ELECTRON BEAM DIAGNOSTICS OF NITROGEN.
MULTIQUANTUM ROTATIONAL TRANSITIONS DURING EXCITATION

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The electron beam diagnostics technique is widely used to determine the parameters of a rarefied gas and is based on recording the electronic vibrational and rotational spectra of molecular gases excited by a beam of fast electrons. In particular, for nitrogen the emitted intensity of the rotational lines can be related through an appropriate model to the gas parameters, so that one can determine the population of the rotational levels of the molecules prior to the electron beam excitation, and when the population has an equilibrium distribution one can determine the rotational temperature. The most important quantities required for the correct construction and application of a model of electron beam diagnostics are the transition probabilities for excitation of molecules by the electron beam from the ground state to an excited electronic vibrational-rotational state of the molecule.

In molecular nitrogen the technique and the simplest model of electron beam diagnostics were described in [1]. According to this model nitrogen molecules from the $N_2(X^1\Sigma_g^+, v=0, k)$ ground state are ionized and excited to the ion state $N_2^+(B^2\Sigma_u^+, v', k')$ by inelastic collisions with primary beam electrons. The intensities of spontaneous emission of rotational lines I_k, in the $N_2^+(B^2\Sigma_u^+, v', k') \to N_2^+(X^2\Sigma_g^+, v'', k'')$ transition (the first negative band system, 1NS N_2^+) in the R branch ($k' = k'' + 1$) of the 00 band are related to the populations of the N_k^X rotational levels of the $N_2(X^1\Sigma_g^+, v, k)$ molecules, under the assumption that dipole selection rules hold for the process of excitation by fast electrons of the beam from this state to the ion state $N_2^+(B^2\Sigma_u^+, v', k')$, i.e., it is assumed that the probabilities of rotational transitions during excitation differ from zero only for $\Delta k = k' - k = \pm 1$.

The use of the electron beam diagnostic technique to study the broadening of a free jet revealed a number of defects of the Muntz model both in its use under equilibrium conditions, and also in a gas without a Boltzmann distribution of rotational level populations of the molecule [2-5]. In particular, it was observed that the rotational level intensities could be affected by secondary electrons arising from ionization of the gas by beam electrons [6, 7]. It was shown in [8, 9] that the rotational transition probabilities during excitation of nitrogen in the $E \geqslant 200$ eV state were different for fast electrons of energy $N_2^+(B^2\Sigma_u^+,$ $v' = 0, k')$ and for slow electrons. Therefore, at least for slow secondary electrons the dipole selection rules must break down and there can be rotational transitions in electron beam excitation of nitrogen with $\Delta k = \pm 1, \pm 3, \pm 5, \ldots$. This suggestion was made first in [6]. In [10] the authors determined the rotational transition probabilities for slow secondary electrons from the measured intensities of the rotational lines of the 1NS of N_2^+ within the electron beam [11].

Coe [12] postulated that even for fast beam electrons the dipole excitation model may not hold and that there could be rotational transitions with $\Delta k = k' - k = \pm 1, \pm 3, \pm 5, \ldots$. He drew this conclusion from measurements of the intensities of rotational lines of the 1NS N_2^+

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in a hypersonic nitrogen jet, having shown that in some range of the conditions in the jet the observed spectra could be explained by postulating a Boltzmann distribution of nitrogen molecules over the rotational levels and that the rotational transitions on electron beam excitation are multiquantum.

Coe's conclusions undoubtedly merit attention, but one can doubt the validity of his model for the following reasons: The experiments were conducted in a narrow range of the gas parameters; one cannot be sure that in the conditions of the experiment the nitrogen molecules had a Boltzmann distribution over the rotational levels, a fact that could distort the processes of rotational relaxation and condensation in the jet [11]; and finally, in determining the probabilities of multiquantum rotational transitions Coe proposed a mechanism for excitation of nitrogen in the $N_2^+(B^2\Sigma_u^+, v', k')$ state, based on the possibility of multiple quadrupole interactions of the electron ejected during ionization with the ion residue, which requires more careful justification.

