

ROTATIONAL AND VIBRATIONAL ENERGY LEVEL DISTRIBUTIONS OF N_2^+ IONS
PRODUCED IN COLLISIONS BETWEEN ELECTRONS AND NITROGEN MOLECULES

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The intensity distribution of the rotational lines observed in the 4278 Å (0, 1) band of the first negative system of the N_2^+ ion (1 n.s. N_2^+) is investigated. The 1 n.s. N_2^+ bands were excited by 25–600-eV electrons traversing a chamber filled with nitrogen at 2×10^{-3} mm Hg. When the electron energy exceeds 100 eV the intensity distribution of the λ 4278-band rotational lines can be described by the Boltzmann formula. Deviations from this formula are observed below 100 eV; the degree of the deviation increases as the electron energy decreases.

The relative intensities of the 1 n.s. N_2^+ bands at 3884 Å (1, 1), 3914 Å (0, 2), 4236 Å (1, 2), 4278 Å (0, 1), 4652 Å (1, 3), and 4709 Å (0, 2) are measured. The relative population of the first vibrational level of the $B^2\Sigma_u^+$ state of N_2^+ is calculated for various electron energies on the basis of the measured relative band intensities. For electron energies below 100 eV the population deviates from the value computed on the basis of the Franck-Condon principle. A correlation is observed between the deviation of the intensity distribution in the rotational structure from the Boltzmann distribution and the degree of deviation of the relative population of the first vibrational level from the value computed on the Franck-Condon principle.

INTRODUCTION

IN earlier work^[1, 2] we investigated the rotational and vibrational energy level distributions of N_2^+ ions produced in collisions of different ions with nitrogen molecules. It was established that the rotational level distribution is not of the Boltzmann type. It was also found that following some of the ion-molecule collisions the relative population of the first vibrational level of the $B^2\Sigma_u^+$ state differs from the value calculated on the basis of the Franck-Condon principle.¹⁾ The magnitudes of all the deviations depend on the kind of ion and its velocity.

The present work was undertaken to determine whether similar effects occur in collisions between electrons and molecules. According to a theoretical calculation in^[4] that has been confirmed by recent experimental work,^[5–8] molecules excited by collisions of sufficiently fast electrons exhibit a Boltzmann distribution of their rotational level energies. No definite conclusion was reached in the case of slow electrons, because in some of the pertinent investigations^[3, 9, 10] the experimental error of rotational line intensities was quite large (15–20%);

the experimental conditions were sometimes quite imprecise.^[9, 10] Even less information is available regarding the vibrational-level populations of the upper electronic states of molecules excited by slow electrons.

It is therefore evident that we have only very incomplete information regarding the rotational and vibrational level distributions of molecules excited to high electronic states by slow electrons. This insufficiency is reduced somewhat by the present work, where, as in^[1, 2] we have investigated the $B^2\Sigma_u^+$ state of N_2^+ ions; in the present instance the nitrogen molecules were excited by electrons.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The excited N_2^+ ions were produced in the emission chamber 1 (Fig. 1), which was filled with nitrogen flowing continuously into the chamber and passing out through ducts 5 into another chamber 7 that was evacuated by an oil diffusion pump. When the nitrogen pressure in the emission chamber was 2×10^{-3} mm the pressure differential in the ducts 5 was 2×10^3 .

An electron beam was emitted by the electron gun 2, which had an oxide cathode. The electron

¹⁾A similar effect has also been observed by Sheridan and Clark.^[3]

