

POSSIBILITY OF FORMING AN INVERTED DISTRIBUTION OVER  
THE ROTATIONAL LEVELS OF NITROGEN IN AN EXPANDING  
GAS STREAM

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A number of theoretical papers have been devoted to an investigation of the relaxation kinetics of the population of a system of rotational levels of molecules in a stream of gas freely expanding from a sonic nozzle [1-3]. The complexity of the task of constructing models of relaxation and of collisions consistent in accuracy, however, as well as the difficulties in solving the resulting system of kinetic and gas-dynamic equations, lead to the necessity of using substantial approximations. Some disagreement between the experimental data and calculated results [1, 2] requires an evaluation of the accuracy of the various approximations used and further refinement of the theoretical models. In contrast to [1], in order to bring out the possible mutual influence of nonequilibrium energy exchange between the degrees of freedom of nitrogen molecules and the variation of the gas-dynamic parameters, the calculation presented below is based on a numerical solution of a self-consistent system of kinetic and gas-dynamic equations for the populations of rotational states and the temperature, density, and velocity of gas in the stream. Collisional probabilities of rotational transitions, calculated with allowance for the long-range part of the potential of the interaction between molecules [4], are used for this.

Equations for Describing Relaxation in a Molecular Gas Stream. Let us consider the formation of a nonequilibrium distribution in the system of rotational levels of molecular nitrogen freely expanding from a sonic nozzle. When a gas expands from a slit or nozzle, its translational temperature decreases rapidly. The internal energy of the expanding gas does not fully relax in this time, resulting in disruption of the equilibrium distribution over the degrees of freedom of the molecules. Having in mind gas temperatures that are not too high ( $T < 300^\circ\text{K}$ ), we can assume that all the molecules are in the electronic and vibrational ground states.

As was done before [1], we shall assume that the processes of translational and rotational relaxation can be separated in time, the translational relaxation takes place faster, and a Maxwellian velocity distribution of the colliding molecules is established, which enables us to convert, in the kinetic equation, from the distribution function over the energies and rotational levels of the molecules to one over the populations of the rotational states,  $P(j)$ :

$$\rho_j(\mathbf{r}, t) = P(j, \mathbf{r}, t)\rho(\mathbf{r}, t)$$

( $\rho(\mathbf{r}, t) = \sum_j \rho_j(\mathbf{r}, t)$  is the gas density and  $\rho_j(\mathbf{r}, t)$  is the partial density of particles in the  $j$ -th rotational state), as well as to use the concept of the temperature  $T$  of the translational degrees of freedom of the molecules.

The kinetic equation for the populations has the form

$$\frac{d}{dt} P(j) = I_{stj} \quad (1)$$

Here the total time derivative in Eulerian variables

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\nabla$$

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is on the left. The collision integral on the right side of (1) represents the rate of change of the number of molecules with the rotational number  $j$  due to collisions, and it can be written as

$$I_{stj} = Zn \sum_{\substack{i, \\ \Delta i, \Delta j}} \left( -P(j) P(i) \mathcal{P}_{j \rightarrow j+\Delta j}^{i \rightarrow i+\Delta i}(T) + P(i + \Delta i) P(j + \Delta j) \mathcal{P}_{j+\Delta j \rightarrow j}^{i+\Delta i \rightarrow i}(T) \right), \quad (2)$$

where  $Z$  is the total number of collisions between molecules per unit time ( $Z = \sqrt{2} \pi d_{ef}^2 \langle v \rangle n$ );  $d_{ef}$  is the effective diameter of an elastic collision between molecules;  $\langle v \rangle$  is the mean thermal velocity of the molecules;  $n$  is the concentration of the molecules;  $\mathcal{P}_{j \rightarrow j+\Delta j}^{i \rightarrow i+\Delta i}$  are the

probabilities of collisional transitions; the indices  $i$  and  $j$  are the numbers of the rotational levels of the electronic and vibrational ground states of the  $N_2$  molecule;  $\Delta i$  and  $\Delta j$  are their changes in a collision act, accompanied by energy exchange between the translational and rotational degrees of freedom. Here a change in the quantum state of one (RT processes) or both (RR' processes) of the colliding molecules is possible. For nitrogen molecules, inelastic processes are confined to even values of  $|\Delta i|$  and  $|\Delta j|$ .

