EXPERIMENTAL INVESTIGATION OF THE POPULATION OF THE ROTATIONAL LEVELS OF MOLECULES IN A FREE JET OF NITROGEN

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INTRODUCTION

The high gradients of gasdynamic parameters and the low density level that occur on expansion into a vacuum lead to a disturbance of the equilibrium between the translational and internal degrees of freedom including rotational. Experimental investigations of the rotational relaxation on expansion, based on measurements of pressure in a Pitot tube [1, 2] and of the velocity distribution function of the molecules [3, 4], enable one to determine the rotational relaxation time, which is in agreement with data from ultrasonic measurements [5]. It is difficult to obtain information on excitation probabilities and the kinetics of level populations from data on the rotational relaxation time. The first investigations with an electron beam [6], which enabled one to determine the population of nitrogen levels, revealed that the upper rotational levels depart from equilibrium more rapidly with translational degrees of freedom. The recorded population distribution differed inappreciably from a Boltzmann distribution, and this difference was ignored when determining the rotational temperature. In later experimental investigations using the same method of measurement [7] the transition from the equilibrium state to the nonequilibrium state was assumed to occur through a continuous series of Boltzmann distributions.

However, calculations of the transition probabilities in the quasiclassical approximation [8] show that the probabilities of single-quantum transitions are less for the upper rotational levels, which is the reason for the relative repopulation of the upper levels during expansion, and may serve as a basis for producing and using inversion in rotational levels [9].

The purpose of the present paper is to investigate the kinetics of the population of the levels on expansion. We chose as the subject of the investigation the region of expansion along an axial current line in a free jet of low-density nitrogen. The populations were measured by the electron-beam diagnostics method. The experiments were carried out on the low-density gasdynamic apparatus at the Institute of Thermal Physics at the Siberian Section of the Academy of Sciences of the USSR [10].

1. Level Populations

The determination of the populations of rotational levels is based on the solution of a system of algebraic equations which relate the intensities of the radiation of the lines of the electron-vibrational–rotational spectrum excited by a beam of electrons with the populations of the levels of nitrogen molecules in the ground state $N_2X^1\Sigma_g^+$. Molecules of nitrogen from the ground state are transferred into the excited state of the ion $N_2^+B^2\Sigma_u^+$ by collisions with fast electrons, and they then transfer spontaneously into the state $N_2^+X^2\Sigma_g^+$ and radiate in the first negative system of bands. The intensity distribution in the rarefied spectrum when using a model of the excitation–radiation processes enables one to calculate the population of the levels of the nitrogen molecules before excitation [11]. The population distribution among the levels in the $N_2^+B^+\Sigma_u^+$ states is described by the relations

$$N_{k+1} = c_1(N_{k+2}P_{(k+2)(k+1)} + N_kR_{k(k+1)}), \tag{1.1}$$

where c_1 is the constant of the given electron-vibrational transition including its probability; N_k and N_{k+2} are the populations of the levels in the ground state; and $P_{(k+2)(k+1)}$, $R_{k(k+1)}$ are the relative excitation probabilities, the so-called Hanle–London factors. The intensity of the radiation in the lines of the R-branch

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$$I_{(k+1)k} = c_2 N_{(k+1)} R_{(k+1)k}, \tag{1.2}$$

where c_2 is a constant which includes c_1 and the Einstein coefficients. Substituting N_k from Eq. (1.1) into Eq. (1.2) we obtain

$$N_k = [(I_{(k+1)k}/R_{(k+1)k}c_2)N_{(k+2)}P_{(k+2)(k+1)}]/R_{k(k+1)}. \tag{1.3}$$

