The Radiative Recombination of Nitrogen Atoms

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The interaction of two reactive atoms can result in the formation of a stable molecule, if the internal energy of the collision pair $[AB]^*$ is lowered by the catalytic interference of a third body M or by radiative energy loss.

$$\begin{array}{lrl} \text{I.} & A+B \rightleftarrows [AB]^*, & k_1/k_{-1}\,; \\ & [AB]^*+M \rightarrow AB+M, & k_2\,; \\ \text{II.} & A+B \rightleftarrows [AB]^*, & k_1/k_{-1}\,; \\ & [AB]^* \rightarrow AB+h\,\nu, & k_3\,. \end{array}$$

Both processes, the three-body recombination (I) and the radiative two-body recombination (II) can be treated by the same theoretical model if a third body in case (II) is introduced as a "phonon field"[1]. Mechanism (I) can also result in "chemiluminescence" if a suitable radiative state of the stabilized molecule AB is populated during the recombination. The lifetime of $[AB]^*$ depends on the energy of the relative motion of the colliding particles, the angular momentum, and on the interaction of the internal energy states. According to recent calculations[1, 2], metastable "resonance" states of the "quasimolecule" $[AB]^*$ seem to be important, at least for the recombination of atoms. These states are assumed to be in quasi-equilibrium with the continuum states of the free atoms by quantum-mechanical tunnelling through a slight potential barrier. Previous calculations for $[H_2]^*$ showed[3] that the lifetimes of such resonance states can be as long as several 10^{-10} sec. On the other hand, lifetimes of the collision pairs above the threshold of resonance states are in the order of 10^{-13} sec, the duration of one vibrational period.

Under most experimental conditions, even for long living resonance states, the rate constant k_{-1} of redissociation is still higher than $k_2 \times (M)$ or k_3, maintaining an equilibrium between $[AB]^*$ and $A+B$. Radiative association is a very rare process at normal pressures and at room temperature, $k_3 \ll k_2(M)$; whereas at higher temperatures, where excited states which correlate with excited atoms or where turning points on repulsive potential curves which are favoured for higher transition probabilities to lower states become accessible, the probability of radiative recombination increases.

Excited molecular states can also be populated by inverse predissociation[4] if the potential curve on which the recombining atoms collide, crosses the potential curves of such excited states in the energy region of dissociation.

Two-body recombinations have been shown to occur for the heavy halogen atoms in hot flames[5] and in shock waves[6, 7]. For astrophysical processes and for reactions in the upper atmospheres of planets two-body recombinations which involve H, C, N, and O atoms should play an important role[8, 9]. Quite recently experimental results from shock tube work[10] gave some evidence for a two-body recombination of $O(^3P)$ atoms via the $O_2(B^3\,\Sigma_u^-)$ state. Experimental results on the radiative recombination of $O(^3P)+N(^4S)$ via the $NO(a^4\,\Pi)$ state with emission from $NO(C^2\,\Pi)$ have also been given[11, 12]. The reported radiative recombination of $O(^3P)+H(^2S)$ at room temperature[13] seems not to be acceptable[14]. The explanation of the N_2^* chemiluminescence in shock waves as a two-body recombination of $N(^4S)$ atoms[15] can be rejected as will be shown by the results of the present work.

This paper reports measurements on the intensity of the first positive bands of nitrogen, $N_2(B^3\,\Pi_g \rightarrow A^3\,\Sigma_u^+)$, as a function of the total pressure in a slowly decaying Lewis-Rayleigh afterglow. These measurements were extended to pressures as low as 10^{-4} Torr in order to find the region where two-body processes compete favourably with three-body reactions.

The experiments were carried out in a spherical reaction chamber of 2×10^5 liters volume[16]. The sphere was evacuated to 10^{-8} Torr before each measurement, and only gases of high purity (99.999%) were used.

