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ROTATIONAL AND VIBRATIONAL ENERGY LEVEL DISTRIBUTION OF N_2^+ *IONS PRODUCED IN COLLISIONS BETWEEN FAST IONS AND NITROGEN MOLECULES*

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A photoelectric method for measuring the spectral line intensities was used to investigate the intensity distribution of the rotational lines in the $\lambda = 3884$ Å (1–1 transition), $\lambda = 3914$ Å (0–0), $\lambda = 4236$ Å (1–2), $\lambda = 4278$ Å (0–1) and $\lambda = 4709$ Å (0–2) bands of the first negative system of the N_2^+ ion excited in collisions of 5–30 keV H^+, H_2^+, He^+, C^+, N^+, O^+, Ne^+, N_2^+, CO^+ and Ar^+ ions with N_2 molecules. In every case, the distribution observed was found to differ from the Boltzmann distribution. As the ion velocity decreased, the deviation increased. The intensity ratios of the same bands were measured when they were excited with the same ions for which the distributions of the rotational line intensities in the band were investigated. The relative populations of the first vibrational level of the $B^2\Sigma_u^+$ state of the N_2^+ ion were calculated from the measured intensity ratios. In some of the investigated ion-molecule collision processes, the population of the first vibrational level of the $B^2\Sigma_u^+$ state of the N_2^+ ion violates the Franck-Condon principle.

INTRODUCTION

A deviation from the Boltzmann distribution was detected in our earlier investigation,[1] which dealt with the distribution of rotational energy levels of N_2^+ ions produced in collisions of 30 keV H^+ ions with N_2 molecules. The magnitude of this deviation was relatively small but we were able to detect it because of the considerable reduction in the experimental error by the use of a photoelectric method of measuring the intensities of rotational lines. Many investigators (for a list of references see[1]), including the authors of a recent paper,[2] have been unable to detect a deviation from the Boltzmann distribution for N_2^+ ions excited in collisions of various ions with N_2 molecules. This is due to the fact that the errors arising from the use of a photographic photometry method in the measurement of the intensities of rotational lines are greater than those arising in our study.

The deviation from the Boltzmann distribution, observed by us for N_2^+ ions formed in collisions with 30 keV protons, has since been investigated further for the purpose of finding the influence of the nature and velocity of ions on the distribution of intensities in the rotational structure of the series of bands in the first negative system of the N_2^+ ion (1 neg. N_2^+).

Simultaneously with the measurement of the relative intensities of the rotational lines in a band, we determined the relative intensities of a series of the 1 neg.N_2^+ bands. These measurements gave additional information on the deviation, observed by Sheridan and Clark,[2] of the relative populations of the levels in the $B^2\Sigma_u^+$ state of excited N_2^+ ions (produced by collisions of various ions with N_2 molecules) from the values which would be expected if the vibrational levels of the $B^2\Sigma_u^+$ state were populated in accordance with the Franck-Condon principle.

RESULTS OF MEASUREMENTS

1. Distribution of intensities in the rotational structure of the 1 neg.N_2^+ bands. The measurements of the relative intensities of the rotational and vibrational lines in the 1 neg.N_2^+ bands were carried out using the apparatus described in[1]. The sensitivity of the photoelectric device, used to measure the relative intensities of the lines and bands, was increased sevenfold by replacing an FÉU-64 photomultiplier with a 6256 S photomultiplier made by the EMI Company. Consequently, we were able to record the rotational structure of the 1 neg.N_2^+ bands when the ion current in the emission chamber was of the order of 1 μA, which made it possible to carry out measurements with ion beams of relatively low energy (up to 5 keV).