This expression represents two independent systems of algebraic equations for even and odd values of k with the number of unknowns N_k one greater than the number of equations. The condition for closure of system (1.3) for odd values of k can be taken as the relation for the intensity of the first line of the P-branch

$$I_{01} = c_2 P_{01} P_{10} N_1,$$

which enables one to solve the system of equations from the lower levels without using additional conditions. However, recurrent calculation gives an accumulation of errors in the upper levels with low populations, which is comparable with the value of their populations. Another method of closure is described in [12]. Assuming $N_k = 0$ when $k > n$ (n is the number of recorded lines in the spectrum), the system of equations was solved starting with a large number of rotational levels. A drawback of this method is the fact that the populations of the levels when $k > n$ are not equal to zero and are comparable in value with those considered. For the closure of the system of equations (1.3) it was assumed that $N_k = 0$ when $k \geq 2n$. The intensity of the lines when $k > n$ was determined by extrapolation [from measurements of the intensity of the five last lines the dependence $I = A\exp(-Bk^2)$ was constructed for $k = n, n+1, \ldots, 2n-1$ using the method of least squares]. The error introduced by the assumption that $N_k = 0$ when $k \geq 2n$ fell down to $k = n$. The error in the extrapolated values was calculated as the variance of the forecast of the method of least squares. Since the matrix of the system contains no errors and the rounding errors are small compared with the conditionality of the system, the error in determining

$$\Delta N_k = [(2k+1)/(k+1)][\Delta I_{k+1}(2k+1)/(k+1) + \Delta N_{k+2}(k+2)/(2k+5)]$$

is 5-15%, which is half the error obtained in [12], and for our experiments does not exceed the measurement errors.

The energy of the rotational degrees of freedom, expressed in degrees, was calculated using the well-known relations [13]

$$E_R = \sum_{1}^{n} k(k+1)\Theta N_k \Big/ \sum_{0}^{\infty} N_k + \delta E_R, \tag{1.4}$$

where $\Theta = B_v hc/kT = 2.878°K$ is the characteristic rotational temperature, B_v is the rotational constant, h is Planck's constant, k is Boltzmann's constant, and c is the velocity of light. The term δE_R takes into account the contribution of unrecorded lines in the spectrum:

$$\delta E_R = \sum_{n+1}^{\infty} k(k+1)\Theta N_k \Big/ \sum_{0}^{\infty} N_k.$$

Here we have used values of N_k from extrapolation for $k > n$. The value of δE_R is usually approximately 1% of E_R.

Method of Measurement

The radiation from the chosen "point," excited by an electron beam of energy 20 keV and a current i = 10 mA, was incident with a 1 : 1 scale image onto the input slit of a DFS-12 spectrometer. The dimensions of the "point" in the flow were defined by the beam diameter (2-3 mm) and the height and width of the slit. The slit of the spectrometer was set parallel to the electron beam and was varied in height from 0.5 (close to the section of the nozzle) to 7 mm (in the far field of flow). An FÉU-79 photomultiplier was placed at the exit slit of the spectrometer; the photomultiplier had a dark current of 10^{-10} A for an anode sensitivity of 10 A/lm. The electrical signal from the photomultiplier was recorded by an ÉPPV-60 potentiometer. The entrance and exit slits of the spectrometer were set to 0.03 mm, which for an inverse linear dispersion of the monochromator of 5 Å/mm ensured that all the R-branch and the first two lines of the P-branch of the 0−0 band of the first negative system were resolved. The time taken to record a single spectrogram was 2-3 min. The beam current was controlled while making the measurements; if the beam current oscillations exceeded 2-3%, the spectrum was recorded.

When recording the spectrogram particular attention was given to recording the upper rotational lines. Their intensity differed from the maximum by 2-3 orders of magnitude, this difference being particularly