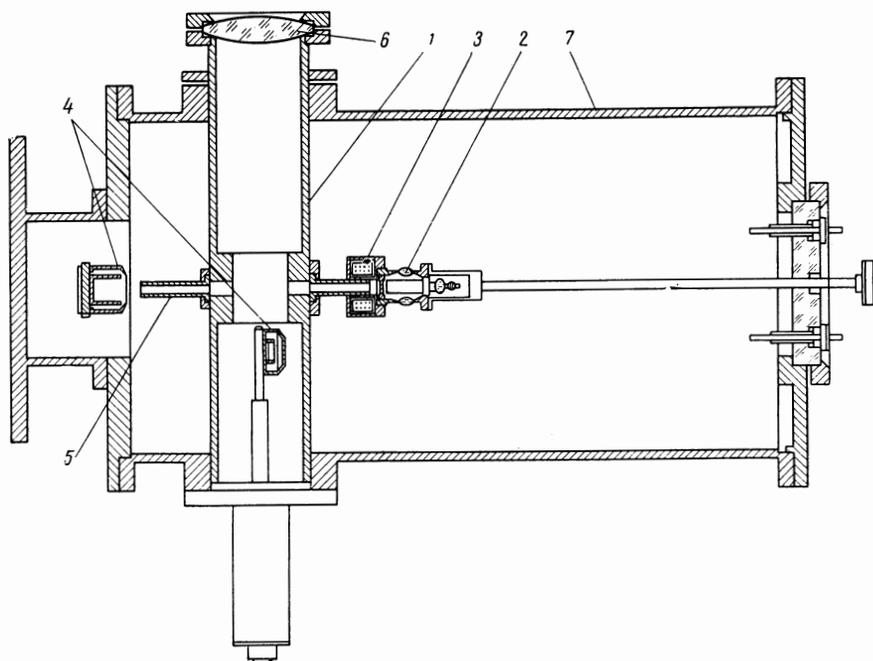


FIG. 1. Scheme of experimental apparatus.

energy was varied by regulating the negative potential of the cathode, and the electron beam was focused by the magnetic lens 3. The beam current was measured by means of two Faraday cups 4. One of these cups measured the beam current in the emission chamber; the other cup was located outside an exit duct of the chamber and measured the beam current traversing the chamber. The electron current strength depended on the electron energy and varied from 50 to 300 μ A.

The nitrogen radiation excited by the electron beam was focused by an achromatic objective lens 6 on the gap of an ISP-51 spectrograph. A photoelectric method was used to measure the relative intensities of the rotational lines in 1 n.s. N_2^+ bands as well as the relative intensities of bands in this system. The measuring apparatus and some details of the technique have been described in [1, 2].

The rotational structure of the band was registered 10–20 times for each fixed electron energy; the mean relative intensities of the rotational lines were then determined, with a statistical error, based on the spread of the observations, equal to 2–3% for $K = 2$ –14 lines and 4–5% for $K = 16$ –20 lines. The analogous error of the relative intensities of bands was 7%.

EXPERIMENTAL RESULTS

The distribution of excited N_2^+ ions among rotational energy levels was obtained by measuring the relative intensities of rotational lines characterized by even rotational quantum numbers. The R

branch of the 4278 Å (0, 1) spectrum of the 1 n.s. N_2^+ was investigated by means of 25–600-eV electrons that traversed an emission chamber filled with nitrogen at 2×10^{-3} mm Hg. The measured relative intensities I_K of the rotational lines were used in a plot of

$$\ln \frac{I_K}{K+1} = f[(K+1)(K+2)] \quad (1)$$

which is known^[11] to be represented by a straight line when the rotational energy level distribution of the emitting molecules is of the Boltzmann type. The slope of this straight line is proportional to the temperature of the radiating molecular system.

Figure 2 shows points of (1) for several electron energies. The points representing $K = 0$ –10 lines are shown only for 600-eV electrons; the corresponding points pertaining to other energies coincide with the former. Figure 2 shows that at 600 and 300 eV the points of (1) fit a straight line whose slope corresponds to a temperature of 306° K; this equals the temperature of the emission chamber walls within the experimental error limits. At 150 eV a very small deviation from a straight line is observed for rotational lines with $K = 18$ and 20. This deviation becomes more pronounced at 100 eV and is enhanced further as the electron energy decreases. We therefore conclude that the rotational energy level distribution of excited N_2^+ ions from ionization by 100-eV electrons does not fit the Boltzmann formula, but deviates therefrom in the same way as for ions colliding with N_2^+ mole-