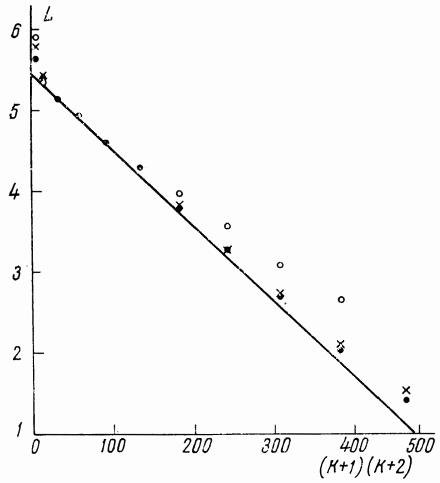
To determine the range of pressures of nitrogen in the emission chamber, in which excited N_2^+ ions were produced by single collisions of various ions with nitrogen molecules, we investigated the distribution of intensities in the rotational structure of the $\lambda = 4278$ Å band (transition 0—1) in the range of nitrogen pressures 5×10^{-4}—2×10^{-2} mm Hg. These experiments showed that in the cited range of nitrogen pressures, the distribution of intensities in the rotational structure of the $\lambda = 4278$ Å band was independent of the nitrogen pressure and, in the case of 30 keV protons, it coincided with the distribution reported in [1]. Further experiments were carried out at a nitrogen pressure of 2×10^{-2} mm Hg.

We investigated the distribution of intensities of the rotational lines in the 1 neg.N_2^+ bands, excited by collisions of H^+, H_2^+, He^+, C^+, N^+, O^+, Ne^+, N_2^+, CO^+, and Ar^+ ions of 5—30 keV energy with N_2 molecules.

The degree of deviation of the distribution of intensities of the rotational lines in a band from the Boltzmann distribution was established as follows. We plotted the dependence of the quantity $L \equiv \ln [I_K/(K+1)]$ on the product $(K+1)(K+2)$ (I_K was the relative intensity of the rotational line, corresponding to a rotational quantum number K). When the distribution of intensities in the rotational structure of a band was of the Boltzmann type, the dependence $L = f[(K+1)(K+2)]$ was linear.[3] The tangent of the angle of slope of this line was proportional to the temperature of the system of emitting molecules. The nature and the magnitude of the deviation from the straight line could be used to judge the nature of the deviation of the investigated distribution of intensities from the Boltzmann distribution.

Before investigating the influence of the ion velocity and the type of ion on the distribution of intensities in the rotational structure of a band, we studied the influence, on the same distribution, of the vibrational quantum numbers of the upper and lower states of a transition. We investigated the distributions of the intensities of the rotational lines in the 1 neg.N_2^+ bands of wavelengths λ equal to 3884 (1—1), 3914 (0—0), 4236 (1—2), 4278 (0—1), and 4709 (0—2) Å, excited with protons of 30 keV energy. For each band, we recorded not less than 10 spectrograms. The values of the rotational line intensities were found by averaging over all the recorded spectrograms. The error in the measurement of the intensities of the rotational lines with K from 2 to 16 was 2—3%, and for lines with K = 18, 20, was 4—5%. The nature and the magnitude of the deviation from the Boltzmann distribution for the investigated 1 neg.N_2^+ bands were independent of the vibrational quantum numbers of the upper and lower state of the transition.

The influence of the velocity of an ion on the distribution of the rotational energy levels of N_2^+ ions is illustrated in the figure, which shows the points representing the dependence $L = f[(K+1)(K+2)]$ for the $\lambda = 4278$ Å band, excited with He^+ ions 5, 15, and 30 keV. The points representing the rotational lines with K = 4, 6, 8 lie on the same straight line, the tangent of whose angle of slope corresponds to the temperature of nitrogen in the emission chamber (T = 310 ± 4°K).[1)] The temperature of nitrogen in the emission chamber was assumed to be equal to the temperature of the chamber walls, measured with a thermocouple.



Dependence of the quantity $L \equiv \ln[I_K/(K+1)]$ on $(K+1)(K+2)$ for the $\lambda = 4278$ Å band excited with He^+ ions of the following energies: ○—5 keV, X—15 keV, ●—30 keV.

It follows from the figure that the nature of the deviation of the distribution of the rotational line intensities from the Boltzmann distribution for He^+ ions is the same as for H^+ ions.[1] The degree of deviation increases as the velocity of He^+ ions decreases.

The distribution of the rotational line intensities in the 1 neg.N_2^+ bands, excited in collisions of other ions with nitrogen molecules, is qualitatively of the same nature as that for H^+ and He^+ ions.