To calculate the kinetics of rotational relaxation in an expanding gas stream, one must supplement the system of kinetic equations (1) and (2) by the conservation laws of gas dynamics, representing the moments of the original kinetic equation [3].

Assuming that the gas flow is established and one-dimensional, and considering that the assumption of the processes of translational and rotational relaxation of an expanding gas can be separated in time corresponds to the equation of state of an ideal gas, we have [3]

$$\begin{aligned} v \frac{d}{dx} P(j) &= F(j), \\ v \frac{d}{dx} \ln \left( \frac{T^{3/2}}{\rho} \right) &= -\frac{1}{kT} \sum_j E(j) F(j), \\ \rho v R(x) &= c_1 = \text{const}, \\ c_p T + \sum_j E(j) P(j) + \frac{1}{2} m_g v^2 &= c_2 = \text{const}. \end{aligned} \quad (3)$$

Here  $T$ ,  $v$ , and  $\rho$  are the temperature, velocity, and density of the expanding gas at a given point of space;  $E(j) = B_0 j(j+1)$  is the energy of the  $j$ -th rotational state;  $B_0$  is the rotational constant of a gas molecule (for nitrogen  $B_0 = 2.88^\circ\text{K}$ );  $m_g$  is the mass of the gas molecules;  $c_p$  is the specific heat of the gas at constant pressure;  $z$  is the dimensionless coordinate along the stream;  $z = 0.566 + x/d_* 0.943$  [1];  $x$  is the distance from the nozzle cut;  $d_*$  is the diameter of the nozzle cut;  $R(x)$  is the cross-sectional area of the expanding gas stream; The system (3) was solved for the quantities  $P(j)$ ,  $T$ ,  $v$ , and  $R$ .

The law of density variation was taken as adiabatic:

$$\rho(z) = \rho_0 \left( 1 + \frac{\gamma-1}{2} M^2(z) \right)^{-\frac{1}{\gamma-1}}$$

( $\gamma = 1.4$ ). The dependence of the Mach number on the coordinate was determined in the form of the empirical approximation

$$\begin{aligned} M(z) &= M(z_1) \exp \{ (z - z_1) M'_z(z_1) / M(z_1) \}, \quad z \leq z_1 \leq 1, \\ M(z) &= a_1 (z - z_3)^{\gamma-1} - \frac{3}{a_1 (z - z_3)^{\gamma-1}} + \frac{a_2}{(z - z_3)^{3(\gamma-1)}}, \quad z \geq 1, \end{aligned}$$

where  $a_1$  and  $a_2$  correspond to the Sherman equation [5] ( $a_1 = 3.65$ ,  $a_2 = 0.2$ );  $z_3 = 0.4$ ;  $z_1 = 1$ .

The system was solved for  $j^* \gtrsim 30$ , i.e., such that the populations of levels  $j \gtrsim j^*$  were negligibly small compared with the populations of lower levels and could not significantly influence the course of relaxation. The populations of several upper levels  $j > j^*$  were calculated from the Boltzmann law with a temperature equal to the temperature of the

distribution over the upper levels  $j^*$  and  $j^* - 2$  of the system. The initial distribution was taken as a Boltzmann distribution with a temperature  $T_0$  equal to the equilibrium value of the translational temperature in the given initial cross section  $z_{in} = z_0$ . The value of  $z_0$  in the calculations was varied (decreased) until the difference between the results of the numerical calculation of the populations with the choice of values  $z_{in} = z_0$  and  $z_{in} = z_0/2$  was less than 1%.

