# POPULATION OF THE ROTATIONAL LEVELS OF NITROGEN
# MOLECULES DURING NONEQUILIBRIUM CONDENSATION
# IN THE FREELY EXPANDING PHASE

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The temperature drop during free expansion of a gas from a nozzle into a vacuum can result in the origination of supersaturation and condensation. Under these conditions, the spoilage of the equilibrium between the translational and internal degrees of freedom of the molecules, including the rotational, is possible [1]. Reports about measurements of the rotational temperature in condensing gas flows, carried out by using an electron beam for diagnostics [2], as well as Raman scattering [3], have appeared in the literature. The authors of the papers mentioned did not detect any disturbances of the Boltzmann distribution in recording the population of the low rotational levels. The disturbance of the Boltzmann distribution was investigated in [4] in a broad range of $p_0 d_*$ ($p_0$ is the stagnation pressure and $d_*$ is the diameter of the nozzle critical section), and the hypothesis that an anomalously high value of the upper level population for large $p_0 d_*$ is caused by the effect of condensation has been expressed.

The purpose of this paper is to investigate the kinetics of the population of the ground state rotational levels of nitrogen molecules during combined rotational relaxation and condensation in an expanding stream of nitrogen and a mixture of nitrogen with carbon dioxide. The measurements were performed on the axis of a free jet where there is no influence from the surrounding gas and the flow is the same as during expansion into a vacuum. The investigation is performed on the gasdynamic low-density apparatus of the Institute of Thermophysics, Siberian Branch, Academy of Sciences of the USSR [5] — the VS-4 stand.

§1. Nozzles with $d_* = 2.11$ and $0.54$ mm in the form of a hole in a thin wall with nozzle edge thickness much less than the diameter were used, which afforded a basis for neglecting the influence of the boundary layer. Technically pure nitrogen and carbon dioxide were the working gases. When working with the mixtures, they were prepared in the nozzle prechamber. The stagnation temperature in the prechamber $T_0$ was checked by a thermocouple and was close to room temperature, $T_0 = 292°K$, in all the experiments. The nitrogen density and the populations of the rotational level of its ground state $X^1\Sigma_g^+$ were measured by electron-beam diagnostic methods [4, 6]. The electron beam penetrated the jet at some distance x from the nozzle exit. Radiation from the "point" of intersection of the beam with the jet axis was transmitted to two monochromators on opposite sides of the vacuum chamber by using a lens. One monochromator (the SPM-2) was to extract the OO band of the first negative system of nitrogen and to measure the density, while the second (the DFS-12) was to record the rotational spectrum of the same band. The dimensions of the "point" during recording of the spectrum were determined by the diameter of the electron beam (~2 mm) and the height of the slit (from 0.5 to 5 mm). The monochromator slit was perpendicular to the electron beam during the density measurements and the section of the beam extracted with respect to the height was 1 mm in this case.

As investigations show [4], the population of the rotational levels in a low-density jet can depend substantially on the background originating during jet interaction with the surrounding gas. To diminish the influence of the background, the pressure in the vacuum chamber was maintained as small as possible for the selected gas discharge. To check the influence of the background, the population of the levels were measured for different surrounding gas pressures. The measurements showed that all the results presented below are free of the influence of the background and correspond to escape into a vacuum.

The following are the methodological uncertainties occurring in measurements in flows with clusters by using an electron beam. First, molecule ionization by electron impact can accelerate condensation on ions exactly as in a Wilson chember; second, the actual influence of the clusters on the radiation of the first negative system of bands is not clear. The acceleration of condensation because of ions should be proportional to their density and, therefore, to the electron beam current. Measurements under conditions when the influence of
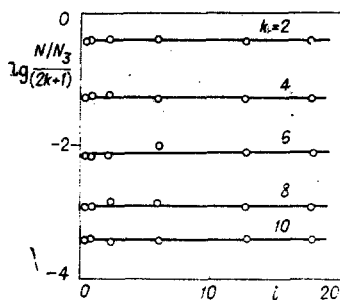
**Fig. 1**

condensation was expected to be maximal in these experiments ($p_0$ = 8000 mm Hg) for different beam currents did not disclose any influence of the magnitude of the current on both the density measurements and the population distribution (Fig. 1, where $N_k$ is the population of the k-th rotational level and i is the beam current, mA).