[1)] There is a misprint on p. 1465 of our earlier investigation.[1] The correct version is: "When a beam of protons was admitted to the emission chamber, the temperature of the chamber rose slightly and became 310 ± 4°K".

Table I

Ion	Velocity, 10^8 cm/sec	δ, %	Ion	Velocity 10^8 cm/sec	δ, %
H^+	2.5	5.2±3	N^+	0.38	23±5
H^+	1.4	11±5	O^+	0.35	21±5
H^+	1	7.3±5	Ne^+	0,39	20±5
H_2^+	1.6	11±5	Ne^+	0,22	38±5
He^+	1.2	5±3	CO^+	0,26	28±5
He^+	0.9	7.3±5	Ar^+	0.18	47±5
He^+	0.5	38±5	N_2^+	0.26	46±5
C^+	0.4	28±5			

The degree of deviation δ from the Boltzmann distribution is given in Table I. Columns 3 of this table give the values of $\delta = \Delta L/L_B$, where L_B is the value of L for a rotational line with K = 18 when the intensity distribution is of the Boltzmann type at the temperature of nitrogen in the emission chamber, ΔL is the deviation of the value of L for a rotational line with K = 18 from the value L_B.

2. Distribution of intensities in the vibrational structure of the 1 neg.N_2^+ bands. We measured the ratios of intensities of the 1 neg.N_2^+ bands:

$$\chi_1 = \frac{I_{3884}(1-1)}{I_{3914}(0-0)}, \quad \chi_2 = \frac{I_{4236}(1-2)}{I_{4278}(0-1)}, \quad \chi_3 = \frac{I_{4652}(1-3)}{I_{4709}(0-2)},$$

which were excited in collisions of nitrogen molecules with the same ions that were employed in a study of the distribution of intensities of the rotational lines in the bands. The measurements of the band intensities were carried out using the maximum intensity of the band profile in a spectrogram.[2)] Because of the small difference between the wavelengths of the bands whose intensity ratios were measured, no correction was made in the ratio of the intensities to allow for the dependence of the sensitivity of the photomultiplier on the wavelength of the recorded radiation.

Using the experimentally determined intensity ratios χ_1, χ_2, and χ_3, we calculated the ratios N_1/N_0 of the populations of the first and zeroth vibrational levels of the $B^2\Sigma_u^+$ state of the N_2^+ ion. The ratios of the populations of the vibrational levels were calculated using the following formula:

$$\frac{I_{ij}}{I_{kl}} = \frac{N_i}{N_k}\frac{A_{ij}}{A_{kl}}\frac{\lambda_{kl}}{\lambda_{ij}}, \tag{1}$$

where N_i and N_k are the populations of the i-th and k-th vibrational levels of the upper electron state, and I_{ij}, A_{ij}, λ_{ij} are, respectively, the intensity of the band, the probability of the transition, and the wavelength, corresponding to a transition from an i-th vibrational level in the upper electron state to a j-th vibrational level in the lower electron state.

The ratios N_i/N_k could be calculated using the values of the Einstein coefficients, the values of the band strengths p_{ij}, proportional to the Einstein coefficients (to within a factor λ_{ij}^3), or the Franck-Condon factors q_{ij}, for constant moment of the electron transition.

The values of A_{ij} and p_{ij} for transitions from the state $B^2\Sigma_u^+$ to the ground state $X^2\Sigma_g^+$ of the N_2^+ ion, were calculated from the measured values of the relative intensities of the 1 neg.N_2^+ bands [4,5] and from the measured lifetimes of the upper electron states of the N_2^+ ion,[6] given in Nicholls's paper.[7] The values of p_{ij} were calculated from the relative intensities of the 1 neg.N_2^+ bands, measured by Herzberg [8] and reported by Bates.[9] The Franck-Condon factors for transitions between the states $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ of the N_2^+ ion were calculated by Nicholls.[10]

Table 2 lists the values of the ratio N_1/N_0 of the populations of the first and zeroth vibrational levels of the state $B^2\Sigma_u^+$ of the N_2^+ ion, calculated from the intensity ratios (measured in the present investigation) χ_1, χ_2, and χ_3 of the 1 neg.N_2^+ bands and from the values of A_{ij} taken from [7] (the left-hand column) and the values of p_{ij} taken from [9] (the right-hand column). The comparison was made for the excitation of the $B^2\Sigma_u^+$ state of the N_2^+ ions in collisions of H^+, He^+, and Ne^+ ions with nitrogen molecules.

