POPULATION KINETICS OF ROTATIONAL LEVELS IN A FREE NITROGEN JET

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Rotational−translational relaxation accompanying supersonic expansion occurs with the breakdown of the Boltzmann distribution over the rotational levels. This has been established experimentally with the help of various methods: electron beam [1-3], glow discharge [4], magnetic resonance in a molecular beam [5], and laser radiation [6].

The theoretical description of the process of rotational relaxation must be based on the solution of Boltzmann's kinetic equation for a gas with internal degrees of freedom [7], but this approach is not used in practical calculations because of well-known difficulties in solving this equation, as well as due to the absence of information on cross sections for R−R and R−T processes. Up to the present time, in order to describe the population kinetics of rotational levels, only a hydrodynamic approach has been used, consisting of solving the system of kinetic equations for the population densities and, in addition, in work along these lines [8-10], the process of rotational relaxation was examined in a fixed field of gasdynamic parameters (linear problem). The values of the rotational relaxation rate constants, necessary for the hydrodynamic method, were found by solving the collision dynamics problem for $H_2 + H_2$ [8] and $N_2 + N_2$ [10] or the values were chosen intuitively [9]. In [10], wherein the rotational relaxation of nitrogen in a freely expanding jet was examined, all collisional transitions were neglected, except the two-quantum transitions $\Delta k = \pm 2$ (i.e., the minimum possible taking into account ortho- and paramodifications of nitrogen). Comparison with experiment, carried out in [10], revealed the disagreement between calculations and data from electron beam measurements.

The purpose of this paper is to describe theoretically the results of electron beam measurements of the population densities of rotational levels of nitrogen molecules in a jet flowing into a vacuum.

1. Experiment. The experimental data, used in the present paper, were obtained on a low-density gasdynamic setup at the Institute of Thermal Physics of the Siberian Branch of the Academy of Sciences of the USSR (testing unit VS-4) [11], equipped with electron beam diagnostics [12]. Axisymmetrical sonic nozzles served as gas sources. The stagnation temperature in all experiments was room temperature (290-300°K). The pressure level in the background gas did not exceed 0.25 Pa, so that the effect of molecules penetrating from the background on the measurements was negligibly small and the flow in the core of the jet was the same as for flow into a vacuum [3]. The experiments consisted of measurements of the first negative band system in nitrogen, excited by an electron beam, along the axis of the jet. The results of the measurements are presented in detail in [13].

2. Calculation of Population Densities of Rotational Levels. In the hydrodynamic approximation, the system of kinetic equations for the population densities of molecular rotational levels has the following form [8]:

$$\frac{dn_i}{dt} + n_i \nabla u = n^2 \sum_{j,l,m} [N_l N_m K_{l,m,i,j} - N_i N_j K_{i,j,l,m}], \qquad (2.1)$$

where u is the velocity of the gas; n_i is the number density of molecules in i-th rotational state; $n = \sum_i n_i$ is the number density of gas molecules; $N_i = n_i/n$ is the relative population density of the i-th rotational level; $K_{l,m,i,j}$ and $K_{i,j,l,m}$ are the microscopic rate constants [14] for binary collisions of molecules $(i, j) \rightleftharpoons (l, m)$ with rotational quantum numbers i, j, l, m. In what follows, we assume that the rate constant $K_{i,j,l,m}$ does not depend on the values of j and m and equals zero when $j \neq m$, i.e., one of the colliding molecules is a structureless particle. Taking into account transitions with $j \neq m$ (R−R transitions), as done in [9], showed that they play a relatively small role. In this case, for one-dimensional stationary flow in a stream tube, the system of kinetic equations (2.1) takes the form

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$$u\frac{dN_k}{dx} = n\sum_{\Delta k}\{[K_{k+\Delta k,k}N_{k+\Delta k} - K_{k,k+\Delta k}N_k] - [K_{k,k-\Delta k}N_k - K_{k-\Delta k,k}N_{k-\Delta k}]\}, \tag{2.2}$$

where x is the distance along the stream tube. Here, the indices i and *l* are replaced by the standard index k for a homonuclear diatomic molecule. Due to the fact that collisional transitions between ortho- and paramodifications of nitrogen are strongly forbidden [15], only transitions with even values of Δk are allowed. For this reason, the system of Eqs. (2.2) decomposes into two uncoupled systems for the even and odd level numbers k. For nitrogen, the relative nuclear degeneracies of the rotational levels g(k) equal 2/3 and 1/3, respectively, for ortho- (k even) and para- (k odd) modifications [15]. In agreement with the principle of detailed balance, we will write the system of Eqs. (2.2) in the form

