Broadening of spectral lines and distribution of the velocities of electron-excited molecules in a nonequilibrium plasma

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The emission line profiles of the 2^+ system of nitrogen excited by metastable N_2^* and Ar^* particles in a gas-discharge plasma were used to determine the nonequilibrium velocity distributions of $N_2(C\,^3\Pi)$ molecules. The distributions were deduced by solving incorrectly posed problems in two stages: a) elimination of the instrumental effects; b) differentiation of the true profile. It was found that the molecule velocity distributions depended on the energy of the bound state and the nature of changes in the distributions was studied in a wide range of pressures of mixtures of N_2 with He and Ar. A comparison of the energies of the internal degrees of freedom and translational motion provided a method for identifying the channels of exothermal processes of molecular excitation.

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I. INTRODUCTION

Electron-excited molecular states from which optical transitions take place in a weakly ionized low-pressure ($p \sim 1$ Torr) plasma usually have lifetimes shorter than or comparable with the typical thermalization times of internal (vibrational and rotational) and external (translational) degrees of freedom. Therefore, characteristics of the vibrational, rotational, and translational distributions of electron-excited molecules are governed largely by the specific nature of the excitation mechanisms.

The existence of parallel molecular excitation channels in a plasma gives rise to distributions of molecules between the rotational levels which are distorted from the Boltzmann form.[1] If the excitation is due to electron impact, then electronic–vibrational levels become populated in accordance with the Franck–Condon principle,[2] and the rotational distributions "copy" the distributions from the ground electronic state if $kT_g \gg B$ (T_g is the temperature of a neutral gas and B is the rotational constant).[3] If an elementary excitation event represents a nonresonant interaction between heavy particles, "hot" groups of molecules are created and the average energy of rotational motion in these groups is considerably higher than the thermal energy.[1,4,5] It follows from the conservation of energy and momentum that electron-excited molecules are formed with an initially nonthermal velocity distribution, and we must allow for the possibility of anomalous Doppler broadening of spectral lines.

Anomalous broadening of lines was observed experimentally in Ref. 6 in the specific case of the 2^+ system of N_2 excited by metastable particles.

We shall describe a systematic investigation of the spectral line profiles of the 2^+ system of N_2 ($C^3\Pi - B^3\Pi$ transition), which were used to find and analyze the molecular velocity distributions.

II. EXPERIMENT

The spectral line profiles were investigated using apparatus consisting of a Fabry–Perot interferometer crossed with a DFS-8 monochromator; in each case the slits were rectangular. The light sources were glow discharges in N_2–He and N_2–Ar mixtures in a quartz tube with a discharge gap of 600 mm and an internal diameter 20 mm or hollow-cathode discharges in the same mixtures; the cathode was a steel can with an internal diameter of 10 mm and 64 mm long. The walls of the discharge tube and the hollow cathode could be cooled with liquid nitrogen or running water. The tube electrodes were located in side branches and only the radiation emitted by the positive column was recorded. The recording part of the apparatus was described earlier.[1] The pressure-scanned Fabry–Perot interferometer was placed in a pressure chamber.

Measurements were carried out at a low circulation velocity (~1 cm/sec) of the gas through the discharge in order to avoid contamination. The influence of the radial inhomogeneity of the source and the width of the instrumental function were minimized by iris diaphragms which selected the axial zone of the discharge.

Measurements were carried out on the R-branch lines of the (0, 0) band of the 2^+ system of N_2. A reliable determination of the profiles of each of the components of the Λ doublet was possible only in the case of the R_1-branch lines corresponding to transitions from the component $^3\Pi_0$ of the $C^3\Pi$ state. The profiles of the R_2 and R_3 lines were superimposed because of the smallness of the Λ splitting of the $^3\Pi_{1,2}$ components.[7] In most cases the spectral interval selected by the monochromator contained not only the investigated R_1 lines but also the R_2 lines separated by 0.2–0.4 Å. The superposition of the interference orders was eliminated by a suitable selection of the interferometer base. The agreements of the results obtained for bases of different length (usually from 2 to 6 mm) confirmed the

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absence of accidental superposition of the interference orders. An analysis was made of the true line profiles, i.e., those obtained after subtraction of the instrumental function because this function varied with the interferometer base. The instrumental function was determined with the aid of an He–Ne laser and by recording line profiles with known broadening.[8]

III. PROCEDURES IN THE ANALYSIS OF RESULTS

The purpose of our calculation procedures was to find the velocity distribution of the emitting particles from the measured spectral line profiles. An important feature was the minimal *a priori* information of the nature of the distributions to be found.

