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UDC 533.6.011.8

In order to describe the rotational relaxation for small deviations from equilibrium one can use the simplest relaxation equation [1]

$$\frac{\partial E_R}{\partial t} + u \frac{\partial E_R}{\partial x} = - (E_R - E_t) / \tau_R, \quad (1)$$

where  $E_R$ ,  $E_t$  are the energies of the rotational degrees of freedom in nonequilibrium and equilibrium conditions;  $\tau_R$  is the rotational relaxation time;  $t$  is time;  $u$  is the gas velocity;  $x$  is the coordinate. Small deviations from equilibrium take place during propagation of ultrasounds in a molecular gas [2], flow of polyatomic gases in capillary tubes [3], and in weak shock waves [4]. The calculation of the transport coefficients is carried out in the approximation of small deviations from equilibrium [5]. In free jets or in expansion of gases from nozzles various values of the deviation from equilibrium can result, including small ones. Interpretation of experiments, performed in free jets, usually applies Eq. (1), although, as is shown in [6], the rotational relaxation time depends on the character of population of the levels and the degree of deviation from equilibrium and it is unknown beforehand for what values of the deviation Eq. (1) is applicable.

Usually the determination of the rotational relaxation time or of its ratio to the translational relaxation time  $Z_R = \tau_R / \tau_t$  is performed by matching in comparing the calculation of  $E_R$  from Eq. (1) with experimental data [7, 8]. In such determination of  $\tau_R$  it is hard to establish the dependence of  $\tau_R$  on the gas temperature and to find the conditions of applicability of Eq. (1).

In the present work the dependence of the rotational relaxation time on the gas temperature and conditions of expansion is found by means of Eq. (1) from electron-beam measurements of rotational energy on the axis of a stationary free argon jet with a small admixture of nitrogen.

The experiments were performed on a low-density gas-dynamics apparatus in the Thermophysics Institute of the Siberian Branch, Academy of Sciences of the USSR — stand VS-4 [9]. The mixture of 95% Ar and 5%  $N_2$  was heated in an ohmic heater and expanded into a vacuum chamber through a sonic nozzle of diameter  $d_* = 5$  mm. The heater was placed on the coordinate table which allowed one to orient the studied jet with respect to the fixed electron beam and the spectral equipment. The radiation induced by the beam in the optical spectral range was registered by the spectrometer DFS-12. The radiation was observed in the direction perpendicular to the electron beam. The size of the region from which the radiation was detected varied from 2 mm near the end of the nozzle to 7 mm away from it by the height of the beam. All measurements were performed on the beam's axis and on its kernel where the flow is unperturbed by the background. The smallness of the effect of the background was assured by the low pressure in the vacuum chamber. The drag pressure was measured by U-shaped manometers and master vacuummeters. The drag temperature was determined by measuring the flow. A detailed description of the apparatus and experimental methods is given in [9] together with random error analysis of the spectral measurements. These errors do not exceed the sizes of the points on the graphs where the confidence intervals are now shown.

To compute the relaxation time by Eq. (1) it is necessary to find the dependence of energy of the rotational degrees of freedom in the state  $N_2 X^1 \Sigma_g$ ,  $v = 0$ , further denoted by  $X^1$ , on the coordinate  $x$  ( $x = 0$  corresponds to the end of the nozzle). In the experiments the rotational spectra were taken from the band (00) of the first negative band system radiated due to the spontaneous transitions between the states  $N_2^+ B^2 \Sigma_u^+$  and  $N_2^+ X^2 \Sigma_g^+$  denoted below

by  $B^2$  and  $X^2$ , respectively. Excitation of the state  $B^2$  was achieved by a direct electron impact [10]. We will find the relation between the intensity of radiation of rotational lines in the spectrum and rotational energy in the state  $X^1$ :

$$E_R^X = \sum_1^{\infty} k(k+1) \Theta^X N_k^X, \quad (2)$$

where  $\Theta = 2875$  K is the characteristic temperature in the state  $X^1$ ;  $N_k^X$  is the normalized population of the  $k$ -th rotational level. In the state  $B^2$  the rotational energy is

$$E_R^B = \sum_1^{\infty} k'(k'+1) \Theta^B N_{k'}^B. \quad (3)$$

Here  $\Theta^B$ ,  $N_{k'}^B$ ,  $k'$  is the characteristic temperature, the population of levels, and rotational quantum number in the state  $B^2$  where

$$N_{k'}^B = I_{k'l'k''} / D_{k'l'k''}^B = \sum P_{k'l'k} N_k^X, \quad (4)$$

where  $I_{k'l'k''}$  and  $P_{k'l'k''}$  are the intensities of rotational lines and the Hönl-London factors for the R-branch of the (00)-band in emission;  $P_{k'l'k}$  are the probabilities of rotational transitions in excitation from  $X^1$  to  $B^2$  by electron impact by the primary beam electrons. According to [10],

$$P_{k'l'k} = (2k'+1) \sum P_{l0} \begin{pmatrix} k & l & k' \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (5)$$