For the same ions, Sheridan and Clark[2] measured the band intensity ratios χ_2 and χ_3. Using the value of χ_3 and the quantities A_{ij} taken from [7], Sheridan and Clark calculated the ratios N_1/N_0 which are given on the right-hand side of Table II. Moreover, we used the values of χ_2 and χ_3, reported by Sheridan and Clark,[2] and the values of A_{ij} from [7] and p_{ij} from [9] in the former case and p_{ij} taken from [9] in the latter case, to calculate the values of N_1/N_0, which are also given on the right-hand side of Table II.

It follows from Table II that the scatter of the values of N_1/N_0, calculated using various band intensity ratios (measured by different authors) is less if the values of p_{ij} given in [9] are used in the calculations. A small scatter is also obtained when the ratios N_1/N_0 are calculated using the Franck-Condon factors given in [10]. The greatest scatter of the values of N_1/N_0 is obtained when

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[2)] The measurements of the relative intensities, carried out in the present investigation using the band edges, gave values which were in good agreement with those reported by Sheridan and Clark, [2] who measured the intensities from the areas under the band profiles in microphotograms.

Table II. Ratio of populations of the first and zeroth vibrational levels N_1/N_0

Ion	Velocity 10^8 cm/sec	Results of present study						Results reported in [2]			
		χ_1		χ_2		χ_3		χ_2		χ_3	
		[7]	[9]	[7]	[9]	[7]	[9]	[7]	[9]	[7]	[9]
H^+	2.5	0.29	0.15	0.18	0.15	0.09	0.13	0.17	0.14	0.10	0.14
H^+	1.4	0.17	0.09	0.08	0.07	0.07	0.09	—	—	—	—
He^+	1.2	0.32	0.17	0.22	0.18	0.09	0.13	0.22	0.18	0.21	0.29
He^+	0,9	0,30	0.16	0.16	0,13	0.08	0,11	0,17	0.14	0.10	0.14
He^+	0.5	0,30	0.16	0.15	0.12	0.10	0.14	—	—	—	—
Ne^+	0.39	0,31	0.17	0.17	0,14	—	—	0.19	0.17	0.21	0.29

Table III

Ion	Velocity, 10^8 cm/sec	N_1/N_0	Ion	Velocity, 10^8 cm/sec	N_1/N_0
H^+	2.5	0.14±0.01	O^+	0,35	0,15±0,01
H^+	1.4	0.08±0.01	CO^+	0,26	0,18±0,02
H_2^+	1.6	0,09±0,01	N_2^+	0,26	0,18±0,02
He^+	1.2	0,16±0.02	N^+	0,38	0,18±0,02
He^+	0.9	0.13±0,02	Ne^+	0,39	0,15±0,02
He^+	0,5	0,14±0,01	Ne^+	0,22	0,14±0,01
C^+	0.4	0.16±0,01	Ar^+	0,18	0,18±0,02

the values of A_{ij} are taken from [7].3) In our subsequent calculations of the values of N_1/N_0, we shall use the band strengths p_{ij} given in [9]. The results of these calculations are listed in Table III, which gives the average of three values of the ratio N_1/N_0, calculated from the intensity ratios χ_1, χ_2, and χ_3.

DISCUSSION OF RESULTS

1. Distribution of the rotational energy levels of N_2^+ ions. The results of investigations of the distribution of rotational line intensities in the 1 neg.N_2^+ bands, excited in collisions of various ions with nitrogen molecules, show that in all the investigated cases there is a deviation from the Boltzmann distribution. Thus, the results given in [1], where this deviation has been observed for H^+ ions, have been confirmed for a number of other ions.

