. These various observations are compatible with the partial dissociation of nitrogen in the airglow if we adopt the following plausible assumptions: In the low pressure discharge the N lines are observed only in very pure nitrogen, indicating that impurities, but not nitrogen atoms or molecules, deactivate the metastable N atoms. In the airglow the absence of the N lines may be due to deactivation by oxygen. In the aurora, where the N lines sometimes appear, it is possible that they are emitted at high altitudes where collisions are very rare. Therefore, the absence of N lines in the airglow and their occasional presence in the aurora leads to the speculation that in any case N atoms are present and excited to metastable levels but are able to radiate only if not quenched by oxygen. Presumably the emission of the forbidden lines in the aurora takes place in altitudes much higher than that of the airglow. This prediction ought to be accessible to direct observation.

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Processes Involving Ions and Metastable Atoms in Mercury Afterglows

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Atomic collision processes occurring in mercury vapor are determined from microwave measurements of the electron density during the afterglow. The electrons are brought into thermal equilibrium with the gas by adding helium to the mercury vapor to act as a "recoil gas." Measurements of the ambipolar diffusion coefficient, D_a, of Hg^+ ions and electrons in helium yield the value $D_an=2.6\times10^{19}$ (cm²/sec)(atoms/cc) at 290°K. The corresponding value for Hg^+ ions in mercury is $D_an=3.6\times10^{17}$ at 350°K. Conversion of the atomic mercury ions to molecular ions according to the reaction $Hg^++Hg+He\rightarrow Hg_2^++He$ occurs at the rate of 140 ($p_{Hg}\cdot p_{He}$) sec^{-1}. The measured recombination coefficient of Hg_2^+ ions with electrons is $\alpha=5.5\times10^{-7}$ cc/sec at 400°K. Studies of the ionization produced by the collisions of pairs of mercury metastable atoms yield the values $D_mn=1.5\times10^{18}$ (cm²/sec)(atoms/cc) for the diffusion coefficient and $\sigma_d=8\times10^{-17}$ cm² for the de-excitation cross section of $^3P_2$ metastables at 350°K.

IN recent years, atomic collision processes occurring in ionized gases have been studied by the use of microwave techniques. Measurements of the variation of the electron density in the afterglow of a pulsed discharge have yielded information concerning processes involving electrons, ions, and excited atoms. Under conditions in which the electrons have been in thermal equilibrium with the gas, it has been possible to obtain quantitative measurements for the probabilities of the various collision processes.

Studies of electron removal in mercury afterglows have been carried out by Mierdel[1] and by Dandurand and Holt,[2] using Langmuir probe and microwave techniques, respectively. In these investigations the electrons were not in thermal equilibrium with the gas. As a result, only qualitative remarks could be made concerning the processes occurring in mercury. In the present experiment the electrons are brought into thermal equilibrium with the gas by adding helium to the mercury vapor to act as a "recoil gas." Quantitative values for the various collision processes are then obtained from the afterglow measurements.

I. EXPERIMENTAL METHOD

Microwave techniques are used to measure the electron density during the afterglow following a pulsed discharge in mercury. Detailed descriptions of the

[1] G. Mierdel, Z. Physik **121**, 574 (1943).
[2] P. Dandurand and R. Holt, Phys. Rev. **82**, 868 (1951).