The problem of determining the true profile of a spectral line $\varphi(\nu)$ from the observed profile $f(\nu)$ reduces to solution of an integral Fredholm equation of the first kind:

$$\int_{-\infty}^{\infty} a(\nu-\nu')\varphi(\nu')d\nu'=f(\nu)=f_0(\nu)+\varepsilon(\nu), \tag{1}$$

where $a(\nu)$ is the instrumental function of the apparatus; $f_0(\nu)$ is the experimental signal after subtraction of the noise; $\varepsilon(\nu)$ is the noise with zero average; ν is the frequency.

The intensity distribution in a true spectral line profile $\varphi(\nu)$ is converted to the distribution function $P(v)$ of the absolute values of the molecular velocities by means of the equation[9]

$$\int_{\mu^*}^{\infty} k(v,\nu)P(v)dv=\varphi(\nu), \quad \mu^*=\frac{|\nu-\nu_0|}{\nu_0}c, \tag{2}$$

where ν_0 is the frequency at the center of the profile and c is the velocity of light. It follows from Eq. (9) that in the case of an isotropic medium the kernel is $k(v, \nu) = 1/v$ and Eq. (2) can be written in the form

$$\int_{\mu^*}^{\infty} \frac{P(v)}{v}dv=\varphi(\nu). \tag{3}$$

Equation (1) can be solved by various regularization schemes: a) the Fourier variant of the Tikhonov method[10]; b) the method of statistical regularization in its general form[11]; c) the iteration method of Kryanev.[12]

Experience in practical calculations and solutions of model problems have demonstrated that the Fourier variant of the Tikhonov method (a) should be best for our purpose both in respect of the "speed" of the algorithm and in respect of the quality of the reconstruction. We modified this variant somewhat compared with that given in Ref. 10 by introducing a determined function which represents the zeroth approximation of the required form and by using minimal *a priori* information. In an earlier communication[8] we discussed in detail the problems of eliminating the instrumental functions, in accordance with Eq. (3), methods for differentiation of regularized solutions, allowance for the noise correlations, and calculation of the errors in the final results. The calculation problems encountered in the reconstruction of the velocity distribution of particles from the emission line profile were also dealt with recently in Ref. 13.

IV. TRANSLATIONAL MOTION OF N_2 ($C^3\Pi$, $v'=0$) MOLECULES

1. Selection of lines

The profiles of the (0, 0) lines of the 2$^+$ system of N_2 were investigated allowing for the characteristic features of the distribution of the $N_2(C^3\Pi)$ molecules between the rotational levels. In all the investigated cases (both in the discharge tube and in the hollow cathode) we found two groups of rotationally excited molecules. The first—"cold"—group with a relatively low rotational temperature $T_r \approx T_g$ was due to the excitation of the N_2 molecules from the ground state $X^1\Sigma$ by direct electron impact[1]:

$$N_2(X^1\Sigma)+e\rightarrow N_2(C^3\Pi)+e. \tag{4}$$

The second—"hot"—group represented an ensemble of those molecules whose average energy was considerably greater than the thermal value. This group was formed as a result of nonresonant interactions of heavy particles[1,4,5]:

$$N_2(X^1\Sigma)+Ar^*\rightarrow N_2(C^3\Pi)+Ar(3p^6\,{}^1S_0)+\Delta E_1, \tag{5}$$

$$N_2(X^1\Sigma)+N_2^*\rightarrow N_2(C^3\Pi)+N_2(X^1\Sigma)+\Delta E_2. \tag{6}$$

Figure 1 show, by way of example, the dependences of the quantity $\ln\{cN_{K'}/g_{K'}\}$ ($N_{K'}$ is the population and $g_{K'}$ is the statistical weight of a rotational level K' and c = const) on the energy of the rotational terms $F(K')$ of the $N_2(C^3\Pi)$ molecules in a discharge tube cooled with liquid nitrogen and containing an N_2–He mixture of the 1:10 composition at a pressure $p = 1$ Torr when the discharge current was $i = 20$ mA. The dashed line describes the distribution of the populations of the cold molecules obtained allowing for the superposition of the distributions in accordance with the conclusions reached in Ref. 14. We can see that high rotational levels (in the present case those with $K' > 20$) are populated with molecules of the hot group created by the process (6), whereas the low levels (those with $K' < 13$) are mainly molecules of the cold group formed as a result of the process (4). Changes in the compositions of the gas mixtures and cooling conditions alter the ef-

