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CONCERNING THE DISTRIBUTION OF ROTATIONAL ENERGY LEVELS OF MOLECULES EXCITED BY ION IMPACT

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The experimental apparatus and technique employed for investigating the intensity distribution in the rotational structure of molecular band spectra are described. The intensity distributions of the rotational lines of the λ = 3914 and λ = 4278 Å bands in the spectrum of the first negative system of N_2^+, excited by the impact of a mixed beam of 30 keV protons and hydrogen atoms, were investigated. The observed distribution of the rotational line intensity was found to deviate from the Boltzmann distribution by an amount greater than the experimental error.

INTRODUCTION

THE passage of a beam of fast particles through a gas in a state of thermodynamic equilibrium is accompanied by the excitation of some of its molecules. An assembly of such excited molecules is a component of the beam–gas system, which is not in thermodynamic equilibrium, and, therefore, the energy distribution of the vibrational and rotational motion of particles in such a system can, in principal, differ from the Boltzmann distribution. However, if the effective cross section for the transfer of energy from an incident to a struck particle is very small, the distribution of the vibrational and rotational states in a system of excited molecules remains, in practice, the same as that for the particles of a gas which have not suffered collisions, i.e., the distribution is still of the Boltzmann type.

The problem of conservation or nonconservation of the Boltzmann distribution of the vibrational and rotational states for a system of excited molecules can be solved by investigating the distribution of intensities in the emission spectrum of these molecules. In the case of the rotational motion, the energy distribution over the states of this motion is investigated by measuring the intensities of the rotational structure lines in the bands of a molecular spectrum.

The distribution of intensities of the rotational structure lines in the bands of a molecular spectrum, excited by heavy-particle impact, has been investigated a number of times[1-6] by studying the distribution of intensities in the rotational structure of the bands in the first negative system of N_2^+ molecules (1n.s.N_2^+).

In the case of the excitation of the bands in the 1n.s.N_2^+ by the impact of protons of energies 3 keV,[2] 30 keV,[3] and 0.5–1 MeV,[4] it has been found that the distribution of intensities of the rotational structure lines in the bands λ = 3914 Å (vibrational transition 0–0) and λ = 4278 Å (vibrational transition 0–1) is identical with the Boltzmann distribution, within the limits of experimental error. The rotational temperature, calculated from the line intensity distribution, has been found to be equal to the gas temperature. Variation of the gas temperature by the heating or cooling of the collision chamber has led to a corresponding change in the rotational temperature of the system of excited molecules.[3] The results reported in [2-4] can be understood by assuming a small effective cross section for the transfer of the rotational energy from a proton to an N_2^+ molecule in a collision accompanied by the formation of an N_2^+ ion in the excited state $B^2\Sigma_u^+$. However, Branscomb et al.[1] have obtained different results: an estimate of the rotational temperature in the excitation of 1n.s.N_2^+ bands by the impact of a mixed beam of protons and hydrogen atoms gave a value between 700 and 1000° K. A similar result, i.e., the conservation of the Boltzmann distribution in the rotational structure of a band accompanied by a simultaneous increase in the rotational temperature so that it becomes higher than the gas temperature, has been reported by Doering.[5] Doering excited the 1n.s.N_2^+ spectrum by the impact of N_2^+ ions of 10 keV energy. An investigation of the distribution of intensities in the rotational structure of the λ = 3914 Å band gave a rotational temperature of 475° K.

The 1n.s.N_2^+ spectrum was excited in [4, 6] by

Li^+ ions of 2–3 keV energy. In the first of these investigations, it was found that the Boltzmann distribution was not obeyed by the rotational structure of the $\lambda = 4278$ Å band. In the second investigation, a rotational structure was observed right up to the rotational line with $K = 47$ (K is the rotational quantum number). The authors of that paper are of the opinion that the intensity distribution observed by them is of the Boltzmann type with a rotational temperature of 3500° K and the deviation from this distribution in the region of low rotational quantum numbers is explained by the superposition of rotational lines of the R- and P-branches.

It is evident from this review that there are only a few papers on the distribution of intensities of the rotational structure lines in the bands of molecular spectra, excited by ion impact. Moreover, the experimental errors of the photographic photometry method of measurement of the intensities of the rotational structure lines used in all these investigations, with the exception of Doering's study,[5] were quite considerable.

In view of this, the problem of the distribution of intensities in the rotational structure of molecular band spectra, excited by ion impact, still remains unsolved. This problem, involving studies of the processes of the transfer of rotational motion in the collisions of ions and electrons with gas molecules, is of considerable scientific importance. Moreover, the investigation of the distribution of intensities in the rotational structure is of great practical significance in the determination of the temperature in the upper layers of the atmosphere from the molecular bands in the spectra of auroras and night airglow.

