Rotational Energy Level Distribution of N_2^+ Ions Produced in Ionization of N_2 Molecules by Slow Electrons

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The distribution with respect to rotational energy levels is studied for $N_2^+(B^2\Sigma_u^+)$ ions produced through ionization of N_2 molecules by 36—300-eV electrons. It is shown that when incidence of the primary electrons on the collision chamber walls is eliminated the distribution of the $N_2^+(B^2\Sigma_u^+)$ ions among rotational levels can be described by the Boltzmann formula. Previously observed deviations from this formula can be attributed to electron-impact desorption of ions from the chamber walls and subsequent charge exchange between these ions and nitrogen molecules.

IT is well known[1-3] that in fast-electron-induced ionization of N_2 molecules the N_2^+ ions formed in the $B^2\Sigma_u^+$ state (the upper state of transitions leading to radiation of bands of the first negative N_2^+ system) are distributed among rotational energy levels according to the Boltzmann formula. It is less clear whether a Boltzmann distribution of the rotational levels also exists when the N_2^+ ions are produced by the impacts of slow electrons. In [4-6] deviations from the Boltzmann distribution were reported, but Moore and Doering[7] concluded that the Boltzmann distribution of $N_2^+(B^2\Sigma_u^+)$ ions is conserved even when they are produced by 30-eV electrons. Since information about the rotational level distribution of diatomic molecules excited by electrons is of great scientific and practical importance, we have investigated this distribution further for $N_2^+(B^2\Sigma_u^+)$ ions in order to account for the mentioned contradiction.

A possible cause of the non-Boltzmann distribution observed in [4-6] could be secondary processes leading to a different rotational distribution of $N_2^+(B^2\Sigma_u^+)$ ions. In our consideration of different secondary processes we directed our attention to the possibility that N_2^+ ions might result from interactions between nitrogen molecules and particles desorbed from the walls of the collision chamber by electron impact. To determine how this effect is involved in the investigated N_2^+ distribution we changed the design of the collision chamber used previously,[4] where the electron beam entered and emerged through long channels of relatively small diameter. In the new collision chamber the primary electrons were prevented from striking metal surfaces situated close to the region from which radiation was emitted into the spectrometer.

The new collision chamber was used to investigate the rotational level distribution of $N_2^+(B^2\Sigma_u^+)$ ions produced by 36–300-eV electrons. For this purpose we studied the intensity distribution in the rotational structure of the λ = 3914 Å band belonging to the first negative system of N_2^+. The nitrogen pressure in the collision chamber was 2×10^{-3} Torr. During the measurements the Faraday cup used to measure the electron beam current was shifted to a point far from the region where luminosity was observed, so that secondary processes involving beam electrons interacting with surfaces of the Faraday cup could not affect the measurements.

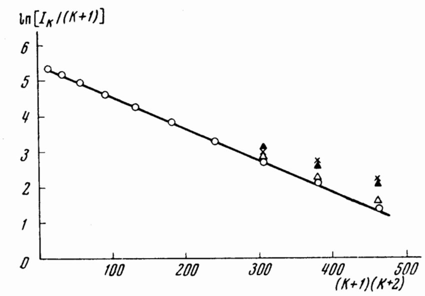

FIG. 1. Graph of Eq. (1) for N_2^+ ions: O—present results, without a metal plate close to the luminous space; X—results in [4]; Δ—present results, with a steel plate close to the luminous space; ▲—the same, with a positive ~10-V potential applied to the steel plate.

To determine the rotational level distribution of the N_2^+ ions we used the customary function

$$\ln [I_K / (K+1)] = f((K+1)(K+2)), \qquad (1)$$

where I_K is the intensity of a rotational line and K is the rotational quantum number. Figure 1 shows this functional dependence for N_2^+ ions produced by 50-eV electrons in both the present work and in our earlier work.[4] The results obtained with the newer collision chamber are well fitted by a straight line and thus indicate a Boltzmann distribution of $N_2^+(B^2\Sigma_u^+)$ rotational levels. The rotational temperature calculated from the tangent of the slope angle of (1) equalled the temperature of nitrogen in the collision chamber. Our present results thus differ from those in [4]. Since in the present work we excluded the incidence of electrons on the collision chamber walls, the deviation from a Boltzmann distribution in [4] is attributable to secondary interactions between nitrogen molecules and particles desorbed from the chamber walls by the impacts of primary electrons. This effect could also have played a part in [5,6].