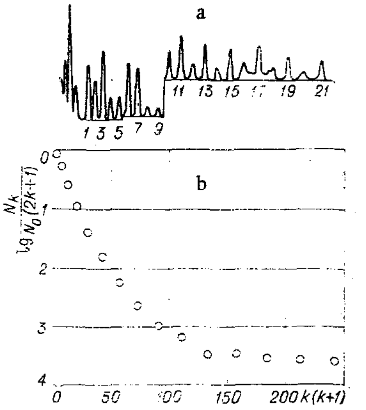

Fig. 1

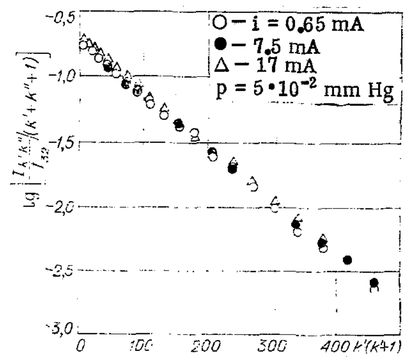

Fig. 2

marked at low temperatures. To record the weak lines the ÉPPV-60 potentiometer, which has four ranges in the 10^{-10}–10^{-6}-A region, was calibrated in such a way that the ratio of the gains in neighboring ranges was 10. The error in measuring the intensity was 5%, 7%, and 20% for the first, second, and third ranges. Figure 1a shows an example of the spectrogram and Fig. 1b shows the results of a calculation of the relative population of the levels for this spectrogram (the population of odd levels is doubled to take into account nuclear spin).

3. The Errors Introduced by the Electron Beam

A plasma is formed in the region of the beam and the measurements may therefore reflect not the state of the gas before excitation, but the state of this plasma. However, estimates [11], measurements of the density under conditions when it is known (for example, [14]), and also measurements of the distribution function of the translational degrees of freedom in helium [15] show that the role of secondary products of the action of the electron beam are negligible, and the radiation excited by it correctly reflects the state of the gas before excitation. A difference is also possible between the excitation–radiation process and the model [11], departures from which were detected experimentally in [16]. The populations of the upper rotational levels for excitation by electrons with energies less than 300 eV differed from a Boltzmann distribution, although the gas in the volume of the chamber was in thermodynamic equilibrium. A later investigation [17] showed that for excitation by an electron beam with an energy of 10 keV the radiative excitation processes are described by the model [11] up to pressures of approximately 1 mm Hg at room temperature.

In the present investigation we checked the effect of the beam current on the results of population measurements. A change in the current by a factor of 25 both in the stationary gas at room temperature (Fig. 2) and at low temperatures in the flow did not disturb the proportionality between the radiation intensity and the current. The temperature of the quiescent gas agreed to within ±2% with room temperature, and the departure from a Boltzmann distribution did not exceed the limits of error.

At pressures greater than 0.3 mm Hg and at room temperature the intensities of the upper rotational lines beginning with $k = 16$ were higher than expected. Identification of the spectra from the data in [18] showed that the rotational lines of the 0–0 band of the first negative system of N_2^+, beginning with the 16th line, overlap the 3–6 band of the second positive system. When the temperature is reduced the population of the upper levels falls and overlapping occurs at lower densities. The dependence on the density is due to the fact that the 3–6 band is mainly excited by secondary electrons whose number is proportional to the square of the density, while the intensity of the 0–0 band depends linearly on the density [11].

4. Qualitative Description of the Processes in Low-Density Jets

This description is necessary for a systematic account of the effect of the surrounding gas on relaxation processes in the jet. The structure of the flow in a free jet, calculated using the model of a nonviscous gas, is shown in Fig. 3a. The gas with stagnation pressure and temperature p_0 and T_0 is expanded from a nozzle into a medium with parameters p_l and T_l forming the characteristic wave structure: a trailing shock wave 1, a Mach disk 2, and a reflected wave 4. The boundary which separates the surrounding space IV and the jet is the contact discontinuity 3. The zone I is the main body of the jet, II is the compressed layer, and III is the region of flow behind the Mach disk. The flow within the main body of the jet is independent of the conditions