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Similar to previous work [17, 18], the measurements were performed in a static system which avoids any uncontrolled concentration gradient. After filling the sphere with active nitrogen which was produced by flowing pure nitrogen through a condensed discharge, the intensity of the Lewis-Rayleigh afterglow between 5680 and 5800 Å was measured during the stepwise or continuous increase of the total pressure by addition of gases, such as He, Ar, or N_2. The atom concentration (N) and the pressure (M) were kept low enough to maintain the decay of the afterglow predominantly controlled by wall recombination of the atoms with a first order decay constant of 1.2×10^{-5} sec^{-1}. At total pressures above 3×10^{-3} Torr the first positive bands were measured by a monochromator with a spectral resolution of about 40 Å. At lower pressures and for comparison also at higher pressures, an interference filter with a spectral band-width of 120 Å centered at a wavelength of 5740 Å was used in front of a photomultiplier (EMI-6255-S).

Fig. 1 shows the pressure dependence of the Lewis-Rayleigh afterglow in the spectral region of 5680 Å to 5800 Å for $M = N_2$. Very similar dependences were found for the other gases which only differ in the levelling off at higher pressures due to electronic quenching and in the initial slope of the intensity versus (M) plot at pressures below 10^{-2} Torr. It can be seen from Fig. 1 that there is a contribution to the afterglow with an intensity independent of total pressure (M). By variation of the atom concentration (N) it was found that the pressure independent emission as well as the pressure dependent one increase in intensity proportional to $(N)^2$. The overall dependence of the afterglow intensity between 5680 and 5800 Å follows relation (1) at pressures below 10^{-2} Torr for all gases.

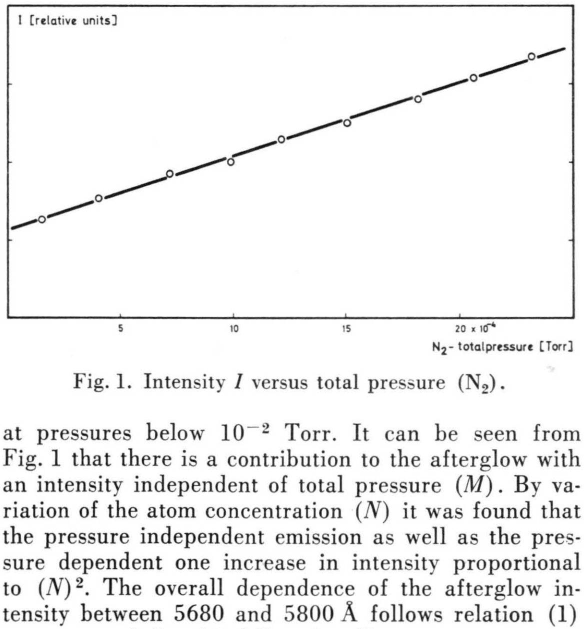

Fig. 1. Intensity I versus total pressure (N_2).

$$I \sim (N)^2[a + b(M)] \, . \qquad (1)$$

It is known [19] that on clean surfaces atom recombinations can yield light emission in the visible spectrum. In order to distinguish between chemiluminescence in the gas phase and a possible one at the surface, a rotatable plate was installed in the centre of the sphere. The material of the plate (stainless steel 4541) was the same as the wall material. The length of the radiating cone within the view of the light detector could be decreased by this plate. A volume emission would follow the change of the optical path length whereas in the case of a surface reaction the plate would not cause any intensity change of the light signal because the detector views always the surface area by the same solid angle, independently of the plate position. It was found that the pressure dependent as well as the pressure independent part of the afterglow intensity between 5680 and 5800 Å was changed by the same relative amount when the plate was turned. Therefore, both emissions originate from volume reactions. The spectral region of the emission excludes CN as well as NO emission bands which are frequently observed in the nitrogen afterglow.