$$u\frac{dN_k}{dx} = n\sum_{\Delta k}\left\{K_{k+\Delta k,k}\left[N_{k+\Delta k} - N_k\left(\frac{N_{k+\Delta k}}{N_k}\right)_t\right] - K_{k,k-\Delta k}\left[N_k - N_{k-\Delta k}\left(\frac{N_k}{N_{k-\Delta k}}\right)_t\right]\right\}, \tag{2.3}$$

where

$$\left(\frac{N_i}{N_j}\right)_t = \frac{(2i+1)}{(2j+1)}\exp\left\{[j(j+1) - i(i+1)]\frac{\Theta}{T_t}\right\}$$

represents the ratio of population densities for equilibrium (Boltzmann) distribution of molecules over rotational levels with the temperature equal to the translational temperature of the gas T_t. Here, Θ = 2.878°K is the rotational constant for nitrogen.

The system of Eqs. (2.3) was used to describe the population kinetics of the rotational levels of nitrogen molecules on the axis of a free jet with an axisymmetrical sonic nozzle. The problem was solved in a linear formulation. The functions u(x), n(x) and $T_t(x)$ were found by solving numerically the system of gasdynamic equations:

$$\begin{gathered}\rho uA = \text{const} = G, \quad 3{,}5RT_t + u^2/2 = \text{const}, \\ \rho u du + dp = 0, \quad p = \rho RT_t,\end{gathered} \tag{2.4}$$

where $R = k_B/m$ is the gas constant; p is the pressure; $\rho = mn$ is the density; A is the area of the stream tube; k_B is Boltzmann's constant; and, m is the mass of a molecule. The function A(x) was tabulated based on a two-dimensional calculation of the flow of a perfect gas with a ratio of specific heat capacities $\gamma = 1.4$ [16]. After putting the system of Eqs. (2.3) into dimensionless form, it can be shown that for a given set of rate constants the functions $N_k(x/d_*)$ will be the same for constant values of the two defining parameters: the stagnation temperature T_0 and the product of the pressure in the fore-chamber p_0 and the diameter of the nozzle edge d_*. The calculations were carried out for T_0 = 290-300°K, $13.3 \le p_0 d_*$ [Pa · mm] $\le 10^4$. It was assumed that in the subsonic part of the nozzle equilibrium exists between the translational and rotational degrees of freedom, while in the nozzle cross section Mach's number equals unity according to the equilibrium velocity of sound. The calculation was started directly from the cross section of the nozzle, where the equilibrium distribution of molecules over the rotational level was given:

$$N_k = \frac{(2k+1)\,g(k)\exp[-k(k+1)\Theta/T_*]}{\sum_k (2k+1)\,g(k)\exp[-k(k+1)\Theta/T_*]}, \tag{2.5}$$

where T_* is the temperature at the edge of the nozzle and, in addition, $T_* = 2T_0/(\gamma+1)$. Twenty-eight rotational levels (from the ground state to the twenty-seventh) were taken into account; in accordance with this, the rate constants $K_{k+\Delta k,k}$ in the system of Eqs. (2.3) were assumed to equal zero for the values $k + \Delta k \ge 29$.

The following procedure was used for solving the system of Eqs. (2.3) numerically. First, the gasdynamic parameters n_2, u_2, T_{t2} were calculated at the point $x_2 = x_1 + h$ (h is the computational step along the axis of the jet) by solving the system of Eqs. (2.4). The equation of motion was approximated in this case as follows [16]:

$$G(u_2 - u_1) + \frac{A_1 + A_2}{2}(p_2 - p_1) = 0,$$

after which the system (2.4) can be reduced to a quadratic equation for u_2. From the two values of the velocity, the solution corresponding to supersonic flow was chosen. Here and in what follows, the index 1 indicates known quantities at the point x_1 and the index 2 indicates the quantities sought at the point x_2. Then, the system of Eqs. (2.3), which was approximated with the help of the following second-order implicit difference scheme, was solved:

$$\frac{N_{k2}-N_{k1}}{h}=\frac{1}{2}\left\{\frac{n_1}{u_1}\sum_{\Delta k}F(\mathbf{N}_1, T_{t1})+\frac{n_2}{u_2}\sum_{\Delta k}F(\mathbf{N}_2, T_{t2})\right\}, \tag{2.6}$$

where F(**N**, T_t) denotes the term in braces in Eqs. (2.3), while **N** indicates the population density vector. Since the quantity F depends linearly on the population densities, the system of difference equations (2.6) can be reduced to a system of algebraic equations for the unknown population densities at the point x_2 (more precisely, to two systems for even and odd levels). These systems of equations were solved with the help of an appropriate standard procedure. The computational scheme described above ensures a stable calculation for any values of the parameter p_0d_*.