In this study we present measurements of the rotational transition probabilities on excitation of $(X^1\Sigma_g^+, v=0, k)$ N_2 molecules by fast electrons of a beam with energy E ~ 10 keV to the state $N_2^+(B^2\Sigma_u^+, v'=0, k')$. We are especially interested in generating an equilibrium Boltzmann distribution of N_2 molecules with known temperature, both in a jet of pure nitrogen, and in a jet of argon where the N_2 molecules are a small impurity. To evaluate the rotational transition probabilities we propose a simple model based on the adiabatic approximation, which describes the experimental data over a wide range of the parameters. We also suggest a method for determining the rotational level populations of molecules under nonequilibrium conditions from the rotational line intensities, accounting for multiquantum rotational transitions.

Probabilities of Rotational Excitation. The intensities of the rotational lines $I_{k'}$ of the R branch of the 00 band of the 1NS N_2^+ are related to the rotational level populations of nitrogen N_k^X molecules in the ground state $N_2(X^1\Sigma_g^+, v=0, k)$ through the probabilities of rotational excitation by an electron beam [13]:

$$I_{k'} = \frac{k'}{2k'+1} C N_{k'}^B = \frac{k'}{2k'+1} C \left\{ \sum_k P_{k'k}(E) N_k^X \chi(r) + D(n_g, r) \sum_k \langle P_{k'k}(e) \rangle N_k^X \right\}. \qquad (1)$$

Here $N_{k'}^B$ are the rotational level populations in the excited state of the $N_2^+(B^2\Sigma_u^+, v'=0, k')$ ion; $P_{k'k}(E)$ are the rotational transition probabilities upon ionization of nitrogen to this state by fast electrons with energy E ≳ 10 keV; $\langle P_{k'k}(e) \rangle$ are the probabilities of rotational transitions due to secondary electrons, averaged over their distribution function; the value of $\chi(r)$ is determined by the radial profile of the electron beam, at the center of which $\chi(0) = 1$; $D(n_g, r)$ is the rate of excitation of nitrogen in the electronic vibrational state $N_2^+(B^2\Sigma_u^+, v'=0)$ by secondary electrons, referenced to the excitation rate to this state by primary electrons at the beam center; C is a constant which includes the Frank-Condon factors, parameters of the beam and of the system for recording the optical emission, and which takes account of quenching of the fluorescence:

$$C \sim n_g/(1 + K_{v',k'}^B n_g),$$

where n_g is the gas density at the measurement point; $K_{v',k'}^B$ is a constant for quenching of the $N_2^+(B^2\Sigma_u^+, v', k')$ ion by nitrogen molecules. If the ion quenching is independent of the rotational number k', i.e., $K_{v',k'}^B \equiv K_{v'}^B$, we can put C = 1 in Eq. (1) without loss of generality in the measurement of the relative $I_{k'}$ of the rotational lines.

The experimental data on the intensity $I_{k'}$ of rotational lines with the aid of Eq. (1) for known populations N_k^X can be used, in principle, to determine the rotational transition probabilities $P_{k'k}(E)$, if we have enough experiments with different distributions of N_k^X. However, such a determination of $P_{k'k}(E)$ is a typical incorrect problem. The result will depend appreciably on the accuracy of the measurements, the number of measured line intensities, and so on. It is more profitable to seek the transition probabilities by using a theoretical model of some kind containing a parametric dependence of the transition probabilities on the quantum numbers k and k'.

One of the main theoretical methods in the study of rotational transitions is the adiabatic approximation [14, 15]. On its basis it has been established that the cross section of an arbitrary rotational transition in a diatomic molecule for $\Sigma - \Sigma$ electronic transitions can be expressed in terms of the cross sections for transitions from the ground rotational state:

$$\sigma_{k'\leftarrow k}(E) = \sum_l (2k'+1)\,\sigma_{l\leftarrow 0}(E) \begin{pmatrix} k' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2,$$

where $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is the $(3-j)$ Wigner symbol.

Analogous relations hold, of course, also for the probabilities of rotational transitions

$$P_{k'k}(E) = (2k'+1) \sum_l P_{l0}(E) \begin{pmatrix} k' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 = \sum_l P_{l0}(E)\, C^2_{k'kl} \tag{2}$$

and correspondingly for the quantities $\langle P_{k'k}(e) \rangle$. The quantity $C^2_{k'kl} = (2k'+1) \begin{pmatrix} k' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2$ is the square of the corresponding Clebsch–Gordan coefficient.