The radiation intensity of the OO band to be recorded in a flow with clusters because of excitation by electrons can be subjected to the dependence

$$I \sim \sum_N \sigma_N n_N,$$

where $\sigma_N$ is the excitation section of the state $X^1\Sigma_g^+$ by electron impact, and $n_N$ is the number of clusters per unit volume consisting of N molecules. This expression is valid upon compliance with the following conditions: When the excitation−radiation processes are not perturbed by kinetic gas collisions and deactivation of the levels occurs only by spontaneous radiation, the radiation of the molecules in the clusters occurs with the same wavelength as in monomers. The first condition is satisfied for monomers with densities $\lesssim 10^{16}$ particles/cm$^3$. As regards the second condition, there is no definite information about this question, and no changes were detected in the spectra which could have been referred to the radiation excited in the condensed phase in these experiments. According to [7], the ionization section of Ar, $CO_2$, and $N_2$ by electron impact is proportional to the number of molecules in the clusters for N < 50 and starts to grow as $N^{2/3}$ for N > 50. Since the first negative system of bands corresponds to transition between ion levels, it can be assumed that the same dependence on the number of molecules in the cluster is conserved even for excitation of the state $N_2^+B^2\Sigma_u^+$. Then for N < 50 the relationship

$$I \sim \sigma \sum_N N n_N$$

should be satisfied, where $\sigma$ is the monomer excitation section. Since the gas density is $n = \sum_N N n_N$, measurements of n should not disclose the presence of clusters prior to N < 50. In the presence of clusters with N > 50, the signal being recorded should be less than from monomers at the same density.

§2. The results of measuring the density and rotational energy as a function of the complex $p_0 d_*$ ($d_*$ = 0.54 mm; $p_0$ is the stagnation pressure in mm Hg) at a distance of $x/d_* = 66.1$ is represented in Fig. 2a, where curves 1 and 2 are the nitrogen density n normalized relative to the stagnation density $n_0$ in pure nitrogen and in a mixture with a 10% molar fraction of carbon dioxide; curve 3 is the energy of the rotational degrees of freedom $E_R = \sum_1^\infty k\ (k+1)\Theta N_k / \sum_0^\infty N_k$; and curve 4 is the translational temperature $T_t$ according to an estimate

of the extrapolation of the "temperature of the population" to the zero value of k [8]. In the expression for the energy, $\Theta$ is the characteristic temperature, and $N_k$ is the population of the k-th rotational level. Data on the population of the levels under these same conditions are presented in Fig. 2b in the form of the "population temperature" $T_k$. These quantities were calculated by means of the formula $N_k = N_0 (2k+1) \exp [-k(k+1)\Theta/T_k]$ by substituting the measured values of $N_k$ and $N_0$. The numbers in Fig. 2b denote the number of the level.

Up to $p_0 d_* \approx 9 \cdot 10^2$ for pure nitrogen, an increase in this complex is accompanied by a diminution in the energy of the rotational degrees of freedom and by the approach to equilibrium between the rotational and translational degrees of freedom. Up to the mentioned $p_0 d_*$, the translational temperature gradually diminished, tending to the isentropic value (it equals 4.1°K for the given $x/d_*$, $T_0 = 292°K$). The relative density (curve 1) varies weakly in this range of $p_0 d_*$. For $p_0 d_* > 9 \cdot 10^2$ a significant drop in the relative density and a rise in the translational temperature are observed; the growth of the energy $E_R$ starts somewhat earlier.
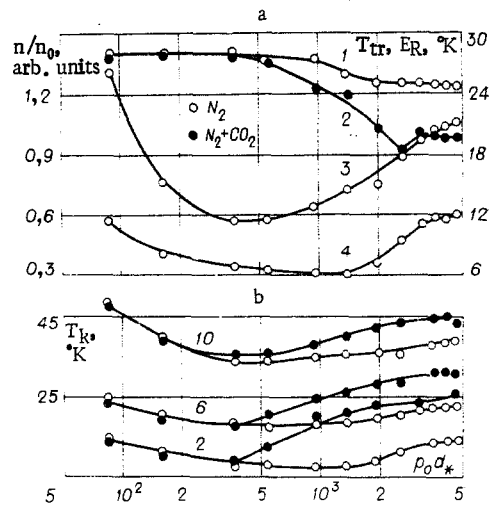
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Fig. 2