Qualitatively the nature of the deviation of the investigated distributions from the Boltzmann distribution is the same in all cases (cf. the figure). The degree of deviation from the Boltzmann distribution increases when the rotational quantum number increases and the line intensities are higher than those corresponding to the Boltzmann distribution. The quantitative values of the degree of deviation from the Boltzmann distribution are denoted by δ in Table I.

Although our investigation was carried out using ions whose velocities were within a narrow range, we were able to determine, in some cases, the influence of the velocity of ions colliding with nitrogen molecules on the degree of deviation of the investigated distribution from the Boltzmann distribution. In the case of He^+ and Ne^+ ions, the degree of deviation from the Boltzmann distribution increases when the ion velocity decreases. For H^+ ions, nothing definite can be said about the dependence of δ on the velocity of these ions, since in this case the deviation itself is small and the experimental error fairly large.

To determine the role of the nature of ions colliding with nitrogen molecules on the degree of deviation from the Boltzmann distribution it is necessary to compare the distribution of intensities in the rotational structure of bands excited by different ions of the same velocity. The experimental material obtained in the present investigation makes it possible to carry out such a comparison for C^+, N^+, O^+, and Ne^+ ions having velocities of $\approx 4 \times 10^7$ cm/sec. It is evident from Table III, that the value of δ for these ions is independent of the nature of the ion, within the limits of the experimental error.

Some of the conclusions about the influence of the nature and velocity of ions on the distribution of intensities of the rotational lines in the 1 neg.N_2^+ bands should be regarded as preliminary. Further investigations of the intensity distribution in the rotational structure of the 1 neg.N_2^+ bands are required over a wider range of velocities. It would be particularly interesting to extend the range in the direction of low velocities, since we may expect that at low velocities the deviation from the Boltzmann distribution should be considerably greater. It would be useful also to extend the range of investigated ions, including particularly alkali-metal ions since the deviation from the Boltzmann distribution in the excitation

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3) It should be mentioned that the value of A_{ij} for the 0–0 transition, given in Table II in [7], was calculated incorrectly since the ratio $A_{0,0}/p_{0,0}$ differed considerably from the corresponding ratios for other transitions.

of the 1 neg.N_2^+ bands by these ions[11,12] is greater than that obtained by us.

2. Distribution of the vibrational energy levels of N_2^+ ions. From the values of N_1/N_0, given in Table III, we can draw some conclusions about the vibrational level distribution of N_2^+ ions in the $B^2\Sigma_u^+$ state, formed in collisions of various ions with nitrogen molecules.

It should be mentioned that in all the investigated cases the distribution of the vibrational energy levels of N_2^+ ions departs very strongly from the Boltzmann distribution, which requires that the number of molecules in each vibrational state should be proportional to $\exp(-E/kT)$ (E is the energy of the vibrational motion of a molecule, T is the temperature of a gas, and k is the Boltzmann constant). According to the Boltzmann distribution, the ratio N_1/N_0 of the number of nitrogen molecules in the first vibrational state to the number of nitrogen molecules in the zeroth vibrational state in the nitrogen present initially in the emission chamber ($T \approx 300°K$) is equal to 1.4×10^{-5}. Comparison of this value with the values of N_1/N_0, given in Table III, leads to the conclusion that the relative population of the first vibrational level of N_2^+ ions formed in elementary processes accompanied by the transition of an ion to the upper electron state, is approximately four orders of magnitude greater than the relative Boltzmann population in the initial state of nitrogen molecules at room temperature.

The reason for such a strong deviation from the Boltzmann distribution is that the populations of the vibrational levels of N_2^+ ions formed under the experimental conditions obtaining in our investigations are governed solely by the probabilities of transitions from the zeroth vibrational level of the ground state of the nitrogen molecule to the vibrational levels of the $B^2\Sigma_u^+$ state of the N_2^+ ion. In view of this, the concept of the vibrational temperature cannot be applied, even in the loosest sense, to a system of N_2^+ ions formed as a result of various elementary excitation processes.

It follows from the data presented in Table III that the relative population of the first vibrational level of the N_2^+ ion is independent of the nature of the ions interacting with nitrogen molecules.