In the special case considered of ionization of nitrogen to the excited state the sum in Eq. (2) will only contain terms with odd values of the number $l = 1, 3, 5, \ldots$, i.e., only rotational transitions are possible with $\Delta k = k' - k = \pm 1, \pm 3, \pm 5, \ldots$, which follows from the properties of the $(3-j)$ Wigner symbol, which for $m_1 = m_2 = m_3 = 0$ equals

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{(j_1+j_2-j_3)!\,(j_1-j_2+j_3)!\,(-j_1+j_2+j_3)!}{(j_1+j_2+j_3+1)!} \times$$
$$\times \left[\frac{p!}{(p-j_1)!\,(p-j_2)!\,(p-j_3)!} \right]^2, \quad 2p = j_1 + j_2 + j_3.$$

The rotational transition probabilities $P_{k'k}(E)$ and $\langle P_{k'k}(e) \rangle$ satisfy the normalization condition

$$\sum_{k'} P_{k'k}(E) = \sum_l P_{l0}(E) \sum_{k'=|k-l|}^{k+l} (2k'+1) \begin{pmatrix} k' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 = \sum_l P_{l0}(E) = 1.$$

If in Eq. (2) we restrict ourselves to only one term with $l = 1$, i.e., $P_{10} = 1$, the transition probabilities reduce automatically to the dipole values

$$P_{k'k}(E) = (2k'+1) \begin{pmatrix} k' & k & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 = C^2_{k'k1} = (k'+1)/(2k'+3)$$
$$\text{for } k = k'+1, \quad = k'/(2k'-1) \quad \text{for } k = k'-1.$$

Thus, the transition probability matrix can be expressed in terms of the unit vector $P_{l0}(E)$ $(l = 1, 3, 5 \ldots)$, which simplifies appreciably the task of determining it from experimental data. For further simplification of the model the transition probabilities P_{l0} were expressed in terms of the single parameter α, determined by comparison with experiment:

$$P_{l0}(E) = (2l+1)\,\alpha^l \Big/ \sum_{l=1,3,5,\ldots} (2l+1)\,\alpha^l = \frac{(2l+1)\,\alpha^{l-1}}{(3+\alpha^2)} (1-\alpha^2)^2. \tag{3}$$

For $\alpha = 0$ Eq. (3) is left with only one dipole term $P_{10} = 1$.

Experimental Determination of the Parameter α. Experimental investigations were conducted in the vacuum facilities of the Institute of Thermophysics, SO Akad. Nauk SSSR, equipped with a vacuum pumping system, including cryogenic pumps, electron beam diagnostic and spectral equipment with which one can record optical and x-ray radiation.

From a fore-chamber gas was expanded through a sonic nozzle of diameter d_* from 0.5 to 15 mm into a vacuum volume with a residual pressure $p_h \sim 10^{-2}$-10^{-1} Pa. The pressure in the fore-chamber (stagnation pressure p_0) was varied in the range 10^2 to 10^5 Pa. The stagnation temperature usually was room temperature, $T_0 \approx 300$°K. An electron gun was used to create an electron beam of diameter $d_b \sim 1$ mm, current $i_b \sim 1$-30 mA and with electron energy $E \sim 10$-15 keV.

From the region of intersection of the electron beam with the jet axis in the direction perpendicular to it we selected the 1NS N_2^+ radiation, recorded by a monochromator and a photomultiplier. The radiation was captured by the narrow slit of the monochromator, positioned parallel to the electron beam, so that it recorded mainly from the central region of the beam. Then the recorded radiation contains appreciably less contribution of secondary electrons from the halo around the beam [11]. The experimental arrangement was described in detail in [11, 16]. First we consider experimental data on the intensities $I_{k'}$ of rotational lines of the R branch of the 00 bands of 1NS N_2^+ excited by the electron beam, taken with various values of $p_0 d_*$ at a certain point x/d_* on the axis of a jet of pure nitrogen. A typical result is shown in Fig. 1 for a value of $x/d_* = 38$ ($T_t = 6.1$°K).

