INTENSITY DISTRIBUTION IN THE ROTATIONAL STRUCTURE OF THE ELECTRON-VIBRATIONAL BANDS OF NITROGEN

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UDC 543.42

The intensity distribution was measured for the rotational lines of the N_2 molecule in the radiation of a glow discharge in the pure gas, at pressure 0.1-5 torr, or with argon, at a total pressure of 2 torr, at a current of 40 mA. The distribution found lags behind a Boltzmann distribution in the 0–3 band (corresponding to the $C^3\Pi - B^3\Pi$ transition; the second positive system) over the pressure range 0.1-2 torr and in the 1–4 band (the $C^3\Pi - B^3\Pi$ transition; second positive system) at a pressure of 0.1 torr. In the $N_2 + Ar$ mixture there is selective amplification of the J = 25, 26 rotational lines.

The radiation of glow discharges produced by a direct current in nitrogen (at pressures of 0.1 to 5 torr) and in a nitrogen–argon mixture (total gas pressure of 2 torr) was studied.

The cylindrical discharge tube with electrodes in side branches was 500 mm long and 8 mm in diameter. In a preliminary evacuation, a pressure of 10^{-5} torr was reached. In the gas mixture, the nitrogen pressure was 0.1 torr and the argon pressure was 1.9 torr.

We measured the intensity of the vibrational structure of the 0–3 (λ = 4059 Å) and 1–4 (λ = 3998 Å) nitrogen bands. The spectrum was produced on an ISP-67 spectrograph. The dispersion of this instrument in this range is 0.88 Å/mm. The triplet structure of the bands was resolved (see Fig. 1). The intensity was measured by means of photographic photometry.

For an equilibrium distribution of molecules among the rotational energy levels, the intensity of a rotational line in the electron-vibrational band is given by

$$I = C\nu^4 i e^{\frac{-E_r'}{\kappa T}}, \quad (1)$$

where C is a constant for a given band; i is the intensity factor, which can be calculated from the equations in [1],

$$E_r' = h \cdot cF'(J) \quad (2)$$

is the rotational energy of the molecules in the excited state; h is the Planck constant; c is the speed of light; and F'(J) is a function of the rotational quantum number, calculated from the equations in [2]. The corresponding graphical dependence of the quantity $\ln I - \ln i$ on F'(J) is a straight line, whose slope is the distribution temperature T_{ro}. In two particular cases this temperature can be equal to the gas temperature T_g: 1) in the radiation of an isothermal plasma; 2) in the radiation of a nonequilibrium low-pressure plasma, if the rotational energy of a molecule is not affected by electronic and vibrational excitation (i.e., if this rotational energy changes by a negligible amount, in particular, $\Delta J = \pm 1$) and if the level is completely depopulated.

We would expect the second condition to be satisfied in an N_2 discharge at a pressure on the order of 1 torr.

V. D. Kuznetsov Siberian Physicotechnical Institute, Tomsk State University. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 9, pp. 17-21, September, 1970. Original article submitted July 7, 1969.

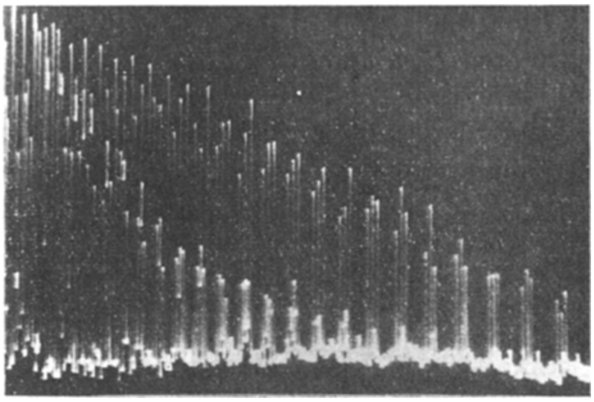

Fig. 1. Photomicrogram of the 0 – 3 (λ = 4059 Å) band in a discharge of pure argon at p = 2 torr.