In order to increase the accuracy, the computed results were compared with experimental results for the magnitudes of line intensities of the first negative band system in nitrogen, which were calculated using the model in [17] from the known values of the population densities:

$$I_{k'}=\left(N_{k'-1}\frac{k'}{2k'-1}+N_{k'+1}\frac{k'+1}{2k'+3}\right)\frac{k'}{2k'+1}.$$

3. Comparison of Calculation with Experiment. In order to compare the calculation with experiment, it is necessary to know the rate constant for rotational relaxation. Up to now, for collisions between nitrogen molecules, there is information in the literature only on the effective probabilities for two-quanta transitions ($\Delta k = \pm 2$) [18]:

$$P_{k+2,k}=\frac{\sigma_i}{\sigma_e}=\frac{193}{\sqrt{T_t}}\frac{1}{\alpha(10+\alpha^2)^2}\frac{(k+2)(k+3)(2k+3)^2}{2k+5}\exp\left[-3\left(\frac{6{,}882(2k+3)}{\alpha\sqrt{T_t}}\right)^{2/3}\left\{1+\exp\left[\frac{\Theta(2k+3)}{T_t}\right]\right\}^2\right],$$

where σ_i and σ_e are the total effective cross sections for inelastic and elastic collisions, respectively; α is a parameter of the potential. The transformation from effective probabilities to rate constants can be made according to the equation

$$K_{k+2,k}=cP_{k+2,k}\,\sigma_g\,\bar{v}, \tag{3.1}$$

where $\bar{v} = (16k_B T_t/\pi m)^{1/2}$ is the average velocity of relative motion; $c = \sigma_e/\sigma_g$; σ_g is the gas-kinetic cross section, which was calculated using Sazerland's equation:

$$\sigma_g=\pi(3{,}22)^2(1+105/T_t)\cdot 10^{-16}\ \text{cm}^2. \tag{3.2}$$

The free parameters α and c were chosen by comparing calculations with experimental results, obtained for $p_0d_* = 8\cdot 10^3$ Pa·mm and $T_0 = 295$°K. These experimental conditions correspond to an insignificant effect of condensation on the population density of levels [19], but at the same time, the deviations of the density and translational temperature from their isentropic values due to the effect of relaxation processes and viscosity in the nozzle [20] are also not large. The parameters α and c were adjusted so that $\alpha = 3$ and $c = 10$, for which the calculation and experiment agree satisfactorily, as is evident from Fig. 1, which shows the behavior of the intensities of rotational lines $I_{k'}$ for odd levels with $k' = 3$ to $k' = 11$. The dots in Fig. 1 indicate experimental data (5 is for $d_* = 5.12$ mm and 6 is for $d_* = 15$ mm), while the lines indicate the computed values. Curve 1 shows the values of $I_{k'}$ with a Boltzmann distribution in the $X^1\Sigma v = 0$ state with translational temperature T_t; curve 2 shows the theoretical calculation with rate constants given by Eq. (3.1), which in what follows we will refer to as the two-quanta model of rotational relaxation. The same figure presents the computed data for the first and second multiquantum models (curves 3 and 4, respectively). These models will be described below.

As a comparison, shown in Fig. 2 (the notation in Fig. 2 is the same as in Fig. 1), between calculations and experiment shows, for $x/d_* = 5$ and $T_0 = 290$°K with $p_0d_* > 8\cdot 10^3$ Pa·mm, the theoretical data on two-quanta model are much closer to the values for equilibrium flow (in Fig. 2, they are shown by the horizontal segments of the dashed lines) than experiment. In addition, this difference increases with increasing rotational quantum number and can be ascribed to the effects of nonequilibrium condensation [19].