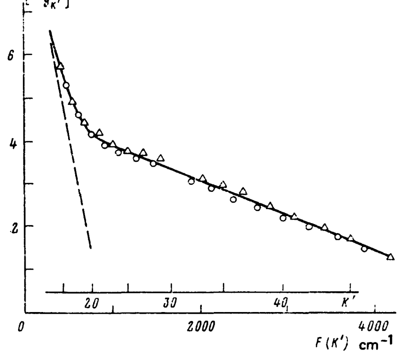

FIG. 1. Dependence of the quantity $\ln\{cN_{K'}/g_{K'}\}$ on the energy of the rotational terms $F(K')$ of $N_2(C^3\Pi,\ v'=0)$. Discharge in N_2–He(1:10) at $p = 1$ Torr for $i = 20$ mA. Cube walls cooled with liquid nitrogen. o) Even values of K'; Δ) odd values of K'. The dashed line gives the populations of the cold $N_2(C^3\Pi)$ molecules at $T_g = 150$°K.

ficiency of population of the various rotational levels of N_2 $(C^3\Pi)$ with molecules from both groups but in most cases the emission spectrum of the 2^+ system of N_2 does contain lines corresponding to transitions in only the hot or only the cold molecules.

Similar distributions of the N_2 molecules between the rotational levels were obtained also for discharges in N_2–Ar mixtures.

2. Line profiles and velocity distributions

Figure 2 shows the true profiles of the $R_1(26)$ lines of the (0, 0) band of the 2^+ system of N_2 obtained for different pressures in an N_2–Ar mixture of the 1 : 9 composition. The tube walls were cooled with liquid nitrogen and the discharge current was $i = 20$ mA. The $R_1(26)$ line corresponds to a radiative transition in the group of hot molecules. For comparison, Fig. 2 gives also the profile of the $R_1(3)$ line corresponding to transition in cold molecules at a pressure of $P = 0.5$ Torr when the current was 20 mA and the gas temperatures was $T_g = 150$°K. We can see that the $R_1(26)$ line profile is considerably wider than that of the $R_1(3)$ line. An increase in the pressure reduces the width of the $R_1(26)$.

Figure 3 shows families of the functions representing the distributions of the N_2 $(C^3\Pi)$ molecules in respect of the translational velocities $P(v)$ obtained by analysis of the $R_1(26)$ line profiles obtained at different pressures in the N_2–Ar(1 : 9) mixture. This figure includes also the Maxwellian distribution of the molecules corresponding to $T_g = 150$°K. The distributions end abruptly at velocities above which the error in the values of $P(v)$ becomes greater than 50% (in the vicinity of the most probable velocity the error does not exceed 5%). We can see that the values of the most probable velocity v_p^{hot} for the N_2^{hot} $(C^3\Pi)$ molecules is considerably greater than the most probable velocity of thermal motion. An increase in the pressure reduces gradually the value of v_p^{hot}.

The results are basically similar also for the N_2–He mixture: the values of the most probable velocities vary from ~10^5 to ~0.66×10^4 cm/sec for pressures ranging from 0.5 to 5 Torr.

At a given pressure the velocity distributions obtained for the discharges in the tube are the same as those obtained for the hollow-cathode discharges.

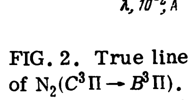

FIG. 2. True line profiles in the (0, 0) band of the 2^+ system of $N_2(C^3\Pi \to B^3\Pi)$. Discharge current $i = 20$ mA. Tube walls cooled with liquid nitrogen. Discharge in N_2–Ar(1:9). 1) Profile of $R_1(26)$ line at $p = 0.1$ Torr; 2) profile of $R_1(26)$ line at $p = 3$ Torr; 3) profile of $R_1(3)$ line at $p = 0.5$ Torr.

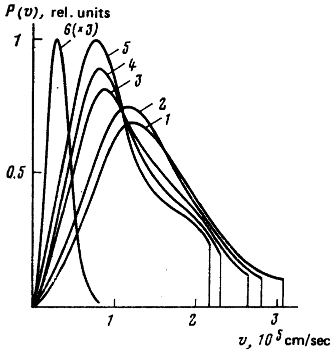

FIG. 3. Distribution functions $P(v)$ of the velocities of $N_2(C^3\Pi, v' = 0, K' = 26)$ molecules in a discharge. Discharge current $i = 20$ mA. Tube walls cooled with liquid nitrogen. All curves normalized to the same area. Discharge in N_2–Ar(1:9): 1) $p = 0.1$ Torr; 2) $p = 0.5$ Torr; 3) $p = 1$ Torr; 4) $p = 2$ Torr; 5) $p = 3$ Torr; 6) Maxwellian distribution for the function of the velocities of N_2 molecules at $T_g = 150$°K.