Our conclusion that particles desorbed from the collision chamber walls distorted the rotational level distribution of $N_2^+(B^2\Sigma_u^+)$ ions was confirmed by experiments that will now be described. We introduced into the collision chamber a steel plate[1)] that could be

[1)]The earlier collision chamber was made of steel.

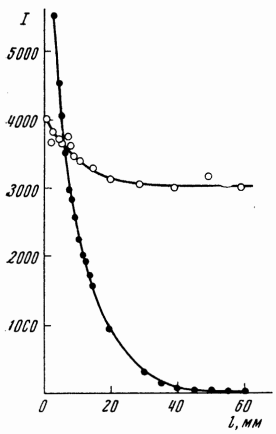

FIG. 2. Graphs of I(l): ●—the λ3914 band of the first negative system of N_2^+ ions; O—the λ3994 band of the second positive system of N_2 molecules (with relative units for I).

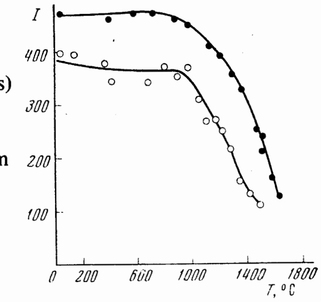

FIG. 3. Intensity (in relative units) versus temperature: ●—the λ3914 band of the first negative system of N_2^+; O—the λ4272 band of the system of comet tail bands of CO^+.

shifted in the direction of the electron beam axis, thus varying the distance from the surface of the plate to the space that emitted radiation into the spectrometer. With the steel plate situated 3 mm from this space and using 36-eV electrons, we measured the intensity distribution of rotational lines in the λ3914 band. The results, which are also shown in Fig. 1, indicate that the presence of a steel plate close to the region of observed luminescence causes the N_2^+ rotational level to deviate from the Boltzmann distribution. This deviation becomes considerably more pronounced when a small positive potential (~ 10 eV) is applied to the plate (see Fig. 1). On the other hand, the deviation is diminished when a negative potential is applied to the plate. When the plate was removed to a distance of 60 mm from the luminous region the rotational levels of $N_2^+(B^2\Sigma_u^+)$ ions did not depart appreciably from a Boltzmann distribution.

The results of the described experiments indicate that secondary processes induced by interactions between desorbed particles and molecules of the investigated gas affect the rotational level distribution of $N_2^+(B^2\Sigma_u^+)$ ions.

Additional experiments were performed to investigate how the band intensities of the first negative system of N_2^+ and the comet tail bands of CO^+ are affected by a metallic surface located close to the observed gas volume. A tungsten plate was used instead of steel, because electron-impact desorption has been well studied for the W–CO[8, 9] and W–N_2[9] systems.

Figure 2 shows graphs of I(l) (where l is the distance from the tungsten plate to the observed region and I is the intensity) for the λ3914 band and also for the λ3994 band of the second positive system of N_2. The λ3914 band becomes greatly intensified as the tungsten plate approaches the luminous region. A similar, but much weaker, effect is observed for the λ3994 band of the neutral nitrogen molecule. Similar I(l) curves were plotted for bands of neutral and ionized carbon monoxide molecules.

If the described effects are associated with desorption, induced by an electron beam, from a gas layer adsorbed on the surface of the tungsten plate, the intensities of the investigated bands should diminish as the temperature of the plate is increased. Figure 3 shows that this temperature effect is actually observed for the λ3914 band of N_2^+ and the λ4272 band of CO^+. Experiments in which a positive or a negative potential is applied to the metal plate show that the desorbed particles involved in enhancing the band intensities of N_2^+ and CO^+ ions are positive ions.

The ions desorbed from the metal surface by electron impact have low energies. Therefore the only possible process that can lead to the appearance of excited N_2^+ and CO^+ ions is charge exchange between the desorbed ions and N_2 or CO molecules.

The hypothesis that the deviation from a Boltzmann rotational level distribution of the $N_2^+(B^2\Sigma_u^+)$ ions is induced by interactions between slow ions, desorbed from the collision chamber walls by the electron beam, and N_2 molecules is in conformity with the data in [10, 11]. These investigations established deviations from a Boltzmann distribution for $N_2^+(B^2\Sigma_u^+)$ ions that were produced by charge exchange between different ions and nitrogen molecules.

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