TABLE 1

J \ p, torr	10^{-1}	0,5	1	2	5
23	1	0	0	0	0
24	8	3	2	0	0
25	17	9	9	2	0
26	22	18	10	6	0
27	28	22	14	15	0
28	32	28	24	20	0
29	32	30	26	23	0
30	40	32	26	26	0

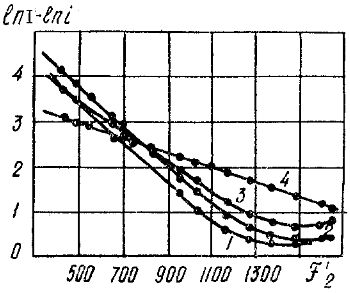

Fig. 2

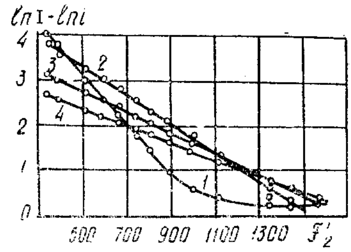

Fig. 3

Fig. 2. Discharge in pure nitrogen. The 0 – 3 band at the following pressures (torr): 1) 0.1; 2) 0.5; 3) 1; 4) 5.

Fig. 3. Discharge in pure nitrogen. The 1 – 4 band at the following pressures (torr): 1) 0.1; 2) 0.5; 3) 1; 4) 5.

RESULTS

In both the bands we measured the intensities of the rotational lines having J = 15 to J = 30 of the two branches R_2 and R_3. Using these intensities, we constructed graphical dependences of the level populations on quantities proportional to the level energy [lnI – lni; F'(J)].

1. Radiation of a Discharge in Pure Nitrogen

Figure 2 shows this dependence in the 0 – 3 band for a nitrogen pressure of 0.1-5 torr in the discharge tube. We see that the radiation of the J ≈ 15-23 lines is at an intensity which depends exponentially on the level energy. The lines with J = 23-30 display an intensity greater than equilibrium; the deviation decreases with increasing discharge pressure and vanishes completely at 5 torr, at which pressure all the experimental points conform to a straight line.

The deviation from a Boltzmann distribution is evaluated from

$$\delta = \frac{\Delta(\ln I - \ln i)}{(\ln I - \ln i)_B} \cdot 100\%, \tag{3}$$

where $(\ln I - \ln i)_B$ is the logarithm of the population for the case of a Boltzmann distribution; and $\Delta(\ln I - \ln i)$ is the deviation of the measured value from that given by Eq. (1). The values of δ for the 0 – 3 band are shown in Table 1.

Figure 3 shows the dependence of lnI – lni on F'(J) for the 1 – 4 band; for pressures in the range 0.5-5 torr the intensities of the rotational lines change exponentially with the energy. At 0.1 torr the higher rotations display a deviation from a Boltzmann distribution with increasing J, as can be seen in Table 2. We calculated the temperatures shown in Table 3 from the slopes of the linear regions of these curves.

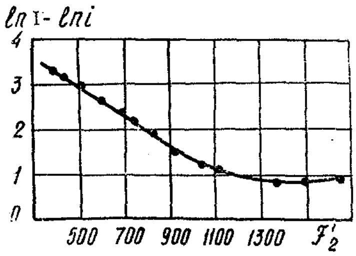

Fig. 4

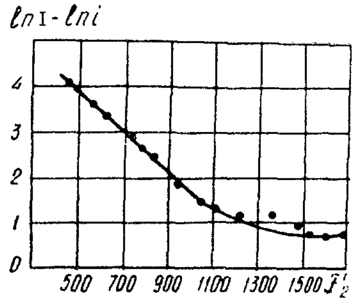

Fig. 5

Fig. 4. Discharge in the mixture N_2 + Ar. The 1–4 band. p_{tot} = 2 torr, p_{N_2} = 0.1 torr.

Fig. 5. Discharge in the mixture. The 0–3 band. p_{tot} = 2 torr; p_{N_2} = 0.1 torr.

TABLE 2

J	23	24	25	26	27	28	29
δ %	10	18	24	26	28	30	32

2. Radiation of a Discharge in a Mixture of N_2 + Ar

Using the intensities measured for the rotational structure for the 0–3 and 1–4 bands in a nitrogen–argon mixture we constructed the curves in Figs. 4 and 5. From Fig. 4 we see that the intensities of the rotational lines in the 1–4 band are not described by Eq. (1). Those of the J = 15-23 lines conform well to a straight line, whose slope yields a temperature of 500°K. The intensities of the lines with J > 23 are greater than predicted by Eq. (1).

Figure 5 shows the intensity distribution in the 0–3 band. The slope of the line plotted through the points corresponding to the intensities of the lines with J = 15-23 yields a temperature of 500°K. At J = 23 we begin to observe a deviation from the exponential law, in the direction of increasing level population.