It is concluded that the pressure independent emission is a result of a radiative recombination of two nitrogen atoms, whereas the pressure dependent emissions was identified as first positive bands originating from $N_2(B^3 \Pi_g, v' \leqq 12)$ molecules which are formed by a three-body recombination of nitrogen atoms. The latter result is in agreement with other recent work at pressures below 0.1 Torr [20–22]. The emission above 3×10^{-3} Torr total pressure definitely showed the structure of the (12,8), (11,7), and (10,6) bands of the first positive band system.

Below 3×10^{-3} Torr both emissions lie within the same spectral region, 5740 ± 60 Å. Lack of intensity did not allow a spectral analysis with higher resolution at the moment. Very likely, the pressure independent emission originates from levels in the vicinity of $B^3 \Pi_g$, $v' = 12$.

Under the conclusion of a radiative recombination of two $N(^4S)$ atoms, from the pressure dependence of the afterglow intensity, Fig. 1, a rate constant k_R for the radiative recombination relative to the rate constant k_D of the chemiluminescence reaction by a three-body recombinaiton can be derived, if the constant a from the pressure function [Eq. (1)] is taken as k_R and the constant b as k_D. For $M = N_2$ the I versus (M) plot in Fig. 1 gives $k_R/k_D = 4 \times 10^{13}$ cm$^3 \times$ molecule^{-1}. With the adopted value of $k_D = 2 \times 10^{-33}$ cm$^6 \times$ molecule^{-2} $\times$ sec^{-1} for the three-body rate constant [23–25] the value of k_R becomes approximately 10^{-19} cm$^3 \times$ molecule^{-1} $\times$ sec^{-1} which should be correct in the order of magnitude. The accuracy of the k_R value is not only limited

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by the experimental errors but also by the uncertainty of k_{D}. Nevertheless, the present results exclude any rate constant much higher than $10^{-19}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1}$ as being related to radiative recombination of nitrogen atoms at room temperature. The pressure independence of the Lewis-Rayleigh afterglow intensity in a previous experiment of GROSS[15] probably has to be explained by electronic quenching of the emitting N_2^* molecules but *not* by a two-body recombination with a rate constant of $k_{\mathrm{R}} = 6 \times 10^{-18}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1}$ at 300 °K.

The values for $k_{\mathrm{R}}/k_{\mathrm{D}}$ and k_{R} respectively, can be used for a rough estimate of the radiative transition probability for the pressure independent emission in two different ways:

I.

If by simplified kinetics from mechanism (II) $k_1/k_{-1} \times k_3$ is taken as k_{R} a transition probability $k_3 = 2 \times 10^{-4}\,\mathrm{sec}^{-1}$ is obtained with

$$k_{\mathrm{R}} = 10^{-19}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1},$$

$$k_1 = 10^{-10}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1}$$

as gas kinetic collision frequency, and with

$$1/k_{-1} = 4 \times 10^{-14}\,\mathrm{sec}$$

as one vibrational period for the lifetime of the collision pair $[\mathrm{N}_2]^*$.

Note: It should be noted that because of the microscopic reversibility any "bottle neck" in the reaction path or a long living resonance state of the collision

$$\mathrm{N}+\mathrm{N} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{N}_2]^* \underset{\alpha_{-1}}{\overset{\alpha_1}{\rightleftarrows}} [\mathrm{N}_2]^{**}$$

pair would not change the overall rate constant k_{R} as long as the emitter $[\mathrm{N}_2]^{**}$ remains in equilibrium with the free atoms and as long as both molecular states have nearly equal statistical weights.

II.

Under the assumption of equal potential curves of the collision pair for three-body as well as for two-body recombination according to mechanism (I) and (II), and taking the rate constant k_2 of the stabilisation by M approximately as $10^{-10}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1}$, from $k_3 = k_2 \times (M)$ at 1.2 mTorr, Fig. 1, a value of $k_3 = 4 \times 10^3\,\mathrm{sec}^{-1}$ is obtained. In this case, no assumption has to be made about the equilibrium constant k_1/k_{-1}.