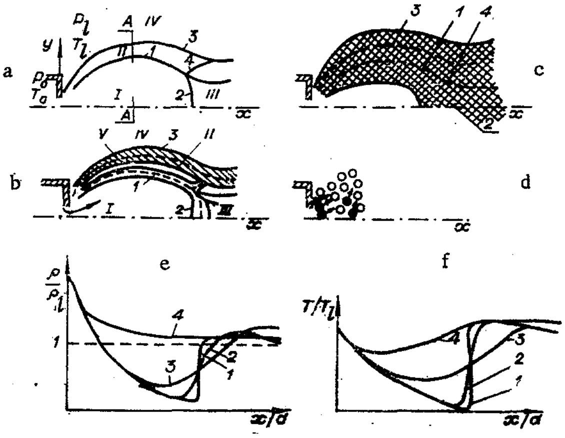

Fig. 3

TABLE 1

p_0d	d, mm	p_0, mm Hg	$p_0/p_l \cdot 10^{-3}$	T_0, K	Re_*	$p_l \cdot 10^3$, mm Hg	Re_L
16,45	5	3,29	1,34	290	335	2,45	9,14
80	5	16	2,775	290	1631	5,77	31
80	5	16,00	0,248	290	1631	64,5	103,0
481	5	96,25	9,85	290	9820	9,77	98,8
13,5	2,066	6,5	1,733	290	274	3,75	6,58
73,5	2,066	35,54	4,52	290	1500	8,87	4,52
493	2,066	238	14,25	290	10050	16,7	84,5
1345	2,066	650	29,9	290	27450	21,75	29,9

in the surrounding space and is the same for outflow into a vacuum. Under practical conditions there is a mixing zone V along the boundary of the jet 3 (Fig. 3b). In a continuous medium the mixing zone and the trailing shock wave are separated by part of the nonviscous compressed layer.

A reduction in the overall level of the density (while preserving the pressure ratio p_0/p_l constant) leads to a transition from a continuous mode to a scattering mode. An important feature of this transition is the expansion of the mixing and shock-wave zones. In the transition state the nonviscous part of the compressed layer is not present, while the mixing zone and the shock waves form a coalescence layer (Fig. 3c). In the scattering mode (Fig. 3d) the characteristic wave structure is not formed, since at relatively small distances from the cross section of the nozzle the energy of directional motion of the molecules of the gas in the jet is converted into thermal energy.

The qualitative nature of the change in the parameters (the density and temperature with respect to the parameters of the surrounding gas) along the axis of the jet in all four modes for $T_0 = T_l$ is shown in Fig. 3e, f. In the continuous medium mode the results of calculations for a nonviscous gas (curves 1) are fully confirmed by the experimental data (curves 2) up to the Mach disk. In the transition mode the gas molecules from the more dense compressed layers and from the surrounding space may penetrate into the main zone up to the axis of the jet. Collisions between the gas molecules in the jet and the penetrating molecules lead to scattering.

The penetrating molecules of the jet together with the scattered molecules form a background gas in which energy dissipation of the directed motion occurs from below with respect to the flow. The influence of the background gas leads to a departure of the density and temperature from the relations for viscous expansion determined by the Reynolds number in the critical section of the nozzle. In view of the fact that the viscosity has practically no effect on the density variations, the density relations for viscous and isentropic expansion are identical. Under scattering conditions the dissipative processes increase to such an extent that the density may even not be reduced below the surrounding density (curve 4 in Fig. 3e), while the temperature will only be slightly reduced below the surrounding temperature (curve 4 in Fig. 3f).

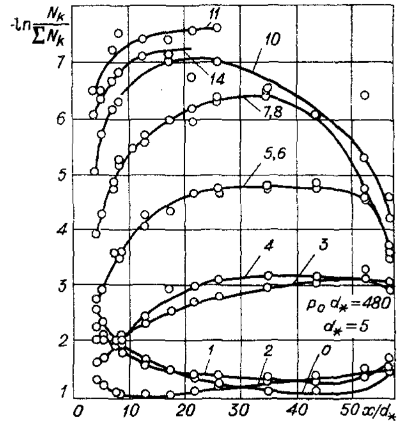

Fig. 4

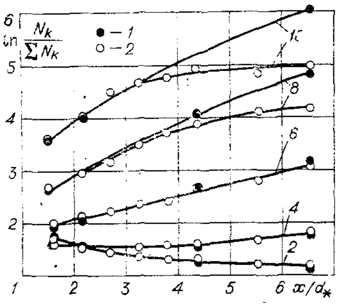

Fig. 5

As a similarity criterion defining the conditions for the interaction between the jet and the surrounding medium when $T_0 = T_l$ we can use the number $Re_L = Re_* / \sqrt{p_0/p_l}$ [19]. When $Re_L > 100$ the flow in the jet can be assumed to be continuous and the main body can be assumed to be unperturbed. The flow with $Re_L < 10$ corresponds to the scattering mode; $10 < Re_L < 100$ is the transition region.