The mentioned changes in the parameters detected for the lower $p_0 d_*$ are more substantial in the mixture of nitrogen with carbon dioxide (curve 2 of the relative density in the mixture).

As is seen from Fig. 2b, there is no Boltzmann distribution in the whole range of $p_0 d_*$ values investigated. An increase in $p_0 d_*$ (and, therefore, an increase in the collision frequency) contributes to a diminution in the "population temperatures" and their approach to the isentropic temperature. However, starting with certain values of $p_0 d_*$, this tendency is spoiled and a rise in the "population temperatures" is observed. Here the value of $p_0 d_*$ at which this growth starts will be smaller, the greater the number of the rotational level. For small $p_0 d_*$, the "population temperatures" of the levels in the flow of pure nitrogen and of the nitrogen in the mixture agree. The "population temperatures" in the mixture grow more substantially with the increase in $p_0 d_*$ than for the pure nitrogen.

An increase in the "population temperatures," the energy of the rotational degrees of freedom, the translational temperature, and also the drop in density observed for certain values of $p_0 d_*$ can be explained by the effect of condensation. A supersaturated state holds in the measurement zone for the whole range of stagnation pressures investigated. However, for high velocities of expansion into a vacuum (as in a free jet) condensation may not even appear. Hence, we present additional proof that the mentioned change in the parameters is caused by condensation in these experiments. According to [9], the velocity of the gas flow increases abruptly in a pure nitrogen flow with the increase in $p_0 d_* > 780$ mm Hg ($d_* = 0.386$ mm, $T_0 = 285°K$) because of liberation of the heat of condensation. A maximum of dimers, trimers, and tetramers is observed for somewhat high $p_0 d_*$, which indicates the development of the nature of condensation. A conversion by means of the correlation formulas [9] to the conditions of this experiment yields the value $p_0 d_* \approx 900$ corresponding to the beginning of the growth in the velocity with respect to $p_0 d_*$. It should be exphasized that the relative cluster concentration for $p_0 d_*$, less by an order of magnitude than the position of the dimer maximum, is sufficiently large [9]; this is disclosed by the behavior of the populations of the upper levels in the mixture. Hence, the population of the levels is determined in the whole range of $p_0 d_*$ studied by the joint progress of rotational relaxation and condensation.

The drop in density in the condensing gas flow is, as is known, related to the increase in the flow velocity; moreover, the density can drop because of an increase in the opening of the streamline [10]. Both these factors are more essential for the mixture of $N_2$ and $CO_2$, since the heat of condensation of $CO_2$ is considerably greater than for $N_2$ and supersaturation in $CO_2$ sets in closer to the nozzle exit than for $N_2$. A greater reduction in the relative density in the mixture stream with the increase in $p_0 d_*$ agrees with all this. A diminution in the signal being recorded is possible upon the formation of large nitrogen clusters ($N > 50$), i.e., an apparent diminution in the density. According to approximate estimates in [11], this should be expected in these experiments with pure nitrogen for $p_0 d_* \gtrsim 2000$. The effect is apparently weak, since the density in pure nitrogen is practically constant in this range of $p_0 d_*$ (see curve 1 in Fig. 2a). For $p_0 d_* \approx 2500$ a minimum is observed in the mixture flow (curve 2), which can be caused by condensation in a two-dimensional flow.