In the expansion of the gas from the fore-chamber into the vacuum the equilibrium distribution of energy over the rotational degrees of freedom in the jet may be disturbed. The reason for this is insufficient collisions of molecules amongst themselves. A kinetic description of this phenomenon has been attempted in [17, 18]. With an increase of the number of collisions in the jet, i.e., with increase of $p_0 d_*$, the deviation from equilibrium conditions decreases. In principle in the gas we should establish a Boltzmann distribution over the rotational levels at temperature T_t equal to the isentropic value. However, for high enough values of gas density the condensation process may begin in the flow, leading to the release of condensation energy to the stream. Therefore, beginning at a certain value of $p_0 d_*$, the populations of the upper rotational levels of N_2 molecules will grow [19], and therefore the relative intensities $I_{k'}$ of the rotational lines will also increase, which is observed on the right hand branches of the curves shown in Fig. 1 (here 1 and 2 correspond to measurements in the nozzles with $d_* = 0.54$ and 5.12 mm). In addition, with increase of p_0 the gas density at the measurement point increases, and there is a corresponding increase in the possibility of secondary processes in the excitation of molecules of the test gas, making it difficult to interpret the results. We note only that the closest to an equilibrium Boltzmann distribution of the $N_2(X^1\Sigma_g^+, v=0, k)$ molecules over the rotational levels with isentropic temperature $T(x/d_*)$

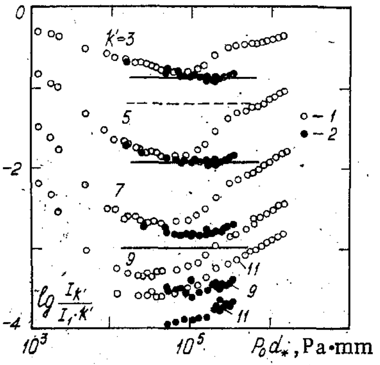

Fig. 1

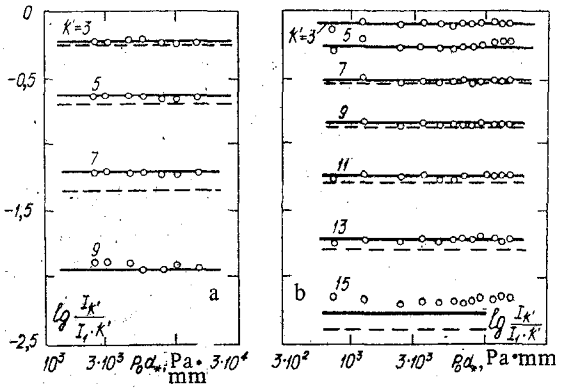

Fig. 2

may be the gas states with values of p_0d_* in the region of the minimum of the distribution of the intensities $I_{k'}/I_1$ in the conditions shown in Fig. 1. A comparison of the measured intensities with the calculated values for the temperature $T(x/d_*)$ according to the Muntz dipole model (broken lines in Fig. 1) shows that either the gas does not reach the equilibrium state or the dipole model is incorrect. The latter conclusion was reached in [12], but the possibility of equilibrium conditions in the gas was not analyzed.

In order to avoid uncertainty in the gas state in this study we conducted investigations in sonic jets of argon with a small impurity (~5%) of nitrogen molecules. In this case one can hope that in the gas mixture conditions will be maintained that are close to equilibrium with the isentropic temperature of the monatomic gas. The measurements in the Ar–N_2 mixture were carried out over a wide range of p_0d_* ($10^3 \leqslant p_0d_* \leqslant 10^5$ Pa·mm) and x/d_* ($0.5 \leqslant x/d_* \leqslant 70$) and for the chosen values of $x/d_* = 1.67$ and 0.67 the results are shown in Fig. 2a and b, where the broken lines are values of the intensities $I_{k'}$ computed with the Muntz model. It can be seen from Fig. 2 that in this case the dipole model does not correctly describe the radiative intensities.

Attention should be directed to the fact that in the Ar–N_2 mixture the values of the relative intensities do not depend on p_0d_*. This means that the N_2 molecules are in equilibrium with the argon because of the higher rate of rotational relaxation than in pure nitrogen. In addition, in the chosen experimental conditions there was no condensation which would lead in pure nitrogen to an increase of gas temperature in the jet at high p_0d_*. The presence of equilibrium in the Ar–N_2 jet and the lack of agreement between the measured intensities with the dipole model theory confirms the conclusion of [12] as to the presence of multiquantum rotational transitions in excitation of nitrogen in the $N_2(B^2\Sigma_u^+,\ v'=0,\ k')$ state by an electron beam.