We investigated the rotational structure of the bands $\lambda = 3914$ Å and $\lambda = 4278$ Å in the 1n.s.N_2^+ spectrum, excited by the impact of particles in a mixed beam of protons and hydrogen atoms of 30 keV energy, using a photoelectric method to measure the line intensities. Because a photoelectric method was used, the results were drawn from a larger number of spectrograms and a statistical treatment of these results ensured a higher accuracy in the measurement of the intensities of rotational lines than in the researches just reviewed.

EXPERIMENTAL APPARATUS AND MEASUREMENT METHOD

In order to obtain a fully resolved rotational structure in a molecular band, it is necessary to use a spectroscopic instrument of sufficiently high resolving power. The relative aperture of such instruments is small and, therefore, to record photoelectrically the rotational structure, it is necessary to increase the intensity of radiation as much as possible and to use a photoelectric instrument of the highest possible sensitivity.

The intensity of emission of excited gas molecules can be increased by increasing the current of the beam of ions entering the radiation chamber. The apparatus used earlier to investigate the emission spectra of various molecular gases[7] was modified for the purpose of increasing this current. The ion-beam current entering the radiation chamber was increased by adopting the following measures: 1) using an ion source producing a strong ion beam; 2) additional focusing of the ion beam, beyond the magnetic analyzer, by the electric field of a quadrupole lens; 3) using a fast diffusion pump for differential pumping of the gas admitted to the radiation chamber, which made it possible to increase the diameter of the entry aperture of the radiation chamber.

The apparatus is shown schematically in Fig. 1. The gun producing a beam of hydrogen ions consisted of an arc ion source 1 discharging in a magnetic field and a three-electrode lens 2, which simultaneously focused the ion beam and accelerated the ions to the maximum energy of 30 keV. The minimum energy of the ions was 10 keV. Using a corrector 3, consisting of two parallel-plate capacitors, we could displace the beam in two mutually perpendicular planes. Protons were extracted from the beam of hydrogen ions by means of a magnetic analyzer 5. A beam of protons issuing from the magnetic analyzer was additionally focused onto the entry channel of the radiation chamber 7 by a quadrupole electrostatic lens 6. The beam current was measured using Faraday cylinders 4 placed in front of the magnetic analyzer, in the radiation chamber (not shown in Fig. 1), and behind the radiation chamber.

The apparatus was pumped with two oil-diffusion pumps working at the rate of 1000 and 2500 liter/sec, respectively. One pump removed the gas entering the ion source, while the second removed the gas admitted to the radiation chamber. The residual gas pressure in the radiation chamber was 1×10^{-5} mm Hg.

The investigation of the 1n.s.N_2^+ bands was carried out at two nitrogen pressures in the radiation chamber: 5×10^{-3} and 2×10^{-2} mm Hg. The corresponding pressures in the space between the mass analyzer and the radiation chamber were 7×10^{-6} and 3×10^{-5} mm Hg, respectively. The composition of the beam at the point, in the radia-

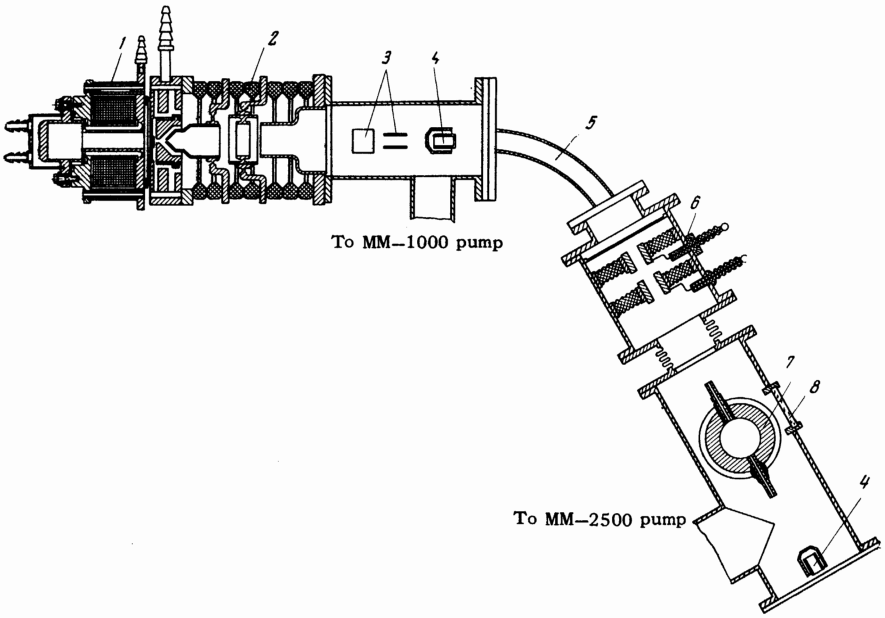

FIG. 1. Schematic diagram of the experimental apparatus.