In the case of He^+ and Ne^+ ions there is no marked dependence of the value of N_1/N_0 on the velocity of ions but it would be incorrect to draw some definite conclusion from this since the investigated range of velocities was very narrow. Sheridan and Clark,[2] whose investigations were concerned with He^+ and Ne^+ ions in the velocity ranges of $(1-1.8) \times 10^8$ cm/sec and $(0.35-0.5) \times 10^8$ cm/sec, found that the value of N_1/N_0 did depend on the velocity of ions.

The following can be said about the dependence of the relative populations of the vibrational levels of molecules excited by electron transitions. If the transition to the upper electron state always takes place in exact agreement with the Franck-Condon principle, then there are no grounds to expect the value of N_1/N_0 to depend on the nature and velocity of ions and on the nature of the excitation process. However, if during an electron transition process the distance between nuclei in a molecule and the nuclear velocities do not remain constant, i.e., the Franck-Condon principle is violated in the transition, we may expect the relative population of the vibrational levels of the upper electron state to depend on the factors referred to above.

Bates[9] calculated the value of N_1/N_0 for the transition $N_2(X^1\Sigma_g^+) \rightarrow N_2^+(B^2\Sigma_u^+)$ in accordance with the Franck-Condon principle and found that this value was 0.11. In the case of excitation of the $B^2\Sigma_u^+$ state of the N_2^+ ion by electron impact and by the impact of H^+ or D^+ ions,[2] the value of N_1/N_0 agreed, within the limits of the experimental error, with the value calculated on the basis of the Franck-Condon principle and, in the velocity range $(1-4) \times 10^8$ cm/sec, it was independent of the velocity of exciting particles.

In the case of excitation of the $B^2\Sigma_u^+$ state of the N_2^+ ion by impact of He^+, N^+ and Ne^+ ions, Sheridan and Clark[2] obtained values for the ratio N_1/N_0 which were considerably higher than the calculated value and which depended on the velocity of exciting particles. The results of the present investigation confirmed this observation, since the values of N_1/N_0 for He^+, C^+, N^+, O^+, Ne^+, CO^+, N_2^+, and Ar^+ ions were also higher than the calculated ones.

Thus, from the results of Sheridan and Clark[2] and those reported in the present paper we may conclude that, in some ion-molecule collision processes, the population of the vibrational levels of the upper electron state violates the Franck-Condon principle. In all the investigated cases the population of the first vibrational level is higher than that which should apply in the case of an electron transition obeying the Franck-Condon principle.

In conclusion, it should be mentioned that a comparison of the data given in Tables I and II shows that there is no marked correlation between the transfer of the rotational and vibrational motion from an ion to a molecule in the same ion-molecule collision process.

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[1] G. N. Polyakova, V. I. Tatus', S. S. Strel'chenko, Ya. M. Fogel', and V. M. Fridman, JETP **50**, 1464 (1966), Soviet Phys. JETP **23**, 973 (1966).

[2] J. R. Sheridan and K. C. Clark, Phys. Rev., **140**, A1033 (1965).

[3] G. Herzberg, Molecular Spectra and Molecular Structure, vol. I, Spectra of Diatomic Molecules, 2nd ed., 1949 (Russ. Transl., IIL, 1949, p. 93).

[4] L. V. Wallace and R. W. Nicholls, J. Atm. Terr. Phys. **7**, 101 (1955).

[5] L. V. Wallace and R. W. Nicholls, J. Atm. Terr. Phys. **27**, 742 (1962).

[6] R. G. Bennett and F. W. Dalby, J. Chem. Phys. **31**, 434 (1959).

[7] R. W. Nicholls, J. Atm. Terr. Phys. **25**, 218 (1963).

[8] G. Herzberg, Ann. Physik **86**, 189 (1928).

[9] D. R. Bates, Proc. Roy. Soc. (London) **A196**, 217 (1949).

[10] R. W. Nicholls, J. Res. Natl. Bur. Stand (U.S.) **65A**, 451 (1961).

[11] E. M. Reeves and R. W. Nicholls, Proc. Phys. Soc. (London), **78**, 588 (1961).

[12] R. P. Lowe and H.I.S. Ferguson, Proc. Phys. Soc. (London) **85**, 813 (1965).

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