§3. Illustrations of the different nature of the progress of rotational relaxation in pure nitrogen and in an $N_2 + CO_2$ mixture are data on the populations of rotational levels at the distance $x/d_* = 10$ [Fig. 3: curve 1) $p_0 d_* = 4035$ in pure nitrogen; curve 2) $p_0 d_* = 4574$ in a mixture with a 13% $CO_2$ addition]. According to the con-
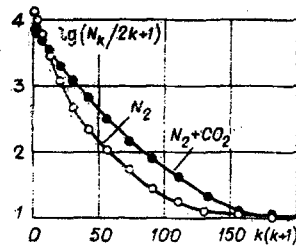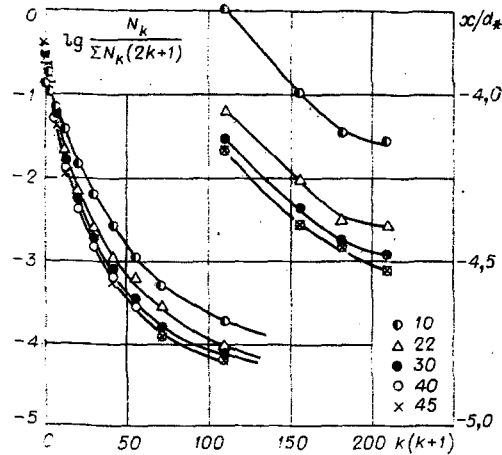
Fig. 3



Fig. 4

densation conditions, these modes are close to the modes of Fig. 2a in the $p_0 d_*$ =1350-1900 range, i.e., with explicit criteria for condensation in both a mixture and in pure nitrogen. An estimate of the translational temperature from the measured "population temperatures" of the low levels for the data in Fig. 3 yields the values 32.3 and 65.5°K, respectively, for nitrogen and the mixture. Under given conditions in the prechamber this means that only $CO_2$ condensed in the mixture up to the measurement point, since the nitrogen pressure at this point is below the vapor saturation pressure. Therefore, rotational relaxation occurred in the nitrogen flow only in the presence of $N_2$ clusters and in the presence of $CO_2$ clusters in the mixture. In this latter case, the fraction of condensate is substantially greater; moreover, the thermal effect of the condensation, just as the presence of the clusters, starts to influence the rotational relaxation considerably earlier with respect to $p_0/d_*$.

As is seen from Fig. 3, the condensation process in the mixture resulted in acceleration of the rotational relaxation. A Boltzmann distribution is built up at the first eight levels, while the population of the 12th to 15th levels does not change even in absolute value.

The data for moderate $p_0 d_*$ (see Fig. 2b), where the populations for the pure nitrogen and the mixture levels do not differ for the same relative concentration of carbon dioxide in the mixture, show that the differences observed in the populations of the levels are caused by the influence of condensation in the mixture and not by the change in rate of the rotational relaxation upon adding carbon dioxide.

A comparison between the results of measuring the populations of the levels for a different degree of concentration simplifies the analysis of the influence of condensation on the population kinetics during the expansion. The results of measurements from $x/d_*$ =10 to $x/d_*$ =40 are represented in Fig. 4 for $d_*$ =2.11 and $p_0$ =650 mm Hg in pure nitrogen and in Fig. 5 for the same nozzle and range of $x/d_*$ in a mixture of $N_2$ and 9% $CO_2$ [$p_0(N_2)$ =2035 mm Hg]. The conditions in pure nitrogen are close, in the degree of condensation, to the mode with $p_0 d_*$ = 1000, and in mixtures, to the mode with $p_0 d_*$ = 3700 (in nitrogen) in Fig. 2a, i.e., the condensation is better developed in the mixture case. In the first case, the gas went into the saturation curve for nitrogen at the distance $x/d_* \approx 3.5$ during expansion, while in the second case the nitrogen was still in the unsaturated state at $x/d_*$ = 10 because of the heat evolution during the $CO_2$ condensation, but downstream its condensation in the mixture occurs more rapidly than for pure $N_2$ after intersection with the nitrogen saturation line because of the presence of condensation nuclei which are particles of the $CO_2$ condensate.
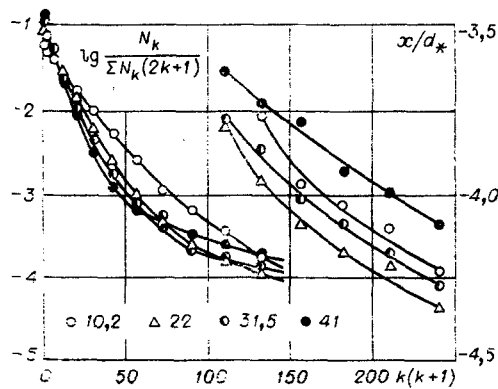
Fig. 5