tion chamber, from which light entered the spectrograph slit was 7% H^+ and 29% H^0 for a nitrogen pressure of 5×10^{-3} mm Hg, and 45% H^+, 55% H^0 for a pressure of 2×10^{-2} mm Hg.

The 1n.s.N_2^+ spectrum was recorded when the current of protons in the radiation chamber was of the order of 30 μA (in [7] the maximum beam current was 1 μA).

The gas temperature in the radiation chamber was measured with a thermocouple. Upon admission of a proton beam to the radiation chamber, the gas temperature in this chamber increased somewhat and became 330 ± 4° K.

A block diagram of the apparatus used to record the radiation spectrum of the gas is given in Fig. 2. The light from the radiation chamber, which passed through a quartz window 8 (Fig. 1), was focused by an achromatic objective with f = 85 mm onto the entry slit of an ISP-51-type spectrograph. A photoelectric attachment, FÉP-1, was added to the spectrograph ISP-51. Only the optico-mechanical part of this attachment was used. The linear dispersion of the spectrograph ISP-51 with the exit objective FÉP-1 was 32 Å/mm for $\lambda = 4713$ Å.

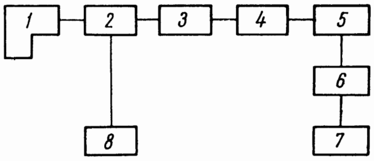

FIG. 2. Block diagram of the apparatus used to measure the intensities of spectral lines by the photoelectric method: 1) ISP-51 spectrograph; 2) photoelectric attachment with cryostat; 3) cathode follower; 4) UIS-2 amplifier; 5) ID-2 discriminator; 6) ISS counting-rate meter; 7) ÉPP-09 electronic potentiometer; 8) VS-10 rectifier.

On leading the exit slit of the FÉP-1 attachment, the light fell on the photocathode of a photomultiplier of the FÉU-64 type, which was placed in a cryostat so that the photocathode temperature could be varied from room temperature to liquid-nitrogen temperature. The FÉU-64 photomultiplier with an antimony–cesium cathode was operated at −70° C because at lower temperatures its sensitivity decreased rapidly.

The voltage applied to the photomultiplier was taken from a stabilized rectifier of the VS-10 type. The pulses from the photomultiplier output were passed through a cathode follower and amplified with an amplifier of the UIS-2 type. The dark pulses of the photomultiplier were discriminated against by a discriminator of the ID-2 type. After discrimination, the pulses were counted with an ISS counting-rate meter. The signal from the counting-rate meter was applied to an electronic potentiometer of the ÉPP-09 type and the spectrum was recorded on the chart of this potentiometer. A more detailed description of the photoelectric apparatus used in the present investigation can be found in [8].

To find a photomultiplier with a low dark-pulse level, we used the photoelectric apparatus described here, as well as an AI-100 pulse-height analyzer, to investigate the amplitude characteristics[8] and the dependence of the signal-to-noise ratio on the wavelength[9] of a number of Soviet and foreign photomultipliers. These investigations led to the selection of a photomultiplier of the FÉU-64 type with an antimony–cesium photocathode. The number of dark pulses per second for this multiplier at a photocathode temperature of −70 °C and at a discrimination level of 20 V was 0.5. This photomultiplier was used in all the investigations described below.

The time taken to record the rotational structure of one line on the chart of the ÉPP-09 potentiometer was 6 min.

During this time, the proton beam current entering the radiation chamber did not remain constant. The fluctuations in this current increased the error in the measurement of the intensities of the rotational structure lines. To reduce the error associated with these fluctuations, we recorded the value of the proton current simultaneously with the rotational structure. In the subsequent analysis, we selected those recordings of the rotational structure for which the current fluctuations did not exceed 4–5% during the recording time.