Here  $\begin{pmatrix} k & l & k' \\ 0 & 0 & 0 \end{pmatrix}$  are the Wigner 3j-symbols;  $P_{l0}$  are the probabilities of transition from the zero rotational level in  $X^1$  to the rotational level  $l$  in  $B^2$ . The vector  $P_{l0}$  is represented parametrically

$$P_{l0} = (2l+1) \alpha^l \sum_{l=1,3,5} (2l+1) \alpha^l. \quad (6)$$

In [10] it is shown that for  $\alpha = 0.28$  a satisfactory description of the spectra can be obtained at equilibrium flow of nitrogen. Substituting (4)-(6) into (3) and using the property of 3j-symbols

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

we obtain

$$E_R^B = \sum_{k,l} \Theta^B N_k^X P_{l0} k(k+1) + \sum_{k,l} P_{l0} \Theta^B l(l+1) N_k^X. \quad (7)$$

Since

$$\sum_l P_{l0} = 1, \quad \sum_k N_k^X = 1, \quad \Theta^B \approx \Theta^X,$$

it follows that

$$E_R^X = E_R^B = \sum_l \Theta^X P_{l0} l(l+1). \quad (8)$$

For  $\alpha = 0.28$   $\sum_l \Theta^X P_{l0} l(l+1) \approx 12.7$  K. The final formula for calculating  $E_R$  has the form

$$E_R^X = \frac{\sum_{k'} I_{k'} (2k'+1) (k'+1) \Theta^X}{\sum_{k'} I_{k'} (2k'+1) / k'} = \sum_l \Theta^X P_{l0} l(l+1). \quad (9)$$

Since in the experiments one registers a finite number of lines in the spectrum, it is necessary to account for the contribution to  $E_R^X$  of the unobserved lines. It is accomplished in the following way. The value of  $E_R^X$  is calculated from the formula (9) from the measured values. The values of  $N_k^X$  are subsequently found from the Boltzmann distribution at  $T_R = E_R^X/k_B$ , the intensities of the unobserved lines are computed from the formula (4), and by means of formula (9) a correction to  $E_R$  is calculated for these values of  $I_k$ .

In Fig. 1 we give an example of calculation of  $E_R^X$  from the spectrum (1 is the observed spectrum; 2 is  $E_R^X$  obtained from the observed spectral lines; 3 is the contribution of the unobserved lines into  $E_R^X$ ; 4 is  $E_R^X$  for the equilibrium temperature of the isentropic expansion).

Since the transition between the ortho- and para- forms of nitrogen in the state  $X^1$  is forbidden, the rotational energy should be computed separately for each form. In the experiments only the resolved lines of the R-branch ( $\Delta k = -1$ ) were registered. The following relation was used to normalize the lines with even values of  $k'$

$$\sum_{k'=2n} N_{k'}^B = 0.5 \sum_{k'=2n+1} N_{k'}^B, \quad (10)$$

which follows from the strong selection rule forbidding transitions between the rotational levels of the same parity in the states  $X^1$  and  $B^2$  in excitation by electron impact.

The results of calculation of the rotational energy from the spectrograms are given in Fig. 2. They are represented in the form of deviation of  $E_R^X$  from the translational temperature of the equilibrium isentropic expansion of a monoatomic gas  $T_t$ . The experimental conditions are given in Table 1 where the row numbers correspond to the labels in Figs. 2 and 3. The tendencies of change in  $E_R^X$  correspond to the picture of leakage of the rotational relaxation in expanding flows: with increasing  $n_0 d_*$  ( $n_0$  is the density in the gas source) the data on  $E_R^X$  approach equilibrium; farther from the end of the nozzle the deviation from the equilibrium flow becomes larger. For the regimes 1 and 3 in Fig. 2 the values of  $E_R^X$  are given that correspond to calculation using even (contour symbols) and odd (full symbols) spectral lines. The results for  $E_R^X$  for the levels of different parity agree within the errors of calculation. Consequently, the ortho- and para- forms of nitrogen relax with identical speed.