In branch R_2 for two lines (J = 25, 26) there is a well-defined selective amplification on each photomicrogram.

DISCUSSION

1. Radiation of the 0 – 3 and 1 – 4 Bands in the Second Positive System of Nitrogen in a Discharge of Pure Nitrogen

Excitation of molecules in a low-pressure glow discharge presumably occurs through collisions with electrons. Figures 1 and 2 show that in a glow discharge the intensities of the rotational lines at high values of J (J > 23) do not have an exponential distribution. The high-J molecular rotation is evidently excited by electron collisions.

The extent of the deviation varies with the pressure: as the pressure in the nitrogen discharge is increased, the deviation decreases, and the dependence of lnI–lni on F'(J) becomes linear at p = 5 torr for the 0–3 band and p = 0.5 torr and above for the 1–4 band. When nitrogen is added, there is an increase in the number of collisions between molecules, and excited molecules of the $C^3\Pi$ state exchange rotational quanta with molecules in the (X'Σ) ground state. The magnitudes of the rotational quanta of the $C^3\Pi$ and X'Σ states are very nearly equal; for the J' = 11 → J" = 10 ($C^3\Pi$) state and the J' = 9 → J" = 8 (X'Σ) state, e.g., the energy of the rotational quantum is $0.55 \cdot 10^{-2}$ eV. We can therefore expect the efficiency of these collisions to be high, leading to the establishment of an equilibrium distribution with respect to rotation with the gas temperature in the exponent. The gas temperature determined from the slope of the linear parts of the curves increases with increasing pressure: as the pressure is increased from 0.5 to 5 torr, the temperature increases from 300 to 1000°K (Table 2).

A nonexponential dependence of the intensity distribution of the rotational lines was found in [3], where nitrogen molecules were excited by electron collision.

TABLE 3

Pressure, torr	Temperature, °K λ=3998Å 1–4	λ=4959Å 0–3
0,1	300	320
0,5	400	420
1,0	430	450
2,0	540	550
5,0	820	1000

The anomalous intensity distribution of the rotational lines of an air discharge (the λ = 4059 Å) band at a pressure of 20 torr was pointed out by Sergeenkova and Vasil'ev [4], who attributed the effect to second-order collisions, although at a pressure of 10 torr a Boltzmann intensity distribution is found.

2. Radiation of the 0 – 3 and 1 – 4 Bands in the Mixture N_2 + Ar

From Fig. 4 we see that in the mixture N_2 + Ar the small-J rotational levels are populated as predicted by Eq. (1); at J = 23 the population begins to increase with increasing J. Comparing the curves for the pure gas and for the mixture with the same nitrogen pressure, we conclude that the addition of argon does not affect the excitation of the nitrogen rotational levels.

The high-J rotational levels in discharges of both pure nitrogen and the N_2 + Ar mixture are apparently excited as the N_2 molecules collide with and are excited by electrons.

Fishburne [5] observed excitation of the rotational structure of the nitrogen spectrum in the mixture N_2 + Ar; comparing the spectra of pure nitrogen at 0.3 torr and that of a mixture with partial pressures P_{N_2} = 0.03 torr and P_{Ar} = 0.27 torr, he attributed this affect to collisions of the second kind between N_2 molecules and metastable Ar atoms, although he did not detect amplification of levels at the most favorable resonance (ΔE = 0.4 cm^{-1}). We believe that it is pertinent to compare the radiation of a mixture with the radiation of a discharge in pure nitrogen at a pressure equal to the partial pressure of N_2 in the mixture.

Further study is required to explain the selective amplification of the two rotational states with J = 25, 26 in the nitrogen–argon mixture.

CONCLUSIONS

1. When molecules in a glow discharge are excited by electron collision, the rotational angular momentum of molecules may be changed as the molecules undergo electronic excitation.

2. Exchange of rotational energy in collisions between nitrogen molecules in the $C^3\Pi$ state and the $X^1\Sigma$ state occurs with a high effective cross section.

LITERATURE CITED

1. Budo, Zeits. f. Phys., 105, 579 (1937).
2. Budo, Zeits, f. Phys., 96, 219 (1935).
3. Ya. M. Fogel' and G. N. Polyakova, Zh. Éksp. Teor. Fiz., 52, 6 (1967).
4. N. A. Sergeenkova and S. S. Vasil'ev, Zh. Fiz. Khim., 41, 8 (1967).
5. E. S. Fishburne, J. Chem. Phys., 47, 1 (1967).