5. Kinetics of the Level Populations

Measurements were made in jets from sonic nozzles of diameter d = 5 and 2 mm for $T_0 = 290°K$ and a pressure $p_0 = 3$–650 mm Hg. The effect of the boundary layer can be neglected and the diameter of the nozzle can be taken as equal to the geometrical value. The experimental conditions are shown in Table 1, where we also give the values of the parameters employed later when simulating: a) the relaxation processes at constant temperature $\rho_0 d$ [6] and b) the effect of viscosity and rarefaction in the jet Re_L [19].

It is convenient to begin the description of the results with the experiment with $p_0 d = 493$ and $Re_L = 84.5$. In accordance with [19] in the main body there is a region not perturbed by the background, and at large distances from the nozzle section we can quite clearly distinguish the effect of the background on the kinetics of the level populations. The change in the relative populations of the levels $N_k \Big/ \sum_0^\infty N_k$ from below with respect to the flow from the nozzle section is shown in Fig. 4, the numbers indicating the number of the rotational levels.

As one moves away from the nozzle section the fall in the translational temperature and the relaxation process of the internal degrees of freedom lead to a reduction in the population of the upper levels and to an increase in the population of the lower levels. Starting at a certain distance, the population of the lower levels (up to the 6th) hardly changes (is stabilized). This distance becomes less the higher the level number. For the 5th and 6th levels stabilization begins at 20 gauges, and for the 0th and 2nd it is not observed over the whole region of the jet investigated. In the upper levels there is no pronounced stabilization section: The population initially falls, passes through a minimum, and then increases. The position of the minimum shifts closer to the nozzle as the number of the rotational level increases.

For expansion into a vacuum we would expect stabilization of the level population to occur due to quenching of the rotational relaxation. The populations of the 6th level and below down to $x/d \approx 50$ have a similar form, whereas the behavior of the populations of the upper levels and the lower ones for $x/d > 50$ contradicts the representation of the behavior of the relaxation process on expansion and may be due to the effect of the background. This effect may occur in two ways: Either the background gas participates in the relaxation process, thereby changing it, or when the rotational relaxation is quenched the recorded spectrum is the superposition of the spectra of the "cold" molecules of the jet and of the background gas. It is difficult to distinguish between these effects at present.

It is characteristic that the higher the rotational level number the less the distance from the nozzle section at which the effect of the background is appreciable. For example, for the chosen experiment (see Fig. 4) the effect of the background on the population of the 0th level was only detected at distances higher than 50 gauges and for the 10th level, at 20 gauges.

The amount of background gas on the axis of the jet in the experiment considered can be estimated under the following assumptions: 1) Until stabilization occurs the background does not change the relative

TABLE 2

k	10	8	6	4	2	0
N_b	0,65	0,4	$8{,}5\cdot10^{-2}$	$1{,}4\cdot10^{-2}$	$3{,}7\cdot10^{-3}$	$1{,}2\cdot10^{-4}$