In calculating the rotational relaxation time the dependences of the flux, velocity and translational temperature of the gas on the coordinate were obtained from the results of a calculation of an isentropic equilibrium expansion of a monoatomic gas ( $\gamma = c_p/c_v = 1.67$ ). To determine the derivatives of the rotational energy a smoothing cubic spline was applied [11]. The results are given in Fig. 3 in the form of a product of the relaxation times with the gas number density  $\tau_{RN}$ . It is clear that  $\tau_{RN}$  for all experiments increases with increasing gas temperature and parameter  $n_0 d_*$ . However, for sufficiently large values of  $n_0 d_*$  when the deviations from equilibrium are small, i.e.,  $(E_R^X - E_t^X)/E_t^X < 1$ ,  $\tau_{RN}$  no longer depends on  $n_0 d_*$ . Precisely in this region  $\tau_R$  can take on the meaning of relaxation time of rotational energy. The quantities obtained in this manner have the temperature dependence

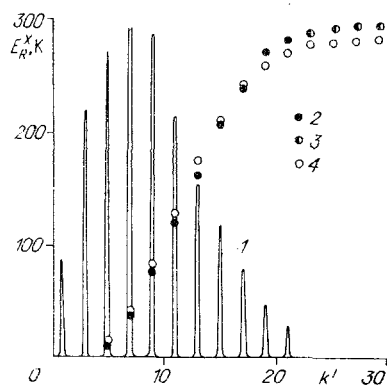


Fig. 1

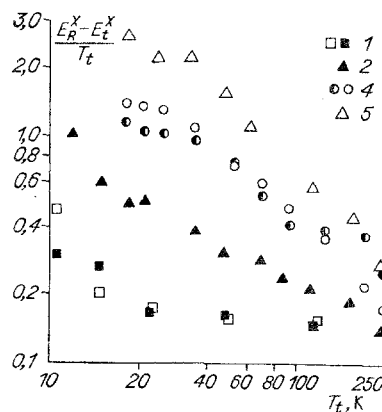


Fig. 2

TABLE 1

Number of regime	$n_0 d_* \cdot 10^{16}$ , $\text{cm}^{-2}$	$T_0$ , K	$(x/d_*)_t$	Range of measurements of $x/d_*$
1	70,1	990	15	0,8—13,7
2	26,1	900	15	0,8—9,7
3	12,1	730	7	0,8—10
4	6,6	730	3	0,8—6,8
5	2,9	670	1,4	0,8—5,8
6	3,0	295	3	0,35—5,0

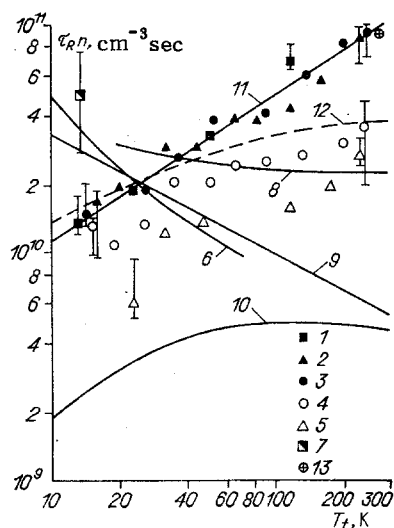


Fig. 3

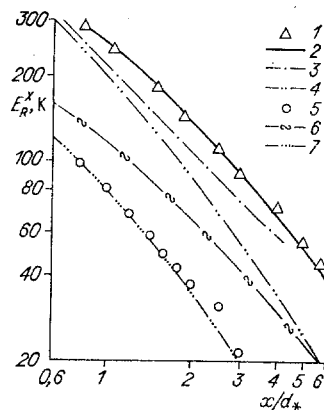


Fig. 4

$$\tau_{Rn} = 0.233 \cdot 10^{10} T_t^{0,66} (\text{cm}^{-3} \cdot \text{sec}) \quad (11)$$

represented by curve 11 in Fig. 3. The shown error consists mainly of the error of determination of the rotational energy  $E_R$  and the error of calculation of the derivative  $dE_R^X/dx$ .

In Fig. 3 our results are compared with the scarce data for  $\tau_{Rn}$  of nitrogen in argon, available in literature. The point 7 represents the value from [8] for a supersonic jet of the mixture of 50%  $N_2$  and 50% Ar. Point 13 is computed from the constants of the velocities of rotational transitions of the nitrogen molecules in argon  $K_{0l}$  [12] from the experiments observing the broadening of spectral lines of combination scattering. To calculate  $\tau_{Rn}$  we used the expression

$$(\tau_{Rn})^{-1} = \sum_i \sum_{j>i} K_{ij} N_j^* (\varepsilon_j - \varepsilon_i)^2 (\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2)^{-1}, \quad (12)$$

