Kinetic investigations of the distribution function in excited nitrogen by the Raman scattering method

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The evolution of the distribution function of N_2 molecules over the vibrational levels $v = 0$–16 was experimentally investigated, for the first time ever, in the time interval 0.5–500 μsec following the pulsed electric discharge. A deviation of the time dependence of the function from a Boltzmann distribution is observed. The gas heating greatly exceeds the known rate of the $V-T$ process.

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The evolution of the population distribution function over the vibrational levels of an anharmonic oscillator has a number of singularities connected with the energy decrease $\Delta E = E_{v+1} - E_v$ between two neighboring levels with increasing number v, and with increasing ratio of the rate of the vibrational-translational ($V-T$) relaxation processes and vibrational-vibrational ($V-V$) exchange between the molecules.[1,2] The presently available data on the $V-V$ processes pertain to molecules that have a constant dipole moment, and the studies of the $V-T$ processes were devoted mainly to relaxation from the first excited vibrational level. An investigation of the first positive band of N_2[3] in a stationary microwave discharge yielded only a qualitative picture of the distribution function and of its dynamics.

We have experimentally investigated the kinetics of the state of vibrationally excited nitrogen at a pressure ~0.2 atm. We used for this purpose the method of high speed spectroscopy of spontaneous Raman scattering (RS) of light.[4] The vibrational levels of the nitrogen were populated with a pulsed electric discharge.

The experimental setup of a high-speed RS spectrometer is described in[5]. The RS spectra were excited with 10-nsec pulses of an AYG:Nd^{3+} laser (second harmonic, repetition frequency 12.5 Hz) in the central part of the discharge region. The rate of flow of gas through the investigated volume was such as to replenish the gas in the discharge gap during the time between two laser pulses. The required time delay τ_d between the discharge and the instant of the RS spectrum registration was set with a delayed-pulse generator with accuracy not worse than 0.01 $\tau_d \pm 20$ nsec.

Figure 1 shows the Stokes RS spectrum of vibrationally excited nitrogen ($\tau_d = 50$ μsec) obtained after 2.5×10^3 laser pulses. The appearance in the RS spectrum of a diatomic molecule, besides the principal $0 \rightarrow 1$ transition (the S and O branches are relatively weak and are not resolved in this spectrum) of other numerous lines is caused by the population of higher (up to $v \sim 18$) vibrational levels. Owing to the anharmonicity of the N_2 molecules, the RS spectral lines corresponding to the transitions $v \rightarrow v+1$ do not overlap and are separated by ~28.3 cm^{-1}. This makes it possible

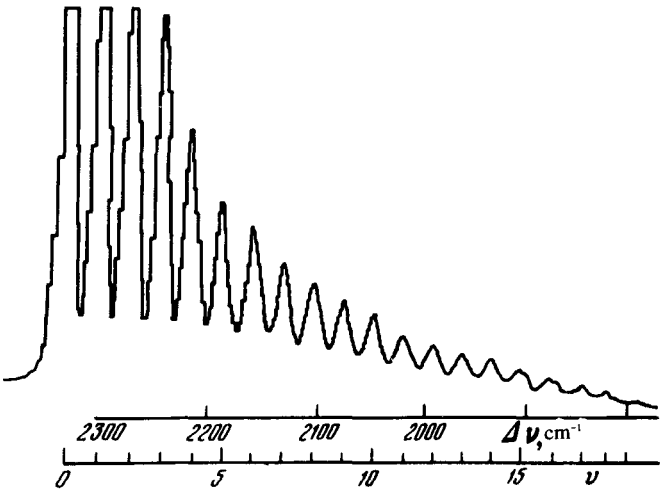

FIG. 1. RS spectrum of vibrationally excited nitrogen (without correction of the intensity for the uneven field sensitivity of the receiving apparatus).

to measure the intensity of the lines corresponding to individual transitions. The population of the vibrational levels n_v is connected with the intensity I_v of the Stokes RS lines in the following manner[5]

$$n_v \approx n_0 \frac{I_v}{I_0(v+1)} \left(\frac{\omega_0}{\omega_v}\right)^4, \tag{1}$$

where ω_v is the absolute frequency of the scattering. The equality in (1) is only approximate because it is derived by using the functions of the harmonic oscillator. The corresponding corrections to n_v, which take the anharmonicity into account, were obtained by calculating the matrix elements of the $v \to v+1$ transitions by perturbation theory and were taken into account when n_v was determined.[6]