The disagreement between computed and experimental data is also observed for smaller values of p_0d_*, i.e., for conditions when the effects of condensation in the flow are insignificant, at least, for most of the rotational levels. The disagreement indicated increases with increasing p_0d_*, since the calculation using the two-quantum model predicts a slower relaxation rate for the process than is observed experimentally.

The problem of finding the rate constants from experimental data on the population densities of the levels for the two-quanta transition model is a problem involving a number of unknown constants $K_{k+2,k}$ equal to the number of equations [Eqs. (2.3)]. For this reason, the lack of correspondence between the calculation using the two-quanta transition model and experiment demonstrated in Fig. 2, except for the experiment with

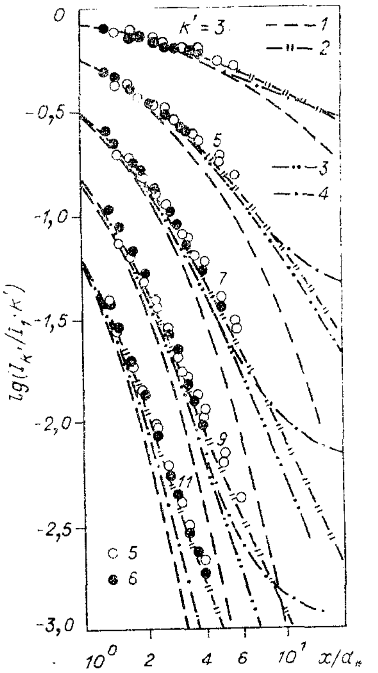

Fig. 1

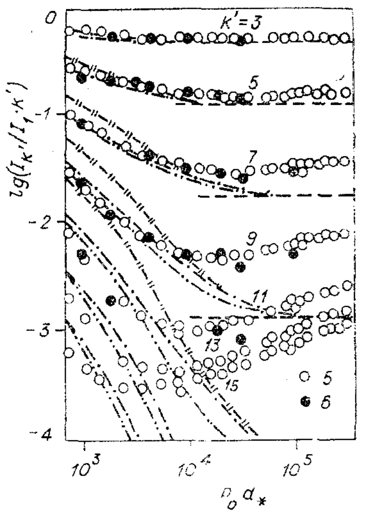

Fig. 2

$p_0 d_* = 8 \cdot 10^3$ Pa·mm, indicates the necessity of taking into account transitions with $\Delta k > 2$. This is also indicated by quantum mechanical calculations of the cross sections of inelastic N_2 + Ar collisions [21]. There is as yet no information in the literature on the rate constants of rotational relaxation with $N_2 + N_2$ collisions, while the system of kinetic equations (2.3) cannot be solved uniquely for the rate constants of multiquantum transitions, as can be done for models involving two-quanta transitions.

Information theory was used to set the multiquantum rate constants [22]. The equations for the rate constants were used in the same form as for the cross sections in this theory. In the notation of the paper cited, the equation for calculating the deactivation constants has the form

$$K_{k+\Delta k,k} = K_{k+\Delta k,k+\Delta k-2}\frac{\Phi(k,\Delta k)}{\Phi(k,2)}\frac{(2k+1)}{2(k+\Delta k)-3}, \tag{3.3}$$

where

$$\Phi(k,\Delta k) = (T_t + E_{k+\Delta k} - E_k)^{1/2}\exp\left(-c_1\frac{E_{k+\Delta k} - E_k}{T_k + E_{k+\Delta k}}\right).$$

Here, c_1 is an adjustable factor, while $E_i = i(i+1)\Theta$. The two-quanta transition constants were calculated using Eq. (3.1) with $\alpha = 3$. The best agreement between theoretical and experimental data is obtained with $c_1 = 4$. In Figs. 1 and 2, calculations according to this model of rotational relaxation (first multiquantum) are indicated by the number 3. In contrast to the two-quanta transition model, this model describes the experimental data in the range $p_0 d_* = 10^3$–$8 \cdot 10^3$ Pa·mm.

The same satisfactory description of the experiments was also obtained for another set of rate constants for rotational relaxation, in particular, for deactivation constants, given in the form [23]

$$K_{k+\Delta k,k} = B\exp\left(-c_2\frac{E_{k+\Delta k} - E_k}{T_t}\right), \tag{3.4}$$

with adjustable parameters B and c_2. We will refer to this model as the second multiquantum model. By fitting, the values $B = 7.39 \cdot 10^{-11}$ cm^3·sec^{-1} and $c_2 = 0.35$ were obtained, for which the experimental data, presented in Fig. 2 for $p_0 d_* < 8 \cdot 10^3$ Pa·mm, are described by this model just as well (curve 4) as by calculations using the first multiquantum model. A similar description of the experiments is also obtained for other values of x/d_*.