A comparison of the results shows that the molecules at different rotational levels have different most probable velocities of translational motion, i.e., the excited molecules are sorted in a characteristic way in accordance with their velocities.

The observed $P(v)$ distributions are formed under the influence of two factors. Firstly, the excitation creates directly molecules with a certain distribution of the translational velocities $P^0(v)$ [we shall call $P^0(v)$ the source function] and, secondly, during the lifetime of the molecules in an excited electronic state the relaxation processes transform the function $P^0(v)$ into $P(v)$, which is recorded experimentally.

3. Source function

The model of collisions between hard spheres is used in Ref. 15 to find the velocity distribution functions of the products of a bimolecular reaction

$$m_1+m_2 \to m_3+m_4, \tag{7}$$

when the distributions of the velocities of the initial reacting particles and the excess of the kinetic energy E_R evolved in the reaction are all known. We used the results of Ref. 15 to calculate the velocity distribution function of the $N_2(C^3\Pi, v' = 0, K' = 26)$ molecules formed by the reaction (5). In this calculation we allowed for the fact that the $N_2(X^1\Sigma)$ molecules may be in different vibrational–rotational states (v^0, K^0) and also that the excited argon atoms can be in different electronic states (e') corresponding to the $3p^54s$ configuration. Therefore, the required distribution function is the sum

$$P(v) = \sum_{e', v^0, K^0} P(e', v^0, K^0). \tag{8}$$

Figure 4 shows our source function for the $N_2(C^3\Pi, v' = 0, K' = 26)$ molecules obtained in the case when the excitation is transferred to nitrogen from the lowest (and as indicated by our line absorption measurements) most populated state $Ar(^3P_2)$. In these calculations we assumed that all the $N_2(X^1\Sigma)$ molecules are in the

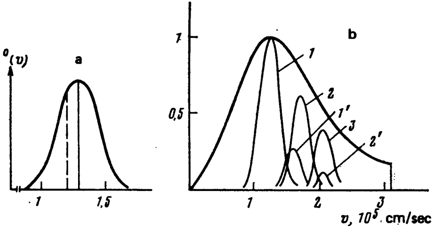

FIG. 4. Distribution functions $P(v)$ of the velocities of $N_2(C^3\Pi$, $v'=0$, $K'=26)$ molecules and source functions $P^0(v)$ in N_2–Ar (1:9) discharge. Tube walls cooled with liquid nitrogen. Discharge current $i = 20$ mA, $T_g = 150$°K. a) Source function $P^0(v)$ (v) calculated on the assumption of excitation of $N_2(C_3\Pi)$ by collisions with $Ar(^3P_2)$.

ground vibrational state $(v^0=0)$ and have a Boltzmann distribution among the rotational states with the gas temperature $T_g = 150°K$. Clearly, in the limit $T_g \to 0$ we should obtain a δ-like distribution of the molecule velocities, i.e., all the $N_2(C^3\Pi)$ molecules formed by the reaction in question would move at the same velocity

$$v^{T_\Gamma\to 0}\left[\frac{2\Delta E}{m_{N_2}(1+m_{N_2}/m_{Ar})}\right]^{1/2}, \tag{9}$$

where m_{N_2} and m_{Ar} are, respectively, the masses of the N_2 molecule and the Ar atom,

$$\Delta E=E(^3P_2)-E(C^3\Pi,\ v'=0,\ K'=26); \quad E(^3P_2)\ \text{и}\ E(C^3\Pi,\ v'=0,\ K'=26)$$

are the energies of the corresponding states.[1] The value of this velocity is identified in Fig. 4a by the vertical dashed line. Thermal (both translational and rotational) motion "smears out" the distribution and the most probable velocity shifts toward higher velocities relative to $v^{T_g\to 0}$. We can show (see below) that

$$v_p^{T_g}=v_p^{T_g\to 0}\left[1+\left(1+\frac{3}{2}\frac{m_{Ar}+m_{N_2}}{m_{Ar}}\right)\frac{kT_g}{\Delta E}\right]^{1/2}. \tag{10}$$

The value $v_p^{T_g}$ is given very accurately by Eq. (10). It follows from the calculations that in the temperature range $T_g = 50$–$1000°K$ for energies $\Delta E = 500$–$10\,000\ cm^{-1}$ the difference between the maximum of the distribution found from Eq. (10) and that deduced by exact calculations in accordance with the theory of Ref. 15 does not exceed 2–4%.