where  $K_{ij}$  is the constant of transition velocities from the rotational level  $j$  on the level  $i$ ;  $N_j^*$  is the equilibrium distribution of populations of the rotational levels;  $\varepsilon_i$  is the rotational energy of the level  $i$ ;  $\langle \varepsilon^n \rangle = \sum_i N_i^* \varepsilon_i^n$ . The expression (12) can be obtained from the kinetic equation by assuming small deviations of the populations from the equilibrium values of  $N_i^*$  [13]. The constants of transition velocities  $K_{ij}$  for  $j > i$  were given with the aid of the approximation of sudden collisions

$$K_{ij} = (2i + 1) \sum_l (2l + 1) K_{0l} \begin{pmatrix} i & j & l \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (j > i)$$

with the constants  $K_{0l}$  [12]. It is clear that the value  $\tau_{Rn}$  computed from the results of [12] is in agreement with curve 11.

Curve 8 in Fig. 3 corresponds to the calculations carried out by means of (12) using the velocity constants  $K_{ij}$  from [14]. Curve 12 is a calculation according to the Parker

theory [15] with the parameter  $T_{*} = 141$  K, taken from [16], however, the absolute values of  $\tau_{RN}$  are selected arbitrarily in this model, since for the system  $N_2$ -Ar there is no reliable data on the asymmetry parameter. Curve 6 shows the results of [17].

The comparison indicates that the experimental sets of data are in a fair agreement while the theoretical results do not reflect the temperature dependence of experimental values of  $\tau_{RN}$  although they agree with them within the order of magnitude. In Fig. 3 the values of  $\tau_{tN}$  are also given that are calculated for the hard-sphere model with cross-section  $\sigma_t = 30.23 \cdot 10^{-16}$  cm<sup>2</sup> and for the Sutherland cross section (curves 9, 10)  $\sigma_t = \sigma_0(1 + C/T_t)$  (the values of the constants  $\sigma_0$  and  $C = 122$  K are taken from [18]). It is obvious that the characteristic number of collisions  $Z_R$  depends on the choice of the cross sections  $\sigma_t$  and, since they are undetermined, can provide only qualitative characteristics of rotational relaxation. It is clear that for all temperatures, except  $T_t < 20$  K,  $Z_R$  is greater than one and for 300 K attains 20.

In Fig. 4 for the regime 3 we compare the measured values of  $E_R^X$  (points 1) with the values calculated by means of Eq. (1) and by means of the data from [14] (curves 2, 3). The equilibrium values of  $E_R^X$  are also given (curve 4). The formula (11) describes well the experimental results confirming the correctness of calculations of  $\tau_{RN}$ . The theoretical dependence from [14] gives somewhat underestimated values of  $E_R^X$ . This is apparently related to the overestimated values of the constants of velocity of rotational relaxation in [14] for the transitions involving the upper rotational levels. On the same plot we compare the results of experiments in room drag temperature (points 5, regime 6) with the equilibrium calculation (curve 7) and a calculation using Eq. (1) with the relaxation time given by the formula (11). The experiment agrees with the equilibrium calculation although the opposite was expected. The reasons for this contradiction are unclear.

The calculation of the rotational relaxation time by Eq. (1) was performed with the following assumptions. In the flux equilibrium takes place in the translational degrees of freedom of the molecules. The presence of a small admixture of nitrogen changes very little the gas-dynamic parameters determined by the isentropic calculation of the monoatomic gas flow. Eq. (1) is applicable to the conditions of experiments for which the relaxation time calculation is carried out. On the basis of estimates we will briefly analyze each of these assumptions.

Due to the indeterminacy of the choice of the cross sections for the translational relaxation at low temperatures (see Fig. 3) the estimate of the degree of violation of the translational equilibrium is rather arbitrary. It is best to use the experiments, but unfortunately, they are performed in the room drag temperature [19], i.e., in the range of low temperatures of the gas in the flow which does not contain the range of measurements of the present work. The estimate of the translational equilibrium can be done according to [20] using the value of the local Knudsen number:  $P_B = 1/vn \cdot dn/dt$  ( $v$  is the frequency of collisions). In calculating  $v$  the gas-kinetic cross-section was determined from the formula (12) with the constants taken from [18]. According to [20] the violation of the translational equilibrium starts at  $P_B > 0.3$ . The distance from the end of the nozzle, where  $P_B = 0.3$ , is shown in Table 1 as  $(x/d_{*})_t$ . The range of distances in which the measurements are performed is also given there. The comparison shows that in regimes 4 and 5 the measurements are performed basically in conditions where equilibrium in translational degrees of freedom is violated. In regimes 1-3 in the whole measurement range there are no violations of the translational equilibrium. Exactly for those regimes the values  $\tau_{RN}$  do not depend on  $n_0 d_{*}$ .