Probabilities of Collisional Transitions in the Rotational Energy Spectrum. The collision integral (2) contains the probabilities of excitation of rotational degrees of freedom of the colliding molecules, the calculation of which is associated with great computational difficulties. Expressions obtained in the quasiclassical approximation [4], for the case when the total energy of the colliding molecules is high compared with the depth  $\epsilon_0$  of the potential well of the intermolecular function, were used for the probabilities in the calculations of [1, 2]. The influence of the long-range part of the potential of the molecular interaction was neglected in this case. The applicability of such probabilities is confined to temperatures of the expanding gas that are not too low.

The more precise averaging of the collisional probabilities of rotational transitions, with respect to the energy of the colliding molecules, calculated in the quasiclassical approximation, carried out in the present work yielded the following temperature dependence of the probabilities, not confined by the condition  $|\epsilon/\epsilon_0| > 1$ :

$$\mathcal{P}_{\substack{j_1 \rightarrow j_1' \\ j_2 \rightarrow j_2'}}(T) = \frac{16\pi^2\mu}{\hbar^2\alpha^2} \epsilon_0 \Phi_{il} \exp\left\{\frac{\Delta E - |\Delta E|}{2kT}\right\} \left\{ \left(\frac{1}{2} D'_{il}(1 + \kappa) - D''_{il}\right)^2 \left[ e^{-2\kappa} + \sqrt{\frac{\pi}{3}} x_0^{\frac{2}{3}} \exp\left\{\frac{-2\kappa \frac{A}{\sqrt{kT}}}{2\kappa \sqrt{x_0} + \frac{A}{\sqrt{kT}}} - x_0\right\} \right] - \right. \\ \left. - \left( \left(\frac{1}{2} D'_{il} - D''_{il}\right)^2 - \frac{1}{4} D_{il}^2 \kappa^2 \right) \sqrt{\frac{\pi}{3}} \left(\frac{A}{\sqrt{kT}}\right) \exp\left\{-3\left(\frac{A}{\sqrt{kT}}\right)^{\frac{2}{3}}\right\} \right\}, \quad (4)$$

$$x_0 = \left(\frac{A}{2\sqrt{kT}}\right)^{\frac{2}{3}} \frac{\epsilon_0 \pi^2}{kT} \left( \sqrt[3]{1 + \left(\frac{kT}{\epsilon_0 \pi^2}\right)^3} - 1 \right), \\ \kappa = \frac{|\Delta E|}{\hbar\alpha} \sqrt{\frac{2\mu}{\epsilon_0}}, \quad A = \frac{\pi|\Delta E|}{\hbar\alpha} \sqrt{2\mu},$$

where  $D'_{il} = B'_{il}/B$  and  $D''_{il} = B''_{il}/B$  are the coefficients of the expansion of the potential of the molecular interaction in the Morse form in Legendre polynomials;  $\Phi_{il}$  are the coefficients of averaging of the probabilities over the projection of the initial angular moments  $m_1$ ,  $m_2$ , and  $m$ , defined in [4];  $\mu$  is the reduced mass of the colliding molecules;  $\alpha$  is the constant of the potential of the molecular interaction;  $\Delta E$  is the energy change in a collision;  $k$  is the Boltzmann constant.

For comparison, in Fig. 1 we give the probabilities of rotational two-quantum RT transitions for  $T = 300, 182,$  and  $91^\circ\text{K}$  (lines 1-3) and  $\epsilon_0 = 0$  and  $80^\circ\text{K}$  (dashed and solid lines), calculated from Eq. (4) in the limit  $\epsilon_0 = 0$  and used in [1, 2] in the approximation of the exponential form of the potential of the molecular interaction:

$$\mathcal{P}_{\substack{j_1 \rightarrow j_1' \\ j_2 \rightarrow j_2'}} = \frac{16\pi^2\mu^2 (\Delta E)^2 (B_{il})^2}{\hbar^4\alpha^4} \Phi_{il} \sqrt{\frac{\pi}{3}} \left(\frac{A}{2\sqrt{kT}}\right) \exp\left\{-3\left(\frac{A}{2\sqrt{kT}}\right)^{\frac{2}{3}} + \frac{\Delta E - |\Delta E|}{2kT}\right\}. \quad (5)$$

We chose the following values of the parameters for nitrogen molecules:  $d_{ef} = 3.0 \cdot 10^{-10}$  m,  $\mu = 14$  amu,  $\alpha = 2.0 \cdot 10^{10} \text{ m}^{-1}$ ,  $\epsilon_0 = 80^\circ\text{K}$ .