In both cases, the estimated k_3 values are lower than the radiative transition probability of the first positive band system which is about[26] $2 \times 10^5\,\mathrm{sec}^{-1}$. For the population of $\mathrm{N}_2(\mathrm{B}^3\Pi_g,\ v' \leqq 12)$ by the three-body mechanism $^5\Sigma_g^+$ (l. c. [23, 27–29]) as well as $\mathrm{A}^3\Sigma_u^+$ (l. c. [25, 29]) have been postulated as precursor states. For the two-body recombination, no collision with M would weaken symmetry rules. Therefore, a radiationless transition $^3\Sigma_u^+ \rightarrow {}^3\Pi_g$ can be rejected on the basis of the $\mathrm{g} \leftarrow\!\!|\!\!\rightarrow \mathrm{u}$ rule[28]. A more likely candidate is $^5\Sigma_g^+$ as precursor state in the case of the radiative recombination. This state correlates with the two $\mathrm{N}(^4\mathrm{S})$ atoms and the formation of $\mathrm{N}_2(^5\Sigma_g^+)$ should be in equilibrium with the free atoms. From this potential curve, on which the $\mathrm{N}(^4\mathrm{S})$ atoms primarily collide, a radiationless transition to $\mathrm{B}\,^3\Pi_g$ can occur with a subsequent radiative transition to $\mathrm{A}\,^3\Sigma_u^+$.

A direct radiative transition $^5\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ with emission of a recombination continuum would explain the experimental results as well. In the case of inverse predissociation, a vibrational structure of the emission can be expected.

The estimated k_3 value from the present measurements presumably is still too high for radiation from $\mathrm{N}_2(^5\Sigma_g^+)$ whereas by recombination with a radiationless crossing to the $\mathrm{B}\,^3\Pi_g$ state, k_3 is too low for the transition probability of the first positive band system. However, if the crossing point lies above the dissociation limit an activation energy term possibly could lower k_1 by $\exp(-E_{\mathrm{a}}/R\,T)$. In this case k_{R} would include $k_3 = 2 \times 10^5\,\mathrm{sec}^{-1}$ as transition probability of the transition $\mathrm{B}\,^3\Pi_g \rightarrow \mathrm{A}\,^3\Sigma_u^+$.

For the three-body recombination of N atoms via the $\mathrm{B}\,^3\Pi_g$ state, $v' = 12$ is the highest vibrational level which has been observed in the Lewis-Rayleigh afterglow[27, 30]. In electrical discharges predissociation in the $v' = 13$ level of $\mathrm{N}_2(\mathrm{B}\,^3\Pi_g)$ molecules was found[31, 32] whereas predissociation from higher rotational states in the $v' = 12$ level is quite uncertain[32]. The $v' = 12$ level without rotation lies 868 cm^{-1} below the dissociation limit $D_0(\mathrm{N}_2) = 78\,719\ \mathrm{cm}^{-1}$ and $v' = 13$ lies 485 cm^{-1} or 1.4 kcal/mole above[33]. If the $v' = 13$ level of $\mathrm{B}\,^3\Pi_g$ becomes predominantly populated during the radiative recombination, an activation energy of $E_{\mathrm{a}} = 1.4$ kcal/mole would lower k_1. Taking $k_3 = 2 \times 10^5\,\mathrm{sec}^{-1}$ in the previous estimations, $k_{\mathrm{R}} = 10^{-19}\,\mathrm{cm}^3 \times \mathrm{molecule}^{-1} \times \mathrm{sec}^{-1}$ is obtained if the collision frequency k_1 is lowered by an activation energy of 1.4 to 2.3 kcal /mole which supports the hypothesis of a radiative recombination of $\mathrm{N}(^4\mathrm{S})$ atoms via the $\mathrm{B}\,^3\Pi_g$, $v' = 13$ state.

Measurements of the Lewis-Rayleigh afterglow at low pressures with higher spectral resolution and studies of the temperature dependences are in progress in order to confirm the assumed mechanism.

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