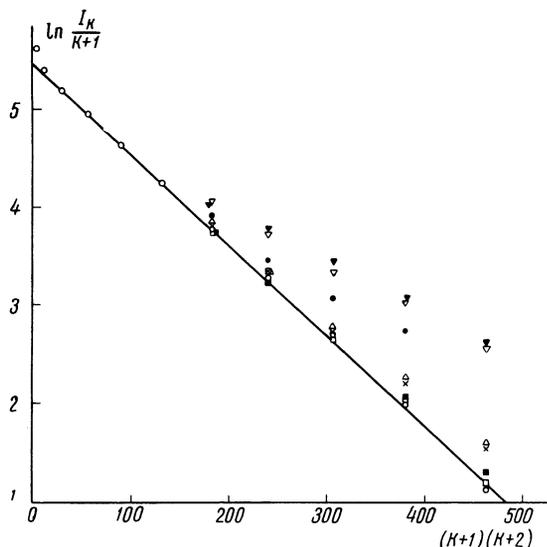


FIG. 2. Plot of Eq. (1) for the 4278-Å band excited by electrons of different energies (in eV): \circ - 600, \square - 300, \blacksquare - 150, \times - 100, \triangle - 70, \bullet - 50, ∇ - 35, \blacktriangledown - 25.

cules,^[1, 2] i.e., the population of high- K rotational levels is increased.

It should be noted that the deviation from a Boltzmann distribution which was observed in our present work was not observed by Sheridan,^[12] who plotted (1) for 40-eV electrons and obtained a straight line with a slope corresponding to 426° K, a temperature much higher than that of the nitrogen traversed by the electron beam.

There is only an apparent discrepancy between our results and those of Sheridan. When a straight line is drawn by means of least squares through the points of (1) for 50-eV electrons²⁾ we find that the slope corresponds to 411° K. It is thus clear that a large error incurred in measuring I_K prevented Sheridan from noticing the non-Boltzmann distribution of points corresponding to large values of K . When he drew a straight line through his experimental points he obtained the unphysical result that the N_2^+ system retained a Boltzmann distribution at a temperature considerably higher than that of the nitrogen in the emission chamber.³⁾

²⁾Some of the points of (1) will not lie on this line.

³⁾In [9] Lindh reported the same result as Sheridan, but from an investigation using 150- and 175-eV electrons. A Boltzmann distribution was retained but the N_2^+ system was found to be considerably above room temperature. However this result is accounted for easily when we remember that the walls of the metal container holding the nitrogen that was traversed by the electron beam could be heated by emission from the cathode. Sheridan's apparatus was designed in such a way that under his experimental conditions the nitrogen could not be heated in this manner.

To determine the ratio N_1/N_0 , where N_1 and N_0 are the populations of the first and zero-point vibrational levels of the N_2^+ state $B^2\Sigma_u^+$, we measured the following band intensity ratios of the 1 n.s. N_2^+ spectrum:

$$\frac{I_{3884}(1, 1)}{I_{3914}(0, 0)}, \quad \frac{I_{4236}(1, 2)}{I_{4278}(0, 2)}, \quad \frac{I_{4652}(1, 3)}{I_{4709}(0, 2)} \quad (2)$$

Using the values given by Bates^[13] for the probabilities of transitions between different vibrational levels of the N_2^+ states $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$, the ratio N_1/N_0 was calculated for each of the given three ratios.^[2, 3]

Figure 3 shows values of N_1/N_0 averaged over the values calculated from the three band intensity ratios as a function of electron energy. Beginning at ~ 100 eV, N_1/N_0 increases as the electron energy decreases. This result indicates that when N_2^+ ions are produced in N_2 ionization induced by electrons having ≤ 100 eV, N_1/N_0 cannot be calculated if it is assumed that the transitions between $X^1\Sigma_g^+$ states of the N_2 molecule and $B^2\Sigma_u^+$ states of the ion N_2^+ obey the Franck-Condon principle.