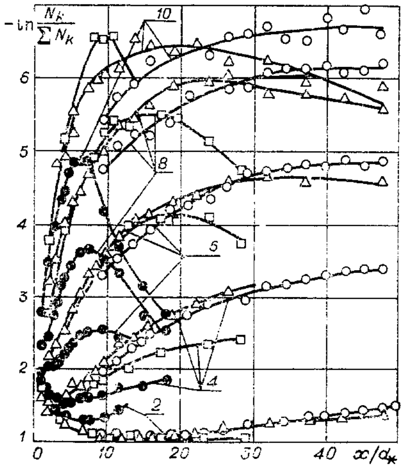

Fig. 6

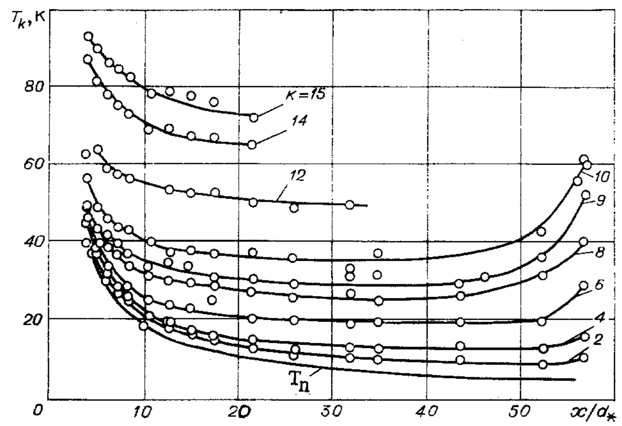

Fig. 7

population of the level used for the estimate; 2) the population distribution of the background molecules is a Boltzmann distribution with a temperature T_l = 290°K. The result of the estimate for the 10th level at 40 gauges from the nozzle section is shown in Table 2, where it is seen that the number of background molecules, though not significant for the populations of the lower levels, makes a considerable contribution to the population of the upper levels.

The effect of the background on the population of the rotational levels is shown in Fig. 5 from measurements at constant $p_0d = 80$ and the two pressure ratios $p_0/p_l = 2.8\cdot10^3$ and $0.25\cdot10^3$, corresponding to points 1 and 2. At distances close to the nozzle section (~up to 3 gauges), the populations of the levels, including the 10th, do not exhibit the effect of the background, and the relaxation process occurs just as in the case of expansion into a vacuum: The populations are the same for high and low pressures. When the distance is increased the populations of the upper levels differ. It follows from the results obtained in this investigation that the dimensions of the main body in which the level populations can be assumed to be unperturbed (for example, by less than 10% of the value for outflow into a vacuum), are considerably less than the region defined as unperturbed in [19] for a 10% departure of the density from the isentropic value.

At the present time it is difficult to analyze the rotational relaxation on expansion taking the effect of the background into account. We will therefore henceforth consider mainly the data which can be related to outflow into a vacuum. The choice of these data for analysis was made on the basis of the qualitative estimates indicated above. It cannot be said, however, that in all cases, particularly for the higher rotational levels, the effect of the background has been completely eliminated.

6. Effect of p_0d on the Population Kinetics

An investigation was made on a nozzle with d = 2 mm. The results of the measurements for 13.5, 73.5, 493, and 1340 mm Hg·mm are given in Fig. 6, where we show only part of the levels. Up to values $p_0d = 493$ the behavior of the level populations as p_0d increases corresponds to the representations of the kinetics of rotational relaxation: The greater p_0d, the closer the population distribution to the state of equilibrium with translational degrees of freedom. The populations of the lower levels increase as p_0d increases, while the upper levels (from the 4th to the 10th) fall. The data for $p_0d = 1340$, when the level populations from the 4th to the 10th are greater, while the 2nd level is less than that corresponding in the experiment with $p_0d = 493$, are an exception. The nature of the variation of the populations along the axis of the jet is approximately the same for all modes of operation. For $p_0d = 13.5$ the relaxation process is quenched in the region of the nozzle section (approximately up to 6 gauges), while for $p_0d = 1340$ quenching is not observed over the whole measurement range up to 70 gauges. From the data shown in Fig. 6 it is easy to see the effect of the background: The

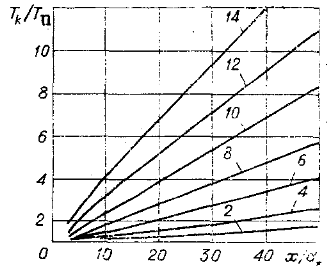

Fig. 8

populations of the levels with $p_0d = 13.5$ ($Re_L = 9$) are perturbed by the effect of the background over the whole measurement range, while in the experiment with $p_0d = 1340$ ($Re_L = 160$) the effect of the background is only appreciable for the upper levels at distances greater than 30-40 gauges.