The probabilities of rotational transitions calculated from (4) have a more clearly expressed dependence on the level number  $j$  of the colliding molecules than the probabilities (5) and decrease insignificantly with a decrease in gas temperature.

Analyzing the reasons for the discrepancy existing between the calculated results of [1, 2] and experimental data, the authors of [2] advance the hypothesis that multiquantum RT processes, which were neglected earlier because the gas temperatures were not very high, may have considerable influence on the course of relaxation in the system of rotational

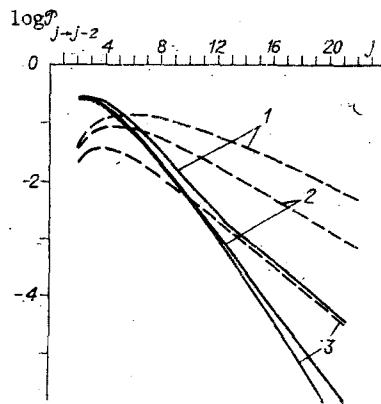


Fig. 1

levels. The calculations made in [2] using model kinetic constants for the multiquantum rotational transitions support this hypothesis.

Numerical calculations of the probabilities of RR' and multiquantum rotational RT transitions, obtained in the quasiclassical approximation [4], are made in the present paper. Numerical estimates of the so-called rates of multi- and two-quantum processes

$$-P(j)K_{j \rightarrow j+\Delta j} + P(j+\Delta j)K_{j+\Delta j \rightarrow j},$$

$$K_{j \rightarrow j+\Delta j} = Z \mathcal{P}_{j \rightarrow j+\Delta j}$$

for different gas temperatures and different population distributions of the rotational levels showed that in the model of rotational relaxation using the probabilities of rotational transitions calculated in the quasiclassical approximation (4), allowance for multiquantum RT processes does not introduce significant changes into the distribution of the molecules over rotational levels. Nor does the presence of RR' exchange processes, in which the quantum numbers of the colliding molecules change ( $j_1 \rightleftharpoons j_1 + \Delta_1 j$ ,  $j_2 \rightleftharpoons j_2 - \Delta_2 j$ ,  $\Delta_1 j = \Delta_2 j$ ), have significant influence on the results of the calculation.

Results of Numerical Calculations. For the numerical solution of the system (3) we chose a second-order, implicit predictor-corrector method. The calculations made confirmed the considerable efficiency in using this scheme of solution of the system of equations of relaxation gas dynamics in comparison with the Runge-Kutta method [1].

The similarity parameter for rotational relaxation [1] in a stream of homogeneous gas at a constant stagnation temperature is  $p_0 d_*$  ( $p_0$  is the stagnation pressure and  $d_*$  is the diameter of the critical cross section of the nozzle). To trace the character of the variation of the kinetics of populations of rotational states corresponding to different regimes of gas expansion, the system of equations (3) of relaxation gas dynamics was solved numerically for different  $p_0 d_*$ . For the transition probabilities we used Eqs. (4) and (5), multiplied by the parameter  $u$ , the value of which was determined from the condition of matching the experimental function  $T(z)$  with the calculated one. The stagnation temperature was  $T_* = 300^\circ\text{K}$ .

The results of the numerical calculations for different  $p_0 d_*$  confirm the main conclusions obtained from the analysis of experimental data. As one would expect, the populations of the system of even and odd rotational levels, although they are close, do vary independently. The relaxation of the system of rotational levels to the equilibrium state with a translational temperature  $T$  occurs through a series of non-Boltzmann distributions of the populations of rotational states. For low rotational levels close to the ground level, the probabilities of rotational transitions are high enough that their populations are able to vary in accordance with the variation of the translational temperature of the gas.