In pure nitrogen (see Fig. 4), the population of the upper and middle levels diminishes with the increase in distance from the nozzle exit, while the population of the lowest level grows. Then the populations are frozen sequentially with further expansion and normalized with respect to the density, are independent of $x/d_*$. The higher the values of the rotational quantum number, the closer to the nozzle exit is freezing observed. There are still no nitrogen clusters at the point $x/d_* = 10$ in the mixture flow (see Fig. 5). The population distribution at the first eight levels is a Boltzmann distribution with temperature 51.6°K and is spoiled at higher levels. The next measurement point $x/d_* = 22$ is already on the phase-transition curve for nitrogen; the relative populations of the levels have changed toward a diminution at the high and middle levels and an increase at the lowest levels, i.e., exactly as in the pure nitrogen stream (see Fig. 4). The population distribution has become more monotonic, and the section with the Botlzmann distribution has disappeared. For $x/d_* > 22$ the relative population of the middle levels in the mixture drops, that of the lowest levels grows in conformity with the rotational relaxation tendencies, while the relative population of the upper levels, starting with the eighth, rises, it almost doubling at several later levels for $x/d_* = 40$. This fact, also detected in the experiments with pure nitrogen not presented here, contradicts the normal behavior of rotational relaxation during expansion and can be related to singularities in the progress of rotational relaxation in the presence of clusters.

§4. It is seen from the results of the experiments elucidated in the preceding sections that the population kinetics of rotational levels in a flow of condensing gas differs substantially from that under no-condensation conditions. The high rate of rotational relaxation in a condensing gas, resulting in a Boltzmann distribution build-up at the low levels (see Fig. 3 and 5) as well as in additional population of the upper levels (see Fig. 5), is the clearest manifestation of this difference.

The former of the mentioned condensation effects is cased mainly by liberation of the heat of condensation, which results in a rise in the translational temperature and, therefore, an increase in the collision probabilities of the rotational transitions. Qualitatively, this is characterized by an increase in the Massey parameter. Results of computations of the rotating-transition-collision probabilities for HCl [12] and $H_2$ [13] might be a quantitative characteristic. Unfortunately, in the literature there are no rotational-transition-collision probabilities for $N_2$ collisions with $N_2$ or $CO_2$, which are needed here for a quantitative estimate of the influence of the temperature on the population kinetics of the levels.

The latter effect can be associated with participation of the clusters in rotational energy transfer. There are still no investigations of rotational energy transfer during the collision of monomers with clusters; hence, the role of the clusters in the population kinetics of the levels can only be estimated qualitatively. Let us examine how the distribution of the population of monomer levels will vary during their interaction with clusters. The flow of condensing molecules is

$$q_c = q_i - q_r - q_e,$$

where $q_i$ is the flow of molecules incident on the cluster; $q_r$ is the flow of reflected molecules, which is that part of $q_i$ not captured by the clusters; and $q_e$ is the flow of molecules evaporating from the clusters.

The flow of incident molecules at each point of the jet under consideration has a population distribution for the levels which is governed by the whole prehistory of the expansion. The difference between the population distributions of the reflected and incident molecule levels is determined by the capture of monomers by clusters and by collisions with rotational energy transfer between the monomers and the clusters. If it is assumed that the probability of capture by clusters diminishes as the rotational quantum number increases,

then the main distinctions in the population distributions of the levels in the reflected flow from the incident flow will be observed at the low levels. By analogy with the collisions of monomers with monomers, it can be expected that the collision probabilities of the rotational transitions between monomers and clusters will be smaller, the higher the rotational quantum number. Exactly as under the influence of the capture process, this should result in negligible changes in the upper level populations. However, collisional transfer should not result in significant changes in populations of the low levels either. This latter is caused by similar values of the "population temperatures" of the low levels and of the cluster temperatures.