For the reasons mentioned above, to determine the parameter α we used experimental data obtained in the Ar–N_2 mixture for $x/d_* = 1.67$ and the corresponding isentropic temperature $T = 44°K$. The best agreement of the rotational line intensities as measured and calculated from Eq. (1), allowing for Eqs. (2) and (3), is reached with $\alpha = 0.28^{+0.03}_{-0.01}$. Here the contribution of secondary electrons is neglected, since $D \ll 1$.

The calculated intensities for this value of the parameter α are shown by the solid lines on Fig. 2. The value of α obtained, and therefore also the values of the rotational transition probabilities, were checked at other values of isentropic temperature, i.e., for other x/d_* in the Ar–N_2 mixture. The results of this comparison of the measured and calculated intensities are shown in Fig. 3a as a function of x/d_*. For comparison Fig. 3a also shows intensities calculated from the Muntz dipole model.

As has already been mentioned, for the experiments in pure nitrogen one must exercise care in checking the model. The closest to the equilibrium state of the gas for a given x/d_* are conditions corresponding to the minimum of the intensities in the dependence on p_0d_*. Under the hypothesis that when the populations are Boltzmann with the isentropic temperature for the diatomic gas, we calculated the rotational level intensities, and the results are shown in Fig. 3b. The agreement obtained is quite satisfactory.

Analysis of the Model. Above, to determine the rotational transition probabilities for excitation of nitrogen to the state $N_2^+(B^2\Sigma_u^+,\ v',\ k')$ by an electron beam we postulated that the 1NS N_2^+ radiation was excited only by beam electrons. With a high gas density various secondary processes are possible, also leading to excitation of the 1NS N_2^+. However, up to gas densities of $n_g \leq 10^{17}$ cm^{-3} the 1NS N_2^+ radiative intensities, according to the experimental investigations, are proportional to the electron beam current [11]. The only secondary process that is linear with beam current is excitation by secondary electrons. Since the probabilities of rotational excitation for fast primary electrons $P_{k'k}(E)$ and slow secondary electrons $\langle P_{k'k}\rangle$ are different [10, 13], the secondary electrons can lead to a redistribution

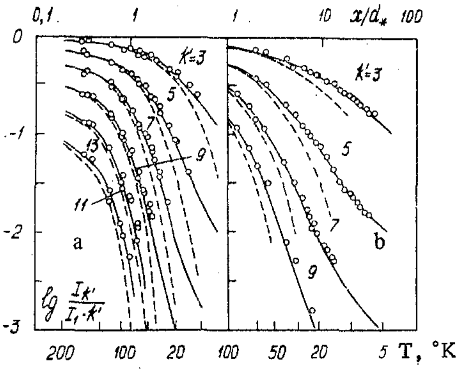

Fig. 3

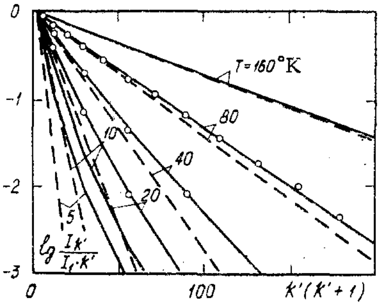

Fig. 4

of the radiative intensities $I_{k'}$ caused by the primary electrons. The amount of this redistribution is determined by the parameter D in Eq. (1) and depends appreciably on the gas density, the region of the recorded radiation, and the geometrical parameters of the beam and the gas flow.

In the experimental data used in this study, obtained at constant values of T_0 and x/d_*, the rotational distribution of the molecules is determined only by pair collisions and does not vary for a given value of p_0d_*. However, the relative intensities of the rotational lines $I_{k'}/I_1$ obtained for a given p_0d_* but for different values of d_*, i.e., for different gas densities at the measurement point, proved to be practically the same for p_0d_* corresponding to the rotational relaxation region (the left hand branches of the curves of $I_{k'}/I_1$ as a function of p_0d_* in Fig. 1). The agreement of the radiative intensities $I_{k'}/I_1$ for different gas densities n_g but the same values of p_0d_* is evidence that secondary electrons do not affect the excitation of the rotational lines of the 1NS N_2^+ in the region of the parameters investigsted, i.e., D << 1.