Figure 3 gives the computed distributions of population densities of rotational levels for $x/d_* = 5$ and $T_0 = 300$°K for different values of $p_0 d_*$ in the coordinates $\ln(N_k/N_0(2k+1)) - k(k+1)$. In these coordinates,

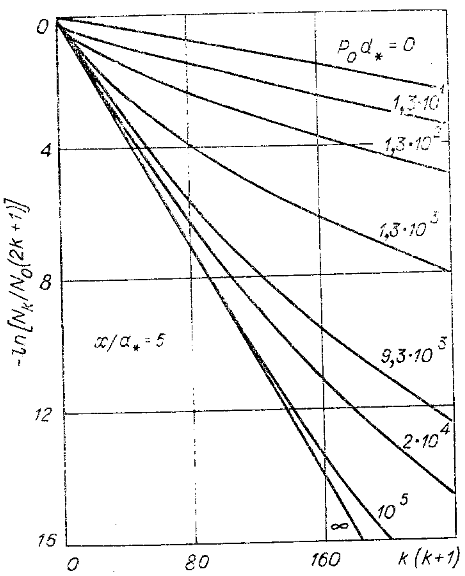

Fig. 3

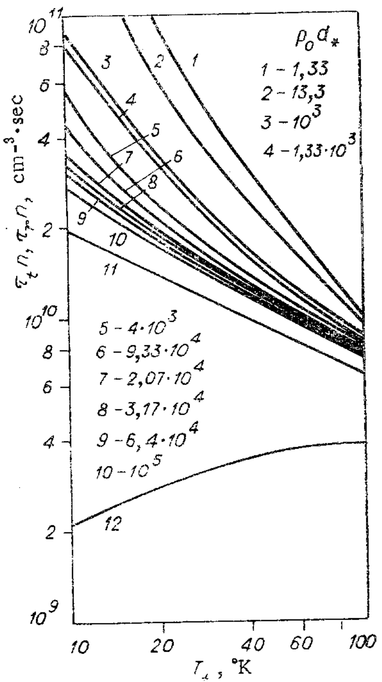

Fig. 4

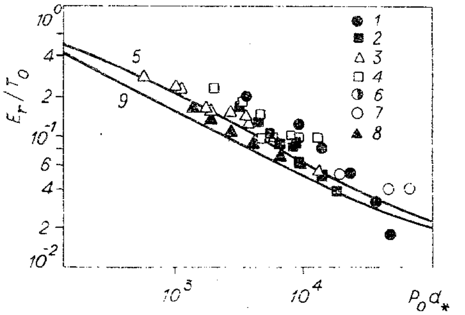

Fig. 5

the Boltzmann distribution with temperature T_r is a straight line with the tangent of the angle of inclination equal to $-\Theta/T_r$. The same figure shows the distributions corresponding to the equilibrium ($p_0d_* = \infty$) and "frozen" ($p_0d_* = 0$) flows. In Fig. 3, the population densities of the odd levels, in accordance with the statistical weights of ortho- and paramodifications, are increased by a factor of 2. It is evident that for all p_0d_* the population densities of even and odd levels are described by single smooth functions of $k(k+1)$. The distributions evolve from equilibrium to "frozen" through a sequence of non-Boltzmann distributions, i.e., distributions for which a rotational temperature cannot be introduced. This evolution of the distributions, which is observed for any x/d_*, is typical for experiments with free jets [3].

4. Relaxation of Rotational Levels. In order to solve a wide range of gasdynamic problems, instead of detailed information contained in the molecular rotational distribution function, it is enough to know the relaxation characteristics of the rotational energy $E_r = \sum\limits_k \Theta k(k+1)\, N_k$. We will examine the problem of the applicability of the relaxation equation