Figure 4b shows the experimental distribution of the velocities of the $N_2(C^3\Pi, v'=0, K'=26)$ molecules in a N_2–Ar discharge at a pressure of $p = 0.1$ Torr for a current of $i = 20$ mA. It also includes the calculated source functions $P_i^0(v)$ obtained for excitation from: 1), 1′) the level $N_2(X^1\Sigma, v^0=0)$; 2), 2′) the level $N_2(X^1\Sigma, v^0=1)$; 3) the level $N_2(X^1\Sigma, v^0=2)$; curves 1, 2, and 3 correspond to excitation from the $Ar(^3P_2)$ state; curves 1′ and 2′ represent the combined contribution of the states $Ar(^3P_0)$, $Ar(^3P_1)$, and $Ar(^1P_1)$ to the excitation of nitrogen. The concentrations of the $Ar^*(3p^54s)$ atoms were determined by the method of line absorption, the cross sections for excitation transfer from Ar to N_2 were averaged using the results given in Refs. 16–19, and the effective vibrational temperature of the $N_2(X^1\Sigma)$ molecules for the three levels was assumed to be $T_v \approx 5000°K$. The relaxation processes flatten out these distributions and, moreover, they give rise to a contribution to the distribution function $P(v)$ of molecules moving at lower velocities $(v < 10^5$ cm/sec).

4. Relaxation of the average kinetic energy

The molecular velocity distributions determined for different gas pressures make it possible to analyze some features of the translational relaxation of excited molecules. At this stage we shall confine ourselves to simple model representations. We shall assume that: 1) the molecules interact as hard spheres; 2) the family of the $P(v)$ distributions can be approximated at all stages of the relaxation by a family of the Maxwellian distributions with the same most probable velocities (in the experimentally investigated cases at pressures $P \gtrsim 0.1$ Torr there are small deviations of the distributions from the Maxwellian form in the range $v > 2v_p$); 3) the buffer gas is not heated in the process of relaxation [this is quite accurately true because the density of electron-excited molecules is $N_2(C^3\Pi) \sim 10^8\ cm^{-3}$ and the density of the cold gas is $\sim 10^{16}\ cm^{-3}$].

We shall now consider the time dependence of the average kinetic energy $\bar{E}_{N_2}$ of the $N_2(C^3\Pi)$ molecule as it moves in a cold gas:

$$d\bar{E}_{N_2}=-n_M\tilde{v}_{N_2,M}\Delta\bar{E}_{N_2}\sigma_{N_2,M}dt. \tag{11}$$

Here, n_M is the density of the cold gas molecules [since the N_2–Ar(1:9) and N_2–He(1:10) mixtures were used mainly in our investigation, we could assume that in practice M = Ar or M = He]; $\tilde{v}_{N_2,M}$ is the average relative velocity of N_2 and M; $\Delta\bar{E}_{N_2}$ is the average energy lost by a molecule in one collision; $\sigma_{N_2,M}$ is the gas-kinetic cross section for the collisions of N_2 with M. We shall use the results of Ref. 20, where the hard-sphere model is also used and it is assumed that both the fast particles and the cold gas are described by the Maxwellian velocity distributions. The following expressions for $\tilde{v}_{N_2,M}$ and $\Delta\bar{E}_{N_2}$ are obtained in Ref. 20 (rewritten in our notation):

$$\tilde{v}_{N_2,M}=\bar{v}_{N_2}\left(\frac{m_{N_2}}{m_M}\frac{T_M}{T_{N_2}}+1\right)^{1/2}, \tag{12}$$

$$\Delta\bar{E}_{N_2}=\bar{E}_{N_2}\mu\left(1-\frac{T_M}{T_{N_2}}\right), \quad \mu=\frac{8}{3}\frac{m_{N_2}m_M}{(m_{N_2}+m_M)^2}, \tag{13}$$

(m_{N_2} and m_M are the masses of N_2 and M; T_{N_2} and T_M are the corresponding temperatures; v_{N_2} is the average velocity of the N_2 molecules). Using Eqs. (12) and (13), we can transform the relaxation equation to

$$-\frac{d\bar{E}_{N_2}}{dt}=4n_M\sigma_{N_2,M}\mu(3\pi m_{N_2})^{-1/2}\left(\frac{m_{N_2}}{m_M}\bar{E}_M+\bar{E}_{N_2}\right)^{1/2}(\bar{E}_{N_2}-\bar{E}_M). \tag{14}$$