To characterize the nonequilibrium distribution, it is convenient to introduce the concept of the population temperature of a rotational level,  $T_r^j = -B_0(j+1)/\ln [P(j)g_0/(P(0)g_j)]$ , where  $g_j$  is the statistical weight of level  $j$ . The population temperatures of the lower levels are  $T_r^j \approx T$ . The number of such levels increases with an increase in  $p_0 d_*$  and  $T$ , which is determined by the rise in the frequency of collisions for the corresponding rotational transitions. For sufficiently abrupt cooling of the gas (low values of  $p_0 d_*$ ) a situation is possible in which this group of levels is absent.

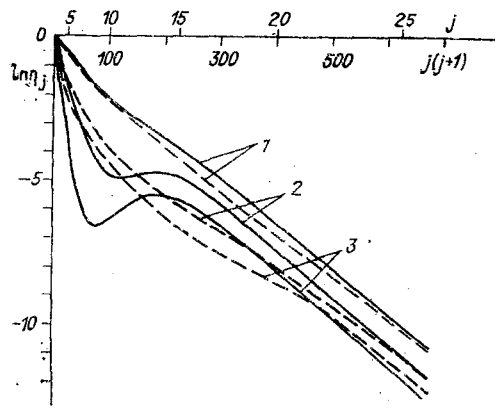


Fig. 2

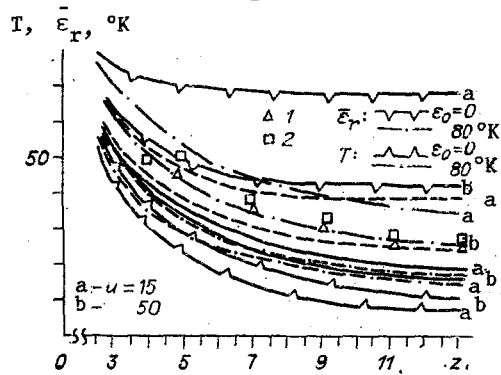


Fig. 3

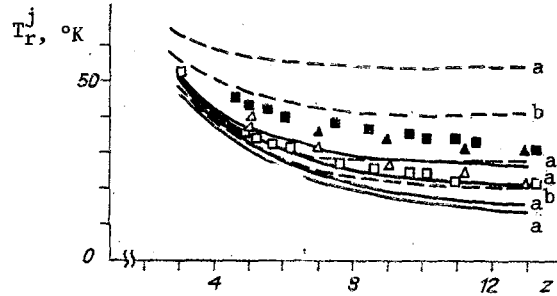


Fig. 4

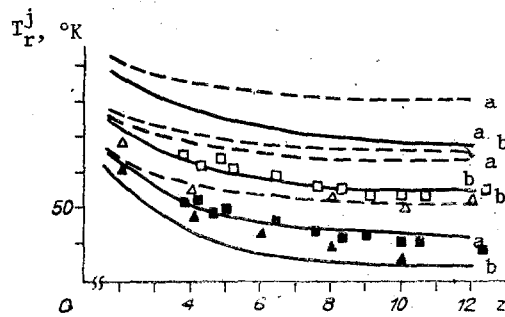


Fig. 5

For upper levels the collision probabilities are not high enough to alter their populations during the rapid decrease in translational temperature. Their relative populations remain "frozen-in." The population temperatures of these levels are  $T_r^j \approx T_0$ . With an increase in  $p_0 d_x$  and  $T_0$ , this group of levels starts with a higher number. Between these two groups there is a third, the intermediate group of levels, the population temperatures of