The adiabatic approximation (2), along with Eq. (3) for $P_{l_0}(E)$ as a function of the quantum number l and an experimentally determined value of the fitting parameter $\alpha \approx 0.28$, constitute a very simple model for the probabilities of multiquantum rotational transitions $P_{k'k}$. Table 1 gives values of $P_{k'k}$. For comparison Table 1 also gives the probabilities for dipole transitions and the probabilities determined in [12]. It is interesting that elements of the matrix of [12] and of the model presented here show rather good agreement for not very large values of $\Delta k = |k' - k| \leqslant 5$. This is evidence that in pure nitrogen in the region of the minima of $I_{k'}/I_1$ as a function of p_0d_* the state of the gas is close to equilibrium, and is supplementary confirmation of the proposed model.

To illustrate the influence of multiquantum transitions Fig. 4 shows the distributions at several temperatures of rotational level intensities $I_{k'}/I_1$, calculated from Eqs. (2) and (3) for the case of a Boltzmann distribution of rotational level populations of $N_2(X^1\Sigma_g^+$, v = 0, k) molecules. Figure 4 also shows the experimental results, measured in a hypersonic jet under conditions close to equilibrium, and also measurements under static conditions at temperature $T_1 \approx 78$°K. It can be seen that from the equilibrium distribution of the $N_2(X^1\Sigma_g^+$, v = 0, k) molecules over the rotational levels N_k^X arises a non-Boltzmann distribution $N_{k'}^B$, in the state $N_2^+(B^2\Sigma_u^+,\ v'=0,\ k')$. However, with increase of the nitrogen temperature T the distribution of the excited ions $N_{k'}^B$, becomes closer to equilibrium with a limit temperature $T^B = T + \Delta T(\alpha)$, where $\Delta T(\alpha = 0.28) \approx 11.6$. An analogous result is also obtained for the dipole mode, where $\Delta T(\alpha = \theta) = 2\Theta$ (Θ is the characteristic rotational temperature of N_2). It is

TABLE 1

$h \backslash k'$	0	1	2	3	4	5	6	7
0	0	0,8277 0,8346 1	0	0,1514 0,1350 0	0	0,0187 0,0233 0	0	0,0020 0,0051 0
1	0,2759 0,2668 0,3333	0	0,6167 0,6201 0,6667	0	0,0950 0,0923 0	0	0,0111 0,0159 0	0
2	0	0,3700 0,3706 0,4000	0	0,5427 0,5384 0,6000	0	0,0775 0,0747 0	0	0,0088 0.0124 0
3	0,0216 0.0193 0	0	0,3876 0,3879 0,4286	0	0,5122 0,5108 0,5714	0	0,0699 0,0677 0	0
4	0	0,0317 0,0310 0	0	0,3984 0,3975 0,4444	0	0,4963 0,4948 0,5555	0	0,0657 0,0635 0
5	0,0017 0,0021 0	0	0,0352 0,0344 0	0	0,4061 0,4051 0,4545	0	0,4865 0,4850 0,5455	0
6	0	0,0027 0,0037 0	0	0,0377 0,0365 0	0	0,4117 0,4105 0,4615	0	0,4799 0,4783 0,5365
7	0,00014 0,0003 0	0	0,0029 0.0042 0	0	0,0374 0,0382 0	0	0,4159 0,4147 0,4667	0

convenient to describe the nonequilibrium distribution $N^B_{k'}$ with the aid of population temperatures $T^B_{k'}$, defined as follows:

$$\ln (I_{k'}/k'I_1) = \ln \frac{3N^B_{k'}}{(2k'+1)\,N^B_1} = -\frac{\varepsilon_{k'}-\varepsilon_1}{T^B_{k'}},$$

where $\varepsilon_k = k(k+1)\Theta$.