DISCUSSION OF RESULTS

It has been shown in the preceding section that when N_2 is ionized by electrons with ≤ 100 eV a non-Boltzmann rotational energy level distribution of the N_2^+ ions is produced. The relative populations of high- K rotational levels exceed the Boltzmann values; the relative populations of low- K levels will accordingly be lower. This redistribution is shown in Fig. 4, which consists of a Boltzmann distribution $I_K(K)$ of N_2^+ ions at 306° K (the nitrogen temperature in the emission chamber) and the measured distribution produced by 50-eV electrons (showing the upward shift of high- K levels). The experimental shift is inconsistent with the selection rule $\Delta K = \pm 1$ for rotational transitions; therefore the observed deviation from a Boltzmann distribution furnishes evidence that when N_2^+ ions are produced by sufficiently slow electrons striking

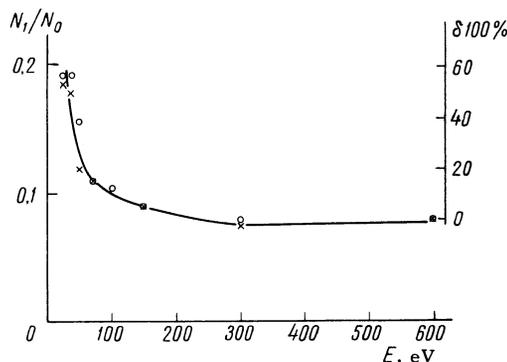


FIG. 3. Plots of $\delta(E)$ and $N_1/N_0 = f(E)$. \times - N_1/N_0 ; \circ - δ .

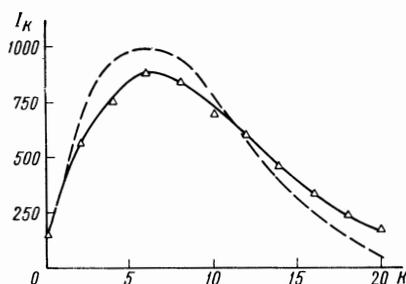


FIG. 4. Plots of $I_K(K)$. Dashed curve – Boltzmann distribution at 306°K; solid curve – experimental distribution of N_2^+ ions from N_2 ionization by 50-eV electrons.

N_2 molecules the given selection rule is violated and transitions with $|\Delta K| > 1$ begin to occur.

The increasing shift of the $I_K(K)$ curve towards high values of K as the electron energy is reduced indicates a corresponding increase in the fraction of electron translational energy that is converted into nuclear rotational energy in the struck molecules. It must be emphasized that a similar situation exists in the conversion of electron translational motion into nuclear vibrational energy in N_2^+ ions. This follows from the fact that beginning with 100-eV electrons the relative population of the first vibrational level of the N_2^+ state $B^2\Sigma_u^+$ is augmented as the electron energy is reduced (Fig. 3) and the vibrational energy transferred to the N_2^+ ions is accordingly increased.

A definite correlation exists between the transfers of rotational and vibrational energy to N_2^+ ions from electrons colliding with N_2 molecules. This correlation is manifested primarily by the fact that an identical electron energy is associated with the beginning of the deviation from a Boltzmann rotational level distribution and with the deviation of relative vibrational level populations in an upper electron state of N_2^+ from the value based on the Franck-Condon principle. However, the relationship between the transfers of rotational and vibrational energy to N_2^+ ions is not limited only by the identical observed thresholds. We characterize the degree of deviation from the Boltzmann distribution by the quantity

$$\delta = \left(\Delta \ln \frac{I_K}{K+1} \right) / \left(\ln \frac{I_K}{K+1} \right)_B$$

where the denominator is the value of $\ln [I_K/(K+1)]$ for the $K = 18$ rotational line when $I_K(K)$ is a Boltzmann distribution and corresponds to the nitrogen temperature in the emission chamber, and the numerator is the deviation of $\ln [I_K/(K+1)]$ for the observed $K = 18$ rotational line. It can then be shown that the dependence of this quantity on electron energy is identical with the electron-

energy dependence of N_1/N_0 . Thus, we use the points in Fig. 2 to plot $\delta(E)$ in Fig. 3 and connect the $\delta(E)$ curve to the $N_1/N_0 = f(E)$ curve in the region where both δ and N_1/N_0 are independent of the electron energy. In Fig. 3 the two curves coincide in the region ≤ 100 eV.