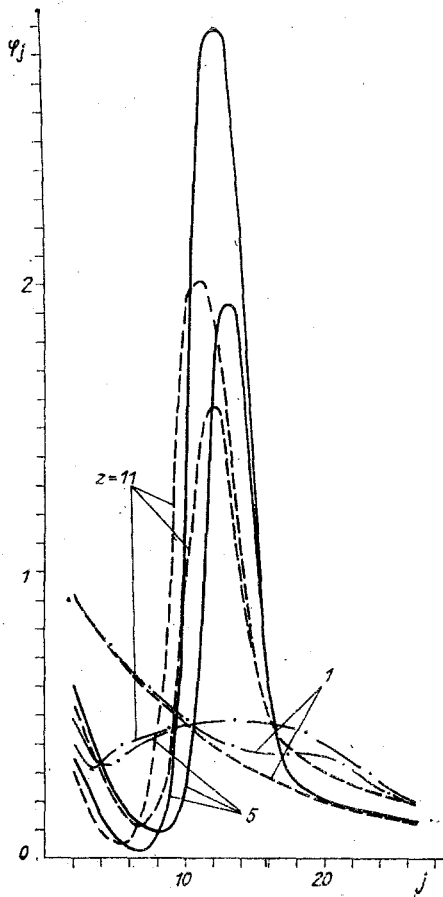


Fig. 6

which lie in the range from the initial translation temperature  $T_0$  to the current value:  $T < T_r^j < T_0 < T_*$ .

The rapid relaxation of the populations of the lower levels and the practically "frozen-in" populations of the upper ones lead to the possibility of the formation of an inverted distribution in the third group of levels. In the results of calculations of the relative population  $\eta_j = g_0 P(j) / (g_j P(0))$ , using Eq. (4), allowing for the influence of the long-range attraction of the interaction potential, for the probabilities of rotational transitions, we observed the formation of an inversion in the populations of the group of rotational levels (Fig. 2, where 1-3 correspond to  $z = 1, 3$  and  $7$ ;  $u = 15$ ;  $\epsilon_0 = 0$  and  $80^\circ\text{K}$  for dashed and solid lines). Calculations using probabilities in the approximation of an exponential form of the potential of the molecular interaction [1] showed no inversion.

In Fig. 3 we present experimental data (1 and 2 for  $p_0 d_* = 19.26$  and  $65.72 \text{ Pa}\cdot\text{m}$ ) and calculated results ( $\bar{\epsilon}_r$  and  $T$  for dashed solid lines) for the variation of the translational

temperature and average rotation energy  $\bar{\epsilon}_r = \sum_{j=0}^{j_*} P(j) E(j)$  of molecules of an expanding gas stream [1]. The calculations of rotational relaxation using Eq. (4) for the probabilities yielded functions  $\bar{\epsilon}_r$  and  $T$  closest to experiment. The joint solution of the system of equations of relaxation gas dynamics led to the fact that with an increase in  $p_0 d_*$ , the translational temperature of the gas increases somewhat in comparison with the results of previous calculations [1], where the system of kinetic equations was solved against the background of a given field of gas-dynamic parameters. In this case the average rotational energy decreases. Actually, with an increase in  $p_0 d_*$ , which corresponds to more intense development of rotational relaxation, the process of energy transfer from rotational to translational degrees of freedom becomes decisive, which can lead to an increase in the temperature of the expanding gas.

In Figs. 4 and 5 we present experimental and calculated data on the populational temperatures of several levels (Fig. 4: dashed lines for  $j = 4$  and  $8$  with  $u = 15$  and  $50$  [a and b] for  $\epsilon_0 = 0$ ; solid lines are the same for  $\epsilon_0 = 80^\circ\text{K}$ ; Fig. 5: same notation, but for  $j = 12$  and  $10$ , respectively).

The qualitative functions  $T_j(z)$  and  $\bar{\varepsilon}_r(z)$  agree sufficiently well with experiment. The experimental results in Figs. 4 and 5 are given for the same levels with  $p_0 d_* = 19.26$  and  $65.72 \text{ Pa}\cdot\text{m}$  ( $\Delta$ ,  $\blacktriangle$  and  $\square$ ,  $\blacksquare$ ; the dark symbols pertain to  $j = 8$  and  $10$ ). The "anomalous" behavior (a rise with an increase in  $p_0 d_*$ ) of the average energy and population temperature of the upper group of levels cannot be explained within the framework of the relaxation model used, however,

The results of the investigation of the formation and development of an inverted distribution in the system of rotational levels in different regimes of gas expansion are presented in Fig. 6, where the inversion parameters  $\phi_j = g_{j-2}P(j)/(g_jP(j-2))$  is given as a function of the level number  $j$  (dash-dot and dashed lines for  $\varepsilon_0 = 0$  and  $80^\circ\text{K}$ ; solid lines for  $u = 50$  and  $\varepsilon_0 = 80^\circ\text{K}$ ).