$$\frac{dE_r}{dt} = u\frac{dE_r}{dx} = \frac{E_r(T_t) - E_r}{\tau_r} \tag{4.1}$$

for describing the computed results for E_r obtained above. In Eq. (4.1), τ_r is the relaxation time. Based on the computed functions $N_k(x)$ and, therefore, knowing the functions $E_r(x)$, for each point x we computed the quantity τ_r from Eq. (4.1). The corresponding results are presented in Fig. 4 for 10 values of p_0d_* and are denoted by the numbers 1-10 for the set of rate constants (3.4) in the form of the functions $n\tau_r(T_t)$. The number 11 indicates the function $n\tau_r^l(T_t)$, obtained directly from the system of Eqs. (2.3) for the case of an infinitely small difference between the translational and rotational temperatures ($T_r - T = \varepsilon \to 0$) by expanding the right sides of Eqs. (2.3) in powers of ε and taking into account terms ~ε. In this case, Eq. (4.1) with $\tau_r = \tau_r^l$ can be obtained for E_r. A similar procedure for calculating τ_r^l was used previously in [24] for a two-quanta transition model. As is evident from Fig. 4, for each value of T_t, there is an appreciable increase in the quantity $n\tau_r$ with decreasing p_0d_*, i.e., with an increase in the deviation from equilibrium between rotational and translational degrees of freedom. This indicates that the quantity $n\tau_r$ depends on the distribution of molecules over rotational levels and, therefore, Eq. (4.1), strictly speaking, cannot describe E_r as accurately as the system of kinetic equations (2.3). The nature of the dependence of $n\tau_r$ on the distribution of population densities is determined by the set of rate constants for rotational relaxation and by the gasdynamic process. We note in this connection that in [9] a special set of constants is indicated for which the equivalent relaxation time does not depend on the distribution of molecules over rotational levels. However, in general, such a dependence exists and, therefore, the relaxation equation (4.1) can be used for describing approximately the relaxation of rotational energy only in a limited range of defining parameters (p_0d_*, T_0, x/d_*). The number 12 in Fig. 4 indicates the dependence of the product of the gas density and the average time between collisions of molecules

$$n\tau_t = \frac{1}{4}\sqrt{\frac{\pi m}{k_B T_t}}\frac{1}{\sigma_g},$$

where σ_g is given by Eq. (3.2). As is evident, in the temperature interval 10-100°K, the quantity $z_r = \tau_r/\tau_t$ increases with increasing T_t from 2-3 at $T_t = 100$°K to 10-100 and higher at $T_t = 10$°K.

Figure 5 shows the results of measurements of E_r, carried out using different methods: according to the energy balance in the molecular beam [25-27], points 1, 2, and 4, respectively; electron beam in a molecular beam [28], points 3. Point 6-8 indicate the results in [13]: 6) $x/d_* = 66.1$, $T_0 = 290$°K; 7) $x/d_* = 66.1$, $T_0 = 295$°K; 8) $x/d_* = 38$, $T_0 = 295$°K. The experimental data in general agree, although the electron beam measurements give smaller values of E_r than the molecular beam measurements. The experimental results [13] agree well with data in [28], where electron beam measurements were carried out in a molecular beam separated out from the jet, i.e., for densities much lower than for measurements in a jet and, therefore, for a smaller effect of secondary electrons. The agreement between the data on E_r provides an additional basis, to that presented in [13], for neglecting the effect of secondary electrons. Figure 5 also shows the computed functions $E_r(p_0d_*)$ at the point $x/d_* = 100$ (the quantity E_r in the range of p_0d_* examined is "frozen" at distances $x/d_* \lesssim 30$-40). Curve 5 was obtained from a solution of the system of kinetic equations (2.3) with constants (3.4); curve 9 is result of a solution of Eq. (4.1) with relaxation time τ_r^l. As can be seen, the kinetic calculation agrees satisfactorily with experiment, while the relaxation equation leads to results that are lower (by 20 to 30%).

The ambiguity of the rate constants for rotational relaxation, demonstrated above, found from the results of measurements of population densities of levels, has a fundamental significance, reflecting the improper nature of the corresponding inverse problem. However, whatever the true values of the rate constants are, the basic characteristics of rotational relaxation in a free jet of a molecular gas remain the same.

1. Supersonic expansion of a gas into a vacuum is accompanied by breakdown of the Boltzmann distribution of the rotational level population densities.

2. Multiquantum R–T transitions ($\Delta k = \pm 4$, ± 6, and so on) play an important role in the kinetics of rotational relaxation.

3. The relaxation time for rotational energy depends on the distribution of molecules over rotational levels and, for this reason, the quantity z_r obtained by analyzing the experiments within the scope of the relaxation equation (4.1) is not a physical characteristic of the gas. This circumstance could be the reason for the large spread in the values of z_r in the literature [26], even those obtained using the same method.

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