The heat capacity ratio for a mixture of 95% Ar and 5%  $N_2$  is equal to 1.66. The calculations [21] for  $\gamma = 1.66$  showed that the dependences of gas-dynamic parameters for this heat capacity ratio differ insignificantly from the same quantities for the flow of monoatomic gas. This is confirmed by experiments performed for the constant  $p_0 d_{*} = 65$  Pa·m and  $T_0 = 290$  K and varying admixture of nitrogen in argon between 2.5 and 20%. For the admixtures of less than 7% the distributions of spectral line intensities obtained in equal distances from the end of the nozzle agree independently of the nitrogen concentration.

The applicability of the isentropic calculation to determination of the velocity and temperature of the gas on the axis of the jet is demonstrated in [10]. The experiments of this work for large values of  $n_0 d_{*}$  (regime 5) in the vicinity of the end of the nozzle, where the flow is close to equilibrium, also agree well with the isentropic calculation. The possibility of using this calculation at small values of  $n_0 d_{*}$  (regimes 4-6) is unclear as in those regimes it is possible to break the equilibrium in the translational degrees of

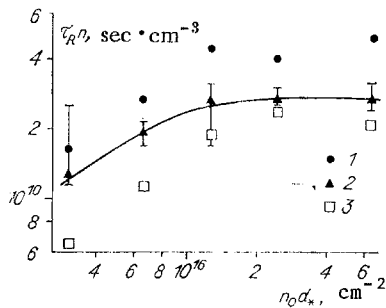


Fig. 5

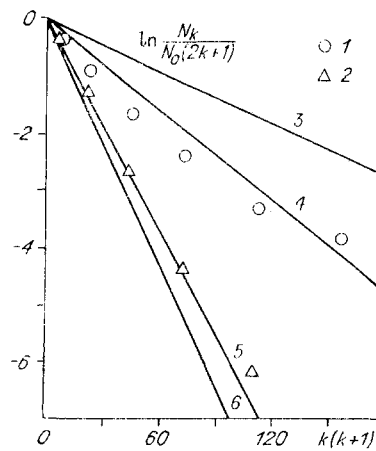


Fig. 6

freedom of the molecules.

As shown in [13] for a multilevel system the relaxation equation (1) is applicable in case of special forms of velocity constants or in case of small deviations from equilibrium in the rotational and translational degrees of freedom. Apparently, those experiments are related to the case of small deviations whose results lead to relaxation times independent of the experimental conditions. In Fig. 5 for the gas temperature 100; 40; 25 K (points 1-3) the dependences of  $\tau_{Rn}$  on the parameter  $n_0 d_*$  are constructed. An increase of  $n_0 d_*$  signifies an increased frequency of collisions and, hence, an approach toward equilibrium. For all three temperatures the values of  $\tau_{Rn}$  initially grow with increasing  $n_0 d_*$ , and starting at some value  $n_0 d_*$ , become independent of this parameter. The conditions under which the values of  $\tau_{Rn}$  become independent of  $n_0 d_*$  correspond to the case of small deviations from equilibrium.

It is known that the rotational relaxation in gas expansion into vacuum takes place with violation of the Boltzmann distribution of the populations of the rotational levels (see, e.g., [6]). In the general case the description of non-Boltzmann distributions of level populations cannot be achieved by means of Eq. (1) with one parameter — the relaxation time. It is necessary to use a more detailed description based on the kinetic equations and microscopic velocity constants.

In Fig. 6 for  $T_t = 40$  K we compare the measured distributions of level populations with the Boltzmann distributions with rotational temperature calculated from (1) and the relaxation time given by formula (11). The points 1 and 2 (curves 3 and 5) correspond to the experiment (calculation) in regimes 1 and 5; 4 and 6 are the equilibrium distributions at  $T_R = E_R^X$  and  $T_R = 40$  K realized in an equilibrium flow.

The analysis of the data in Fig. 6 shows that in a decrease of  $n_0 d_*$  accompanied by a deviation of the rotational energy from the translational energy the equilibrium distribution over the rotational levels is also broken. The relaxation equation (1) describes sufficiently well the distribution of populations close to equilibrium whereas for small  $n_0 d_*$  the results of calculation (curve 3) significantly differ from experiment. The observed difference can be related to the violation of Maxwellian distribution of velocities of the translational motion of the molecules at small values of  $n_0 d_*$ , to the large departure from equilibrium of the rotational degrees of freedom or to the violation of the Boltzmann distribution of the level populations. Which one of these causes is responsible for the differences between the calculation and experiment is still unclear.

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