Figure 3 shows a typical recording of the rotational structure of the λ = 3914 Å band of the 1n.s.N_2^+ spectrum, excited by the impact of 30-keV protons. In the analysis of the rotational structure, it was assumed that the rotational line intensity was proportional to the amplitude of the corresponding peak, measured from the noise level. To reduce the error in the measurement of the rotational line intensities, we recorded one and the same 1n.s.N_2^+ band 10–50 times, keeping the experimental conditions constant. The value of the rotational line intensity was found as the average of the intensity measurements of all recordings in the same group. For a group of 10 recordings, the error in the measurement of the rotational line intensity was 2% for K = 0, 2, 4, 6, 8, 10, 12, 14, and 3% for K = 16, 18, 20 (K is the rotational quantum number). For a group of 20 recordings, the corresponding errors were 1.5 and 2–3%.

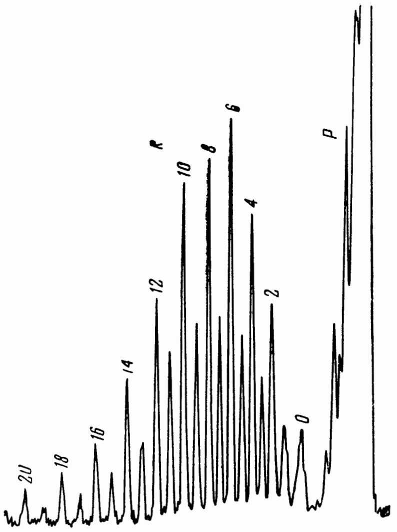

FIG. 3. Recording of the rotational structure of the λ = 3914 Å band of the 1n.s.N_2^+. Proton energy 30 keV. Nitrogen pressure 2×10^{-2} mm Hg. The numbers above the rotational structure lines are values of the rotational quantum number.

RESULTS OF THE MEASUREMENTS AND DISCUSSION

In order to establish the nature of the distribution of intensities of the rotational structure lines in the 1n.s.N_2^+ bands, we recorded the rotational structure of the λ = 3914 Å and λ = 4278 Å bands. At a pressure of 5×10^{-3} mm Hg, we took 10 recordings of the rotational structure of each of the bands; and at a pressure of 2×10^{-2} mm Hg, we took 50 recordings of the λ = 4278 Å band and 40 recordings of the λ = 3914 Å band. For each group of recordings, we determined the average values I of the line intensities in the rotational structure. These values were used to plot dependences similar to those shown in Fig. 4.

It must be mentioned beforehand that the deviation from the Boltzmann distribution of the intensities in the rotational structure of a band, associated with the transfer of the rotational motion to an excited molecule, can be detected experimentally only if the condition $\tau \ll t$ is satisfied (τ is the lifetime of the excited state of a molecule, t is the time between two successive collisions of gas molecules). When $\tau \gg t$, the assembly of excited molecules has time to return to the thermodynamic equilibrium with the gas obtaining before emission, and consequently, irrespective of the excitation mechanism, the distribution of intensities in the

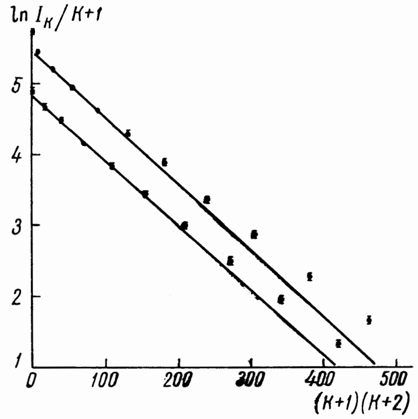

FIG. 4. Plot of ln[I/(K + 1)] = f[(K + 1)(K + 2)] for the λ = 4278 Å band of the 1n.s.N_2^+. Proton energy 30 KeV. Nitrogen pressure 2×10^{-2} mm Hg.

rotational structure of a band remains of the Boltzmann type.

The condition $\tau \ll t$, necessary for the observation of deviations from the Boltzmann distribution, was satisfied at the highest nitrogen pressure used in the present investigation. In fact, the lifetime of the zeroth vibrational level of the excited state $B^2\Sigma_u^+$ of the N_2^+ molecule is, according to Fink and Welge,[10] 5×10^{-8} sec. At a nitrogen pressure of 2×10^{-2} mm Hg, $t \approx 8 \times 10^{-6}$ sec. Thus, the condition $\tau \ll t$ was satisfied.

The distribution of the line intensities in the rotational structure of a molecular band in the spectrum emitted by a gas which is in thermodynamic equilibrium is given by the formula[11]

$$I = C(K+1)\exp\left[-\frac{B(K+1)(K+2)hc}{kT}\right], \qquad (1)$$

where C is a constant, K is the rotational quantum number of the lower level in an optical transition, B is the rotational constant of a gas molecule, and T is the gas temperature.

