Effect of population of higher rotational levels in the course of free expansion of a gas with clusters

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The simultaneous occurrence of various relaxation processes, including condensation, can offer new possibilities for the development of laser media and for changing the properties or states of one of the components in the course of gas separation. Borzehko[1] has previously investigated the violation of the Boltzmann distribution over the rotational levels of nitrogen molecules when the nitrogen was freely expanded from a sonic nozzle. The presence of an "anomaly" in the population of the levels was indicated at large stagnation pressures, when a condensation can take place.

The purpose of the present study was to investigation the kinetics of the populations of rotational levels of nitrogen molecules when rotational relaxation and condensation take place simultaneously in the expanding stream of nitrogen or of a mixture of nitrogen with carbon dioxide. The investigation was carried out with gas-dynamic low-density setup of our institute,[2] using electron-beam diagnostics to determine the populations of the rotational levels in the ground state of the nitrogen molecules.[1] The measurements were made on the axis of jets behind the sonic nozzles with critical diameters $d_*=2.11$ and 0.54 mm at room temperature of stagnation in the P_0d_* range from 100 to 5000 (P_0 is the stagnation pressure in mm Hg). The data obtained pertain to the flow region where the gas pressure exceeds the saturated-vapor pressure. The supersaturation could be quite appreciable, since it is not eliminated by condensation in the case of rapid expansion in a jet.

Figure 1 shows the measured relative nondegenerate populations of the rotational levels of nitrogen at different distances from the edge of the nozzle ($x/d_*=10$—45) as functions of the quantum number. The experiments were performed in pure nitrogen

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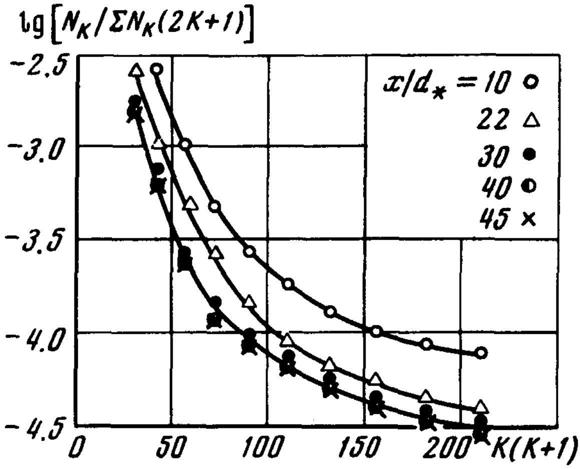

FIG. 1. Kinetics of the populations of the rotational levels in gas expansion without condensation. N_K—population of K th rotational level.

with a nozzle having $d_* = 2.1$ mm at relatively low stagnation pressure $P_0 = 650$ mm Hg, when the role of condensation is immaterial. With increasing distance from the edge of the nozzle, the populations of the upper and middle levels decrease, while those of the lowest ones increase. A deeper expansion leads to a successive quenching of the populations of the upper levels, and consequently to a normalization in density, the levels being independent of x/d_*. The higher the rotational quantum number, the closer to the edge of the nozzle is the quenching observed.

The character of the variation of the level populations in the stream of a condensing gas is substantially different. Figure 2 shows the distribution of populations at approximately the same distances from the edge of the nozzle as in Fig. 1, but at a much higher partial pressure of the nitrogen ($P_0 = 2035$ mm Hg) in the presence of

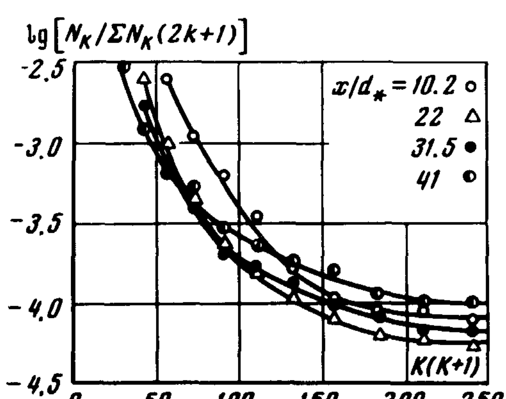

FIG. 2. Kinetics of the population of rotational levels in the case of simultaneous rotational relaxation in the condensation.

$\sim 8\%$ of CO_2. Up to $x/d_* = 10$ it is the carbon dioxide which is mainly condensed. On the first eight levels the populations have a Boltzmann distribution with a temperature $T_R \sim 51.6$ K. The next measurement point $x/d_* = 22$ is already far beyond the phase-transition curve for nitrogen, and the relative populations of the levels of the higher and middle levels have decreased and those of the lowest ones have decreased, i.e., just as in the flow without the influence of condensation (Fig. 1). The section with the Boltzmann distribution has disappeared.

What was unexpected was the behavior of the populations of the upper levels with further expansion. At $x/d_* > 22$ the populations of the central levels dropped, and that of the lower ones increased in accordance with the tendencies of the rotational relaxation. The populations of the upper levels, starting with the eighth, rose, and reached nearly double the values of the last few levels at $x/d_* = 40$. This effect, which was observed also in experiments with pure nitrogen at high stagnation pressure, contradicts the variation of the rotational relaxation when a homogeneous gas expands, and may be due to singularities in the course of the rotational relaxation in the presence of clusters.

It is obvious that the source of the molecules excited to the upper rotational levels exceeds their drain. Such a source can be the emission of molecules from the surface of a cluster.

The mechanism of the additional population is the following. From among the molecules incident on the clusters, it is mainly the molecules having low rotational quantum numbers which are captured. The molecules with large quantum numbers are reflected from the clusters and their distributions change insignificantly. Consequently, additional rotationally excited molecules appear in the stream. The continuous capture and emission processes lead to accumulation of molecules on those upper levels which do not manage to become depleted as the result of rotational relaxation. We note that the pumping of the upper levels is due to the heat of condensation. As indicated above, one of the decisive processes is selective capture of the rotationally excited molecules. The effect of rotational excitation on the condensation process has been discussed in the literature.[3,4] Estimates for the conditions of the experiment illustrated in Fig. 2 show that the average number of binary collisions of each molecule on the path from $x/d_* = 22$ to $x/d_* = 40$, i.e., on the section of additional population, is of the order of 100. This means that at a condensate fraction 10%, which can be expected under the present conditions, each molecule participated numerous times in the capture-emission process. At a cluster temperature close to the saturation temperature (~ 50 K under our conditions), the population of the upper levels by emission from clusters is comparable with the experimentally measured value, thus indicating that the proposed mechanism is realistic.

[1] B.N. Borzenko *et al.*, Zh. Prikl. Mekh. Fiz. No. 5, 20 (1976).

[2] A.A. Bochkarev *et al.*, in: Eksperimental'nye metody v dinamike razrezhennykh gazov (Experimental Methods in the Dynamics of Rarefied Gases), Novosibirsk, Inst. Teplofiz. SO Akad. Nauk SSSR, 1974.

[3] R.E. Leckenby and E.J. Robbins, Proc. R. Soc. London Ser. A **291**, 389 (1966).

[4] V.K. Konyukhov and V.N. Faĭzulaev, Preprint No. 32, Fiz. Inst. Akad. Nauk, 1976.