Figure 5 shows the quantity $T^B_{k'} - T$ as a function of the gas temperature for the dipole model with $\alpha = 0$ and 0.28. The larger the value of α and the lower is the temperature, the more nonequilibrium will be the $N^B_{k'}$ distribution. This makes it difficult, especially at low temperatures, to observe nonequilibrium in the ground state. For a high mean rotational energy of molecules in the flow, when the population temperatures $T^B_{k'} \gtrsim 100$ °K for all $k' > 1$, the large difference in $T^B_{k'}$ means that the distribution is non-Boltzmann in the $N_2(X^1\Sigma_g^+, v, k)$ ground state.

In the general case, to determine the populations N^X_k of rotational levels of N_2 molecules from the measured intensities $I_{k'}$ of rotational lines in the R branch of the 1NS N_2^+ excited by an electron beam is a complex problem even for the dipole model of excitation. The reason is that the system of equations (1) has always a larger number of unknowns N^X_k, than measured line intensities $I_{k'}$, i.e., an appropriate closure method is required. For the Muntz dipole model various closure methods have been proposed in [16, 20]. Below we suggest a formal method of forming the system (1) for the adiabatic transition probabilities (2).

We write system (1) in vector form

$$\mathbf{N}^B = \sum_l P_{l0}\tilde{C}_l^2\mathbf{N}^X, \tag{4}$$

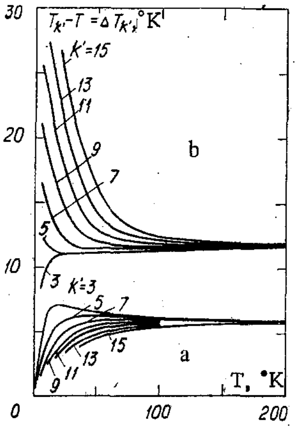

Fig. 5

where $\tilde{C}_l^2$ is the matrix of squares of the Clebsch–Gordan coefficients with elements $C_{k'kl}^2$. For the $\tilde{C}_1^2$ matrix it is easy to find the inverse matrix $\tilde{S}$. Elements of the matrix $\tilde{S}$ are defined as follows:

$$S_{i,i+1}=(2i+1)/(i+1),\quad i=0,\,1,\,2,\,\ldots,$$
$$S_{i,i+1+n}=(-1)^n S_{i,i+1}\prod_{m=1}^{n}(i+2m)/(i+2m+1),$$
$$S_{ij}=0\quad\text{for}\quad j\leqslant i\ \text{and}\ j=i+2n.$$

Then for Eq. (4) we can write the formal solution

$$\mathbf{N}^X=\frac{1}{P_{10}}\{\tilde{I}-\tilde{Q}+\tilde{Q}\cdot\tilde{Q}-\tilde{Q}\cdot\tilde{Q}\cdot\tilde{Q}+\ldots\}\tilde{S}\cdot\mathbf{N}^B, \tag{5}$$

where $\tilde{I}$ is the unit matrix, and $\tilde{Q}$ is the matrix with the elements

$$Q_{ij}=\sum_{l=1,3,5,\ldots}\frac{P_{l0}}{P_{10}}\sum_m S_{im}C_{mjl}^2. \tag{6}$$

The vector $\tilde{S}N^B$ is the solution of N^X for the dipole model, and the operator in the curved brackets in Eq. (5) transforms it to the solution for multiquantum transitions. Since the elements of the matrix Q are proportional to $P_{30} \ll 1$, one can hope that the solution (6) converges quite rapidly.

Since the intensities of a finite number of rotational lines $I_{k'}\sim\frac{k'}{2k'+1}N_{k'}^B$ are measured in the experiment, then to reduce the errors in determining the populations N_k^X one can use Eq. (6) to extrapolate the values of $I_{k'}$ (or $N_{k'}^B$) in the appropriate manner to the region of quantum numbers k' for which no measurements were made. This method will at least give an idea of the size of the error introduced by means of the transformation method.

Another method of determining the populations N_k^X is to assign them in some functional form as a function of the quantum number k, e.g., in the form of a superposition of several Boltzmann distributions:

$$N_k^X=\sum_{i=1}\gamma_i N_k^{X_0}(T_i),\quad \sum_i\gamma_i=1, \tag{7}$$

where $N_k^{X_0}(T_i)$ is the Boltzmann distribution with temperature T_i; γ_i are the fractions of molecules having the distribution at this temperature. Limiting Eq. (7) to a few terms and calculating the intensity $I_{k'}$ with the aid of the transition matrix $P_{k'k}(E)$ we can use the least squares method to determine the fitting parameters T_i and γ_i. In fact, this method is used in [1, 12], where only one term was taken in Eq. (7) with $\gamma_1 = 1$ and $\gamma_i = 0$ for $i > 1$.