7. Rotational Relaxation

The extent to which the population of the rotational levels departs from a Boltzmann distribution can be conveniently represented by the "temperature" of the population T_k, calculated from the equation [19]

$$T_k = -k(k+1)\Theta/\ln[N_k/N_0(2k+1)],$$

where odd N_k are doubled. For a Boltzmann distribution T_k is the same for all levels.

Data on the "temperature" of the population of the levels along the axis of the jet for $p_0d = 480$ are shown in Fig. 7, where the numbers denote the number of the rotational levels. The lower curve T_n is the calculated temperature of the isentropic expansion with $\gamma = c_p/c_v = 1.4$. There is a Boltzmann distribution over the whole range of measurements. The "temperature" of the population increases with the level number. As one moves away from the nozzle section the difference in the "temperature" of the population increases and then begins to stabilize, this occurring earlier the higher the quantum level. After the stabilization section there is initially a rise in the upper levels and then in the lower levels from below with respect to the flow, the latter being due to the effect of the background.

For other values of p_0d the same tendencies were found in the change in the "temperature" of the population. The values of the stabilization temperature of individual levels decrease as p_0d increases. But for $p_0d = 1340$ the values of T_k were higher than those corresponding to $p_0d = 480$. It is possible that this anomaly is due to the effect of condensation, the initial stage of which, according to estimates given in [20], occurs in this mode.

The extent to which the equilibrium between the rotational and translational degrees of freedom is disturbed during the expansion can be followed from the change in T_k/T_n. Under equilibrium conditions $T_k/T_n = 1$, and for a Boltzmann distribution of the populations T_k/T_n is the same for all levels. The variation in T_k/T_n along the axis of the jet for $p_0d = 493$ is shown in Fig. 8. It is obvious that there is a Boltzmann population distribution over the whole range of measurement. The upper levels relax more slowly and the higher the level, the closer to the nozzle section will departure from equilibrium be appreciable. This departure is qualitatively the same for the upper levels: slow close to the nozzle with a gradual increase in the rate of departure, followed by its stabilization. In the part where the rate is stabilized the slopes of the straight lines are a function of the number of the rotational level and p_0d. For other values of p_0d the qualitative variation of T_k/T_n can be described similarly.

8. Energy and Temperature of the Rotational Degrees of Freedom

When the distribution of the level populations is not a Boltzmann distribution the energy of the rotational degrees of freedom expressed in degrees can be calculated as the sum of the contributions of the individual levels E_k in accordance with Eq. (1.4); E_R can be regarded as the rotational temperature, but in this case it does not characterize the population distribution. For a Boltzmann distribution $T_R = T_k = E_R$. Figure 9 shows the change in rotational energy calculated for a different number of terms of the sum $\sum_1^n E_k$ (n = 5; 10; 15; 20) for $p_0d = 480$, compared with the temperature T_n; it is seen that limitation of the sum $\sum_1^n E_k$ can lead to con-