The flux $q_e$ consists of molecules which have been captured by clusters and have evaporated after a certain time. This time is considerably greater than the equilibrium build-up time in the rotational degrees of freedom in a fluid ($\sim 10^{-12}$ sec); hence, it can be expected that the population distribution of the levels of evaporating molecules is a Boltzmann distribution with the cluster temperature.

The mechanism of the additional population is as follows. Molecules having low values of the rotational quantum number are captured from the flux of incident molecules by clusters, are then evaporated with a population distribution governed by the cluster temperature, and are then added to the total number of monomers. The continuous progress of the capture–evaporation processes results in the accumulation of molecules at those levels which the rotational relaxation of monomers by monomers does not succeed in empyting. The relative population of the level $N_k/\Sigma N_k(2K+1)$ in a flow with clusters indeed grows partially because of the departure of molecules in large clusters. The dependence of the capture factor of molecules by clusters on the rotational excitation is mentioned in [14]. The capture and evaporation process considered contributed to the build-up of a Boltzmann distribution at low levels, i.e., is an additional mechanism accelerating the process of rotational relaxation of the low levels in a condensing gas flow.

Estimates for the conditions of the experiment presented in Fig. 5 show that the mean number of binary collisions of each molecule on the path from $x/d_* = 22$ to $x/d_* = 40$, i.e., on that section where the additional population of the upper levels is observed, equals approximately 100. This means that for a several percent fraction of condensate (expected under the considered conditions) each molecule took part multiply in the condensation–evaporation process. If it is assumed that the cluster temperature is 45°K, then an estimate of the increase in relative population because of evaporation in the mentioned range of $x/d_*$ will yield a result commensurate with the experimentally measured increase in $N_k/\Sigma N_k(2K+1)$, which verifies the actuality of the proposed mechanism for additional population of the upper levels.

It follows from the results of this paper that the formation and presence of clusters in the flow complicates the rotational relaxation mechanism and specifies the appearance of relaxation acceleration effects at the low levels and an additional population of the upper levels. The reverse influence of rotational relaxation on condensation, in addition to connecting an additional reservoir for a heat of condensation sink in the form of rotational degrees of freedom, is apparently that the rate of rotational relaxation in monomers and clusters influences the heat of condensation sink.

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# COMPUTATION OF THE ROTATIONAL TRANSITION
# PROBABILITIES OF DIATOMIC MOLECULES WITH A MORSE
# POTENTIAL

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This paper is a continuation of the computations of the excitation probabilities of the rotational degrees of freedom of diatomic molecules during collisions carried out in [1]. In connection with the enormous computational difficulties occurring in quantum-mechanical computations [2], a quasiclassical approach [3] is used which allows obtaining analytical dependence of the probability on both the number of the rotational level characterizing the transition and on the energy of the colliding particles. This last circumstance is a factor of no little importance in the application of the probabilities obtained in the description of the level kinetics of rotational relaxation under different conditions, for instance, under the efflux of gas mixtures from a slot of nozzle into a vacuum.

Analytic expressions are obtained in this paper for the rotational transition probabilities at which the quantum numbers of one (R−T transitions) or both (R−R transitions) molecules change by 1 or 2. A multiplicative integral is used in the solution of the system of equations for the probability amplitudes of the appropriate processes. In contrast to [1, 3], the change in energy in an inelastic collision is taken into account in the classical equation of motion, and the averaging of the probabilities with respect to the total energy is carried out more correctly. An experimental potential and a potential in the Morse form are used in computing the probabilities. The need for such computations is due, in particular, to the substantial influence of attraction on the magnitude of the probability for low energies of the colliding molecules.

Let us recall that according to the method described earlier, the molecule trajectory is considered classical with the use of the spherically symmetric part of the intermolecular potential, while the rotational motion is considered quantum mechanically. The anisotropic part of the potential hence governs the form of the perturbation operation.