If we assume that when an N_2^+ ion is transferred to the $B^2\Sigma_u^+$ state by the collision of a proton with an N_2^+ molecule, the ion does not acquire rotational energy and, therefore, the distribution of intensities of the rotational structure lines in the electron band appearing on the transition of the N_2^+ ion from the $B^2\Sigma_u^+$ state to the ground state of the molecule should be also described by Eq. (1).

It is evident from Eq. (1) that the dependence of $\ln [I/(K + 1)]$ on the product $(K + 1)(K + 2)$ should be linear if the distribution of the line intensities in the rotational structure obeys this formula. The rotational temperature can be calculated from the tangent of the angle of slope of this dependence.

Figure 4 gives the experimental points for this dependence for lines with odd and even rotational quantum numbers in the structure of the $\lambda = 4278$ Å band, excited at a nitrogen pressure of 2×10^{-2} mm Hg. The vertical lines at each point indicate the error in the determination of the intensity of the corresponding rotational line. Figure 4 includes also a straight line for which the tangent of the angle of slope corresponds to a nitrogen temperature of 310 ± 4° K in the collision chamber. The points in Fig. 4 do not fit a straight line drawn as a tangent to a set of points at an angle corresponding to the gas temperature. The points for the rotational lines with odd values of K are distributed in the same way. At a nitrogen pressure of 5×10^{-3} mm Hg in the case of the $\lambda = 4278$ Å band, and at nitrogen pressures of 2×10^{-2} and 5×10^{-3} mm Hg in the case of the $\lambda = 3914$ Å band, we observe a similar distribution of the points with respect to a straight line drawn at an angle corresponding to the nitrogen temperature in the collision chamber.

Thus, it could be assumed that the distribution of the line intensities in the rotational structure of the $\lambda = 4278$ Å and $\lambda = 3914$ Å 1n.s.N_2^+ bands differed from the Boltzmann distribution. The difference was associated with the transfer of the rotational motion to the N_2^+ ion in atomic collisions. The intensities of several lines, corresponding to high values of K, were greater than those corresponding to the Boltzmann distribution at the gas temperature, and the difference increased as the value of K increased. This could be understood by assuming that the effective cross section for the transfer of the rotational motion to the N_2^+ ion increased when the rotational quantum number increased. There was still the problem of the cause of the deviation, from a straight line, of the points corresponding to low values of K. This deviation was probably due to the superposition of the R- and P-branch lines in the rotational structure of the investigated bands. According to Childs,[12] if the resolving power of a spectroscopic instrument is insufficient, an R-branch line with K = 0 can be masked by a P-branch line with K = 27, and an R-branch line with K = 2 may be masked by a P-branch line with K = 29. If a straight line is drawn, by the least-squares method, through all the experimental points of Fig. 4, the deviation of the points corresponding to K = 6, 8, 10, 12, 14, and 20 from this straight line lies outside the limits of the experimental error. The slope of the straight line corresponds to a rotational temperature of 335.4° K, which is slightly higher than the gas temperature in the collision chamber.

Roesler, Fan, and Chamberlain,[3] who investigated the distribution of intensities in the rotational structure of the $\lambda = 4278$ Å band at the same proton energy and the same nitrogen pressure as in the present study, found no deviation from the Boltzmann distribution. This was not surprising because these authors investigated the distribution of the rotational line intensities using a photographic-photometry method and, therefore, they obtained a small number of microphotograms for analysis. It should be mentioned that the measurement error in [3] was considerably greater than in the present investigation and, therefore, Roesler, Fan, and Chamberlain were unable to notice the relatively small deviation from the Boltzmann distribution.

In the other two investigations, in which the 1n.s.N_2^+ spectrum was excited with 3 keV[2] and 0.5–1 MeV protons[4] and no deviation was found from the Boltzmann distribution, the measurement method was similar to the method employed in [3]. Moreover, the effective cross section for the transfer of the rotational energy to the N_2^+ ion by high-energy protons could have been very small and this may have been the cause of the absence of deviations from the Boltzmann distribution in [4].

The very strong deviation from the Boltzmann distribution reported in [4] for the excitation of the 1n.s.N_2^+ spectrum by Li^+ ions of 2–3 keV energy indicates that the effective cross section for the transfer of the rotational motion in ion–molecule collisions depends strongly on the nature of the ion and its velocity. An investigation of this dependence will be carried out in our subsequent studies of the distribution of intensities in the rotational structure of molecular band spectra, appearing in the case of ion–molecule collisions.

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