It should be noted that if the deviations from equilibrium are small, i.e., if $\bar{E}_{N_2} \approx \bar{E}_M$, then Eq. (14) reduces to the well-known equation with a constant relaxation time τ_{rel} (see, for example Refs. 21):

$$-\frac{dE_{N_2}}{dt}=\frac{1}{\tau_{rel}}(\bar{E}_{N_2}-\bar{E}_M), \tag{15}$$

$$\tau_{rel}^{-1}=4n_M\sigma_{N_2,M}\mu\left[\frac{\bar{E}_M}{3\pi m_{N_2}}\left(\frac{m_{N_2}}{m_M}+1\right)\right]^{1/2}.$$

Solution of Eq. (14) subject to the initial condition $\bar{E}_{N_2}(t=0)=\bar{E}_{N_2}^0$ can be written down as follows:

$$\bar{E}_{N_2}(t)=\bar{E}_M\left(1+\frac{m_{N_2}}{m_M}\right)\frac{[C\exp(t/\tau_{rel})+1]^2}{[C\exp(t/\tau_{rel})-1]^2}-\frac{m_{N_2}}{m_M}\bar{E}_M, \tag{16}$$

$$C=\left[\left(\bar{E}_{N_2}{}^0+\frac{m_{N_2}}{m_M}\bar{E}_M\right)^{1/2}+\left(\bar{E}_M\left(1+\frac{m_{N_2}}{m_M}\right)\right)^{1/2}\right]$$
$$\times\left[\left(\bar{E}_{N_2}^0+\frac{m_{N_2}}{m_M}\bar{E}_M\right)^{1/2}-\left(\bar{E}_M\left(1+\frac{m_{N_2}}{m_M}\right)\right)^{1/2}\right]^{-1}. \qquad (17)$$

Figure 5 shows the time dependence $E_{N_2}(t)$ for the case when $M = Ar$, $\bar{E}^0_{N_2} = 2250°K$, and $\bar{E}_M = 150°K$. It is clear from Fig. 5 that the relaxation process is very fast: already after $t = 0.5\tau_{rel}$ the value of $\bar{E}_{N_2}$ decreases by the factor e, whereas after $t = 3\tau_{rel}$ the energy becomes $\bar{E}_{N_2} \approx \bar{E}_M$.

Our measurements give information on the steady-state distributions of the velocities of the excited particles. In discussing the experimental results we must bear in mind that the observed molecules are formed at different times relative to the moment of observation (or deexcitation by emission) and their excited-state lifetimes are different. Therefore, when Eq. (16) is used to analyze the experimental results it is necessary to average over the radiative lifetime of the excited molecules. The probability of emission of a photon by an excited particle in a time from t to $t + dt$ is given by[22]

$$dW(t)=\frac{1}{\tau}e^{-t/\tau}dt, \qquad (18)$$

where τ is the radiative excited-state lifetime, amounting to $\tau = (41 \pm 2.9) \times 10^{-9}$ sec for $N_2(C^3\Pi, v' = 0)$ (Ref. 23). Finally, averaging Eq. (16), we obtain

$$\langle\bar{E}_{N_2}(n_M,\sigma_{N_2M})\rangle=\frac{1}{\tau}\int\limits_0^\infty\bar{E}_{N_2}(n_M,\sigma_{N_2M},t)e^{-t/\tau}dt. \qquad (19)$$

Comparing the dependence (19) with the experimental results, we can determine the effective collision cross sections of the $N_2(C^3\Pi)$ excited molecules with the atoms of argon ($\sigma_{N_2,Ar}$) and helium ($\sigma_{N_2,He}$). Figure 6 shows, by way of example, the dependences of the most probable energies of the $N_2(C^3\Pi, v' = 0, K' = 26)$ molecules on the density of the Ar atoms. The points correspond to the experimental values and the lines are the dependences calculated for different cross sections on the basis of Eq. (19). The best agreement between the calculations and the experimental results is obtained for the values $\sigma_{N_2,Ar} = (4.1 \pm 1.5) \cdot 10^{-15}$ cm^2 and $\sigma_{N_2,He} = (5.8 \pm 0.5) \cdot 10^{-15}$ cm^2. We can see that the calculated dependence is sensitive to the selective cross section. This allows us to determine the effective collision cross section with a relatively small error. It should be noted that in the case of the N_2–Ar(1 : 9) mixture the value $\sigma_{N_2,Ar}$ is practically identical with the gas-kinetic collision cross section particles in the ground electronic states ($\sigma^0_{N_2,Ar} = 4.3 \cdot 10^{-5}$ cm^2— see Ref. 24), whereas in the case of the N_2–He mixture there is some discrepancy ($\sigma^0_{N_2,He} = 2.8 \cdot 10^{-15}$ cm^2— see Ref. 24). Our cross section is twice as large as $\sigma^0_{N_2,He}$. It is difficult to find the cause of these discrepancies at this stage of our investigation. Clearly, further detailed and systematic studies will be needed. We shall simply point out that the cross section for an electron-excited molecule need not be equal to the cross section for a molecule in the ground state colliding with a different particle because the effective size of a molecule in the excited state may generally be greater than in the ground state.