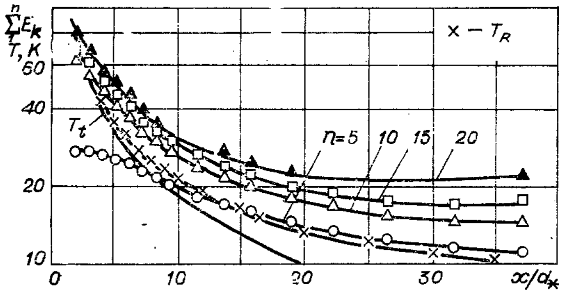

Fig. 9

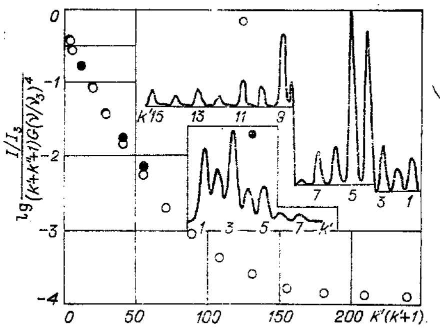

Fig. 10

siderable errors in E_R. As one moves away from the nozzle section a large part of the rotational energy occurs in the lower levels, while the sums of E_k for different n approach one another. Up to a certain distance this is in fact observed (~10 gauges for $p_0d = 480$), and then under the action of the penetrating molecules the population of the upper levels increases, their contribution to E_R increases, and the sums of E_k again diverge.

In the above results a tendency to approach toward an asymptotic limit E_R as the number of terms of the sum is increased (in the region where the penetrating molecules have no effect) can already be observed. However, the necessary number of levels to estimate the rotational energy with an assigned accuracy is difficult to predict in advance (it is a function of p_0d, T_0, and Re_L).

The data obtained on the rotational energy (see Fig. 9) were compared with the results obtained in [6] for the same values of p_0d and Re_L. All the points in [6] lie below $\sum_1^{10} E_k$. This disagreement between the results also occurs for other values of p_0d. In order to find out the reasons for this we compared the spectrograms obtained under the same conditions (Fig. 10): the upper spectrogram is our result and the lower spectrogram is from [6]. It is seen from the comparison that in [6] a considerable portion of the lines was not recorded. For all the spectrograms in [6] the maximum intensity ratio did not exceed 10; in our investigation it reaches 10^3.

In [6], for the spectrogram shown in Fig. 10, the rotational temperature was found from the slope of the line to be $T_R = 26°K$; the departure from this straight line is already appreciable for k = 6, 7, but it lies within the limits of experimental error. For our measurements the absence of a Boltzmann distribution is obvious, while $E_R = 30.8°K$.

It is clear that both in the example considered and under the other conditions in [6] the contribution of the upper levels was not included in the estimate of the rotational energy. Hence, the conclusions regarding the rotational relaxation times obtained in [6] and by subsequent investigators using the same method of measurement must be regarded extremely critically.

We used the method of measuring temperature employed in [11] for weak-gradient flows. Under gas expansion conditions close to spherical (as in this investigation), the introduction of the ideal of temperature is conventional. The rotational temperature measured by the slope method from the population of the lower quantum levels in flows with strong gradients has a value which approximates the translational temperature from above and exceeds it by an amount which depends on the complete prehistory of the flow up to the point of measurement. This temperature represents approximately the energy of the lower quantum levels only.

9. The Reasons for the Departure from a Boltzmann Distribution

One of the reasons for the lack of equilibrium among the rotational levels is the strong dependence of the rate of energy exchange on the level number. This has been shown for one- and two-quantum transitions in [9]. Calculations of the expansion in nozzles [9] carried out using the probabilities from [8] are in qualitative agreement with results of the present investigation – the "temperature" of the population of the lower levels is close to the kinetic value and that of the upper levels is close to the stagnation temperature.

The other reason for the departure from a Boltzmann distribution is the effect of the background. Both dissipative processes caused by penetration of the molecules and nonequilibrium diffusion of hotter gas into the main body of the jet can lead to a distribution of the populations in this mixture which is qualitatively similar to that described above: The lower levels have a population "temperature" close to the temperature of the gas in the jet, while those of the upper levels are higher.

One of the reasons for the occurrence of a nonequilibrium population for large values of p_0d may be connected with the condensation process. The basis for this suggestion is the population distribution of the levels for $p_0d = 1340$ (section 7) which is anomalous from the point of view of rotational relaxation in a homogeneous medium and indicates the occurrence of condensation during the expansion process. In fact, from estimates made on the basis of experimental data [20] for $p_0d = 1340$ an initial condensation stage occurs, the result of which (for large x/d) can be represented very approximately by a certain average size of cluster — about 10 molecules per cluster. The mechanism by which the condensation affects the kinetics of the populations is unknown at the present time.

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