The more pronounced dependence of the collision probabilities (4) on the level number  $j$  in comparison with (5), as well as the weak influence of the temperature variation on them, lead to the fact that as the relaxation process develops, the populations of the upper levels hardly vary, while the relative populations of the lower levels increase through the intense nonuniform depletion of the middle group of levels, for which the probabilities of rotational transitions are rather high. As a result, an inversion is formed in this middle group of rotational levels.

An increase in the parameter  $p_0 d_*$  of rotational relaxation corresponds to the more intense development of an inverted population of the system of rotational levels. In the process, the number of the level at which the maximum value of the inversion parameter is reached increases. This character of the population kinetics is explained by the fact that the probabilities of collisional transitions grow effectively with an increase in  $p_0$ . A similar variation of the development of relaxation kinetics is observed with a change in the value of  $\varepsilon_0$ , an increase in which also leads to a weaker dependence of the probabilities of rotational collisional transitions on  $T$  as it decreases.

An analysis of the results obtained enables us to conclude that long-range molecular attraction has a significant influence on the behavior of relaxation in a system of rotational levels, so that the formation of an inverted distribution is possible for certain values of  $p_0 d_*$ .

One of the mechanisms which could explain the anomalous increase in  $T_r^j$  in high rotational levels is "remote" multiquantum  $RR'$  exchange, when the variation of molecular states during a collision takes place by the scheme  $j_1 \rightleftharpoons j_1 + \Delta_1 j$ ,  $j_2 \rightleftharpoons j_2 - \Delta_2 j$  ( $0 < \Delta_1 j < \Delta_2 j$ ,  $j_1 > j_2$ ). With allowance for the resonance (or nearly resonance) character of such processes, as well as the rather high populations of the lower  $j_2$  states, under the condition

$$\frac{(2j_1 + \Delta_1 j) \Delta_1 j T_r^{j_2} T_r^{j_1} - T}{(2j_2 - \Delta_2 j) \Delta_2 j T_r^{j_1} T_r^{j_2} - T} > 1, \quad T_r^{j_2} \approx T_r^{j_2 + \Delta_2 j}$$

we can obtain an "anomalous" distribution of the population temperatures  $T_r^j$  of the upper levels.

This relation is fully realized under the conditions discussed above. The difference between the experimental data of [1, 2] and the results of the present work, as was indicated earlier [1], is probably also connected with the pronounced role that may be played by the process of clustering of molecules with an increase in the parameter  $p_0 d_*$  [6].

#### LITERATURE CITED

1. A. N. Vargin, N. A. Ganina, et al., "Rotational relaxation of molecule nitrogen in a freely expanding stream," Zh. Prikl. Mekh. Tekh. Fiz., No. 3 (1979).
2. P. A. Skovorodko and R. G. Sharafutdinov, "Rotational relaxation in the transitional regime of free streams of nitrogen," Zh. Prikl. Mekh. Tekh. Fiz., No. 6 (1981).
3. H. Rabitz and S.-H. Lam, "Rotational energy relaxation in molecular hydrogen," J. Chem. Phys., 63, No. 8 (1975).
4. A. N. Vargin, N. A. Ganina, et al., "Calculation of the probabilities of rotational transitions of molecules using the Morse potential," Zh. Prikl. Mekh. Tekh. Fiz., No. 3, (1981).
5. G. V. Dubrovskii and A. V. Kondratsenko, "Models of the interaction and relaxation of rotating and vibrating molecules," Zh. Tekh. Fiz., 51, No. 2 (1981).
6. N. V. Karelov, A. K. Rebrov, and R. G. Sharafutdinov, "Effect of populating of upper rotational levels in the process of free expansion of a gas containing clusters," Pis'ma Zh. Eksp. Teor. Fiz., 27, No. 1 (1978).