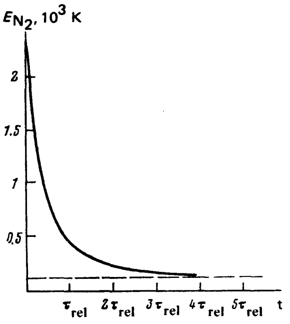

FIG. 5. Time dependences of the average energy of translational motion $\bar{E}_{N_2}$ of the $N_2(C^3\Pi)$ molecules moving in a cold gas (argon). $\bar{E}^0_{N_2} = 2250°K$, $\bar{E}_{Ar} = 150°K$.

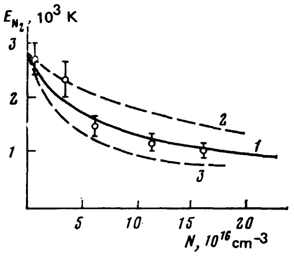

FIG. 6. Dependences of the most probable energies of $N_2(C^3\Pi, v' = 0, K' = 26)$ molecules on the density of Ar. Dependences calculated for N_2–Ar assuming the following cross sections: 1) $\sigma_{N_2,Ar} = 4.1 \times 10^{-5}$ cm^2; 2) $\sigma_{N_2,Ar} = 2 \times 10^{-15}$ cm^2; 3) $\sigma_{N_2,Ar} = 8 \times 10^{-15}$ cm^2. The points are the experimental values.

The good agreement between the calculated and experimental results justifies the application of a simple model to the translational relaxation processes. The cases under discussion are characterized by a strong departure from equilibrium: the initial energy of the hot particles is over an order of magnitude higher than the equilibrium value. These are the cases which are of the greatest interest in the theoretical analysis of the problem.

5. Identification of the excitation mechanisms

The known excess energy E_R and Eq. (8) can be used to find the velocity distribution of excited molecules undistorted by the relaxation processes, i.e., the distribution corresponding to zero density of the buffer gas. Application of the above relaxation model provides a satisfactory approximation for the distribution function when the buffer gas density is finite. However, we can formulate also the inverse problem: the experimentally determined distribution of the molecular velocities can be used to find the excess energy evolved in the excitation process. This is an important task because the knowledge of the energy defect allows us to identify the process resulting in the excitation of molecules.

We shall first consider the process of the transfer of excitation from an atom to a molecule. It follows from the law of conservation of energy that

$$E_e{}^{at}=E^{mol}_{e,v,K}-E_K{}^0+E_t{}'-E_t{}^0, \qquad (20)$$

where E_e^{at} is the energy of an excited state of an atom; $E_{e,v,K}^{mol}$ is the energy of the investigated rovibronic state of a molecule; E_K^0 is the rotational energy of a molecule before the interaction; E_t^0 and E_t' are the translational energies of a system of two particles before and after the interaction, respectively.

If the kinetic energy of the particles of masses m_1 and m_2 is expressed in terms of the center-of-mass energy and the energy of relative motion, and if averaging over the directions of motion of the center of mass is carried out for the isotropic case, the result is

$$E_t'-E_t^0=\frac{M}{2m_2}(m_1v_1'^2-m_1v_1^{02}),\ M=m_1+m_2. \tag{21}$$

Combining Eqs. (21) and (20) and assuming that $E_K^0 = kT_g$, $m_1v_1^{02}/2=3\frac{3}{2}kT_g$, and $m_1v_1'^2/2=\varepsilon_1^0$, we find that

$$E_e^{at}=E_{e,v,K}^{mol}-kT_g\left(1+\frac{3}{2}\frac{M}{m_2}\right)+\frac{M}{m_2}\varepsilon_1^0. \tag{22}$$