It is still impossible to achieve an exhaustive interpretation of our present results. For this purpose we require additional experimental and theoretical investigations of the populating of excited rotational and vibrational electronic levels by electron-molecule collisions at different energies. For the time being the following preliminary remarks are permissible.

A coincidence between the measured value of N_1/N_0 and the value based on the hypothesis that a given molecular transition to a higher electronic state obeys the Franck-Condon principle denotes essentially that the electron energy expended in exciting this electronic transition is expended for this transition alone and is not converted directly into nuclear vibrational motion. On the other hand, an examination of the Franck-Condon principle and of its quantum-mechanical formulation shows that this principle is valid only when the wave function of the exciting electron can be represented by a plane wave, i.e., in the Born approximation. Therefore for electrons that are sufficiently fast to satisfy the Born approximation the Franck-Condon principle will hold true and will yield values of N_1/N_0 that coincide with the measured values. However, when the electron energy is small enough to invalidate the Born approximation the Franck-Condon principle may no longer hold and the respective values of N_1/N_0 may cease to coincide. Therefore the discrepancy that we have observed between the measured and calculated values of N_1/N_0 indicates that for the electronic transition investigated in the present work the Born approximation can be applied only to electrons having energies beyond the 100–150-eV range.

A similar situation evidently exists in connection with the non-Boltzmann rotational level distribution, which is associated, as indicated above, with violation of the selection rule $\Delta K = \pm 1$. The validity of this selection rule is also associated with the applicability of the Born approximation to calculations of rotational level populations in the upper electronic state of the molecule. Therefore the deviation from a Boltzmann distribution is here also associated with the inapplicability of the Born approximation to electronic-rotational transitions induced by slow electrons.

It is noteworthy that the Born approximation cannot be applied to calculations of processes lead-

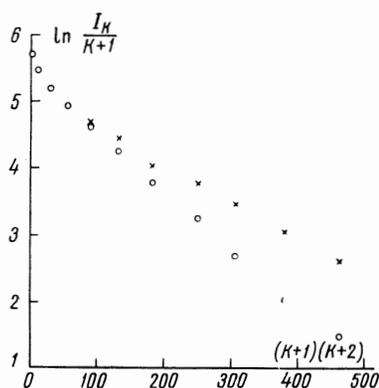


FIG. 5. Plots of Eq. (1) for electrons and protons having almost identical velocities. \times - e, \circ - H^+ .

ing to the populating of rotational and vibrational levels at an identical electron energy. However, for the ionization and excitation of hydrogen atoms by electron impact,^[14, 15] which are processes that differ very much from those studied in the present work, Born-approximation calculations of cross sections begin to yield quantities differing from the actual measurements even below 100 eV.

It should be noted, in conclusion, that the ionization of nitrogen molecules by means of electrons and ions, respectively, does not yield identical rotational and vibrational level distributions of N_2^+ ions. Since a meaningful comparison of these distributions can be made for identical electron and ion velocities, our data can be used to make a comparison for electrons and protons. Figure 5 shows points of (1) for the 4278-Å band of the 1 n.s. N_2^+ that were obtained in two experimental investigations: 1) with electrons at 3×10^8 cm/sec, and 2) with protons at 2.5×10^8 cm/sec (taken from^[11]). It is seen that a greater deviation from the Boltzmann distribution is obtained with the electrons than with the protons. This result cannot be accounted for by an admixture of hydrogen atoms in the proton beam because the character of (1) did not change with an increase of nitrogen pressure in the collision chamber that caused doubling of the beam contamination with hydrogen atoms.

The ratio N_1/N_0 is also found to differ in the two cases; its value is 0.18 for electrons at 3×10^8 cm/sec and 0.14 for the protons at 2.5×10^8 cm/sec.^[2] The foregoing discrepancies are evidently associated with the fact that the Born approximation begins to break down at different electron and proton velocities (at higher electron veloc-

ities, as shown by our present work). A similar effect is also observed in the cases of hydrogen atom ionization by electrons^[14] and protons.^[16]

A possible cause of the stronger excitation of rotational and vibrational molecular motions by electrons as compared with protons is found in the very large change of electron velocity following the ionization and excitation of a nitrogen molecule; this increases the electron-molecule interaction time.

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