In conclusion we note that in this work we determined the rotational transition probabilities $P_{k'k}(E)$ for electron beam excitation of $N_2(X^1\Sigma_g^+, v = 0, k)$ molecules to the $N_2^+(B^2\Sigma_u^+, v' = 0, k')$ state. By using the adiabatic approximation we could evaluate the matrix $P_{k'k}(E)$ as a function of the quantum numbers k and k' (see Eq. (2)) and reduce its determination to calculation of the unit vector $P_{l0}(E)$. The dependence of $P_{l0}(E)$ on the electron energy, as follows from [9, 10], should appear only near the threshold for excitation of the $N_2^+(B^2\Sigma_u^+, v', k')$ state, where the probabilities of multiquantum transitions increase. For example, for electrons near the threshold we have $\alpha \approx 0.5$ [10], and from the experiments of [9] $\alpha \approx 0.42$. But for electrons with energy $E > 100$ eV $\alpha \approx 0.28$. The dependence of P_{l0} on the quantum number l was chosen in the form of Eq. (3), but later this restriction could be removed by more careful direct measurement or by using theoretical considerations.

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NUMERICAL INVESTIGATION OF THE PROPAGATION OF A PULSE OF RADIATION WITH $\lambda = 10.6$ μm THROUGH ABSORBING MEDIA

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The passage of electromagnetic radiation through gaseous media is of special interest when resonantly absorbing impurities are present in the gas. The interaction of radiation with such a medium can lead, for example, to a temporal decrease of the gas temperature or to its strong heating [1-3]. At the same time the index of refraction in the channel of the light beam is altered, which leads to a deviation of the light rays from the initial direction. The main characteristics of such thermal self-action within the framework of linear absorption theory for steady and nonsteady processes have been discussed in [4-12]. Nonequilibrium processes in the medium upon absorption of resonant radiation were not taken into account. The effect of the kinetics of vibrational energy exchange on the state of a medium upon the propagation of radiation through a mixture of CO_2 and N_2 gases was first considered in [2, 13, 14]. However, the simplest models of vibrational energy exchange were used, and saturation of the absorbing transition P20 $[10^00 \to 00^01]$ in the CO_2 molecule was not taken into account. Thus linearized equations of vibrational kinetics were used in [13], and only one channel of relaxation of asymmetric vibrations of CO_2 and excited nitrogen was considered in [14]. The propagation of a pulse of radiation with $\lambda = 10.6$ μm through an absorbing medium is investigated and the influence of the saturation effect and nonlinear processes of vibrational energy exchange on the self-action of light beams of Gaussian profile is studied in this paper.

1. Theoretical Model. The propagation of electromagnetic radiation in a medium with dielectric constant ε in the quasioptics approximation is described by the following equation for the complex amplitude A(z, r, t):

$$2ik\left(\frac{\partial}{\partial z} + \frac{n_0}{c}\frac{\partial}{\partial t}\right)A + \Delta_\perp A + k^2\left(\frac{\varepsilon}{n_0^2} - 1\right)A = 0,$$
$$k = \frac{\omega}{c}n_0, \quad \Delta_\perp = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right), \quad \varepsilon = \left(n + i\frac{c}{2\omega}k_\nu\right)^2, \tag{1.1}$$

where n is the index of refraction (a subscript "0" refers to the unperturbed medium), ω is the frequency of the wave, c is the speed of light, and k_ν is the absorption coefficient.

A change in the state of the medium upon absorption will lead to a change in both the real and imaginary parts of the dielectric constant. Actually, when the temperature of a gas varies, its density ρ changes, which is related to the index of refraction by the Gladstone–Dale law $\delta n = (n_0 - 1)\delta\rho/\rho_0$. On the other hand, the absorption of photons of an electromagnetic field will result in disruption of the initial distribution of molecules by energy levels of the internal degrees of freedom, and as a consequence, in a change in the absorption coefficient k_ν, whose value determines the imaginary part of the dielectric constant. When

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