Here, ε_1^0 is the energy obtained in the limit of zero gas density. We can find ε_1^0 by plotting the dependence of the most probable energy on the density and then extrapolating this dependence to zero density. We shall consider the specific case of the reaction (5), i.e., when $m_1=m_{N_2}$ and $m_2=m_{Ar}$ [combining Eqs. (22) and (9), we obtain Eq. (10)]. It follows from the experimental data for $N_2(C^3\Pi, v'=0, K'=26)$ that $\varepsilon_1^0=2860\pm300$ cm^{-2}, $E_{e,v,K}^{mo}=90\,259$ cm^{-1}, and at $T_g=150$°K we find from Eq. (22) that $E_e^{at}=93\,264\pm360$ cm^{-1}, which is practically identical with the energy of the $Ar(^3P_2)$ state [$E(^3P_2)=93\,144$ cm^{-1}—see Ref. 25]. If other spectral lines of the 2^+ system of N_2 are used, particularly those corresponding to transitions from higher rotational levels ($K'\sim 50$), we can determine the limits of the interval of the states of argon that can excite nitrogen molecules. These states have been identified sufficiently reliably earlier[4] so that the above example is simply illustration of the reliability of the method.

We shall now consider the transfer of excitation from one molecule to another molecule. In this case the law of conservation of energy is

$$E_{e,v}^0=E_{e,v}'-\varepsilon_K^0(1)-\varepsilon_K^0(2)+(E_t'-E_t^0)+\varepsilon_K'(1)+\varepsilon_K'(2), \tag{23}$$

where $E_{e,v}^0$ and $E_{e,v}'$ are the values of the vibronic energy of the system before and after the interaction; $\varepsilon_K^0(1)$, $\varepsilon_K'(1)$ and $\varepsilon_K^0(2)$, $\varepsilon_K'(2)$ are the rotational energies of the first and second molecules before and after the interaction; E_t^0 and E_t' are the translational energies of the system before and after the interaction. Using Eq. (23) and assuming that $\frac{1}{2}m_1v_1^{02}=\frac{3}{2}kT_g$, $\frac{1}{2}m_1v_1'^2=\varepsilon_1^0$, and $\varepsilon_K^0(1)=\varepsilon_K^0(2)=kT_g$, we obtain

$$E_{e,v}^0=E_{e,v}'-kT_g\left(2+\frac{3}{2}\frac{M}{m_2}\right)+\frac{M}{m_2}\varepsilon_1^0+\varepsilon_K'(1)+\varepsilon_K'(2). \tag{24}$$

In the transfer of excitation from one molecule to another, the second molecule carries away not only the translational energy found from the conservation laws, but also the rotational energy $\varepsilon_k'(2)$. In this case we can determine $E_{e,v}^0$ from Eq. (23) only if we have additional information such as the maximum possible value of the rotational energy of the second molecule $\max[\varepsilon_K'(2)]$. It follows from Eq. (24) that the maximum possible rotational energy of the second molecule corresponds to the minimum value of the quantity $[M\varepsilon_1^0/m_2+\varepsilon_K'(1)]$ for the first molecule, i.e.,

$$E_{e,v}^0=E_{e,v}'-kT_g\left(2+\frac{3}{2}\frac{M}{m_2}\right)+\min\left[\frac{M}{m_2}\varepsilon_1^0+\varepsilon_K'(1)\right]+\max[\varepsilon_K'(2)]. \tag{25}$$

We shall now consider the example of the excitation of the 2^+ system of N_2 in a discharge taking place in pure N_2 or in an N_2–He mixture. There are at present at least two points of view on the mechanism of formation of the hot group $N_2^{hot}(C^3\Pi)$ in such discharges: 1) it may be formed as a result of deexcitation of the $N_2(E^3\Sigma)$ molecules[1] or 2) as a result of the deexcitation of the $N_2(C'^3\Pi)$ or $N_2(D^3\Sigma)$ molecules.[26] The products of these reactions are the $N_2(X^1\Sigma)$ and $N_2(C^3)$ molecules. The moments of inertia of $N_2(X^1\Sigma)$ and $N_2(C^3\Pi)$ are very similar so that it is natural to assume that, on the whole, the rotational distributions are similar (this conclusion follows also from the statistical theory of decay of the excited complexes[27]). In the spectrum of the 2^+ system of N_2 representing transitions of molecules of the hot group there are lines up to $K'\sim 50$, so that $\max[\varepsilon_K'(2)]=\varepsilon_K(K'=50)$. It follows from our investigation of the spectral line profile that $\min[2\varepsilon_1^0+\varepsilon_K'(1)]$ corresponds to the $N_2^{hot}(C^3\Pi, v'=0, K'\leqslant 18)$ molecules.[2] In