A family of distribution functions of nitrogen molecules over the vibrational levels as functions of the delay time τ_d is shown in Fig. 2. The corresponding curves were plotted from a series of RS spectra similar to that shown in Fig. 1 and obtained under identical excitation conditions. All the curves are normalized to the population of the first vibrational level, taken to be 10^2. In the delay interval $\tau_d = 0.5$–1.5 μsec (Figs. 2a and 2b), a distribution function has an approximately exponential dependence on v (the curves are approximately linear in the scales on the axes), characterized by a vibrational temperature $T_v \approx 5800$ K. This value greatly exceeds the initial translational temperature (~ 300 K). Thus, the initial post-discharge conditions can be characterized by a large deviation from the equilibrium state. It follows from theoretical premises[1] that the relaxation of the vibrational energy from such states should be accompanied by a repopulation of the intermediate vibrational levels. Indeed, starting with $\tau_d = 5$ μsec and further, the distribution functions show a distinct tendency for the population of the upper level to increase, whereas the population of levels with small v decreases. This behavior of the distribution function can be attributed to the V–V exchange process, which predominates over the V–T relaxation in the region $v \sim 9$–20.

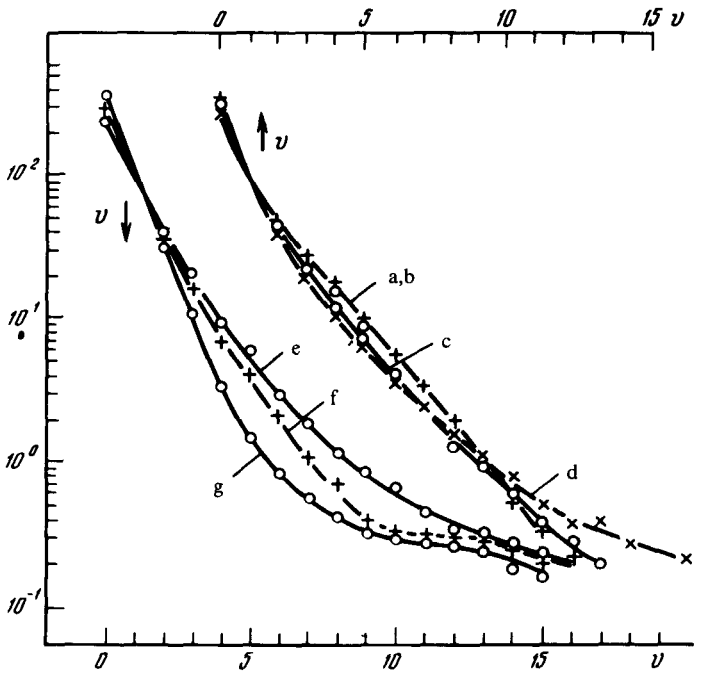

FIG. 2. Distribution function of nitrogen molecules over the vibrational levels at τ_d: a—0.5 μsec, b—1.5 μsec, c—5 μsec, d—15 μsec, e—50 μsec, f—170 μsec, g—500 μsec.

The fact that the obtained RS spectra contain no lines corresponding to levels with $v > 20$ indicates a relatively low population of these levels. Preventing the increase of the population of these levels on account of the V–V exchange is the V–T process, whose effectiveness increases strongly with increasing translational temperature T_{tr}. It is important that the rise of T_{tr} takes place much earlier than expected when account is taken of the known V–T relaxation rate.[7] Thus, the value of T_{tr} estimated by us from the change of the gas density as a result of its heating (from the summary intensity of the RS spectral lines) turn out to be ~ 1300 K already at $\tau_d = 170$ μsec. A similar phenomenon was revealed in N_2 by an estimate of the gas density under post-discharge conditions.[8] The appreciable heating of the gas even in the initial stages after the discharge can be explained as being due to the conversion of the energy defect $\Delta E_{v,v'}$ into heat in the relatively rapid V–V exchange process. During the later stage, a noticable contribution to the gas heating is made by the V–T process. As follows from the curves of Fig. 2, the initial increase of the populations of the upper vibrational levels (at relatively low T_{tr}) gives way to a decrease already at $\tau_d \sim 50$ μsec (Fig. 2e). We attribute this behavior of the distribution function to a change in the ratio of the V–T and V–V rates as a result of the gas heating.

A feature of curves 2a and 2b (which correspond to small τ_d) is presence of a wiggle at the point $v = 0$. We attribute this feature to inhomogeneity of the electric discharge over its cross section and over the length of the laser "neck" from which the

RS radiation is drawn. With increasing τ_d, this anomaly vanishes gradually as a result of the increase of the initially excited volume of the gas and the smoothing of the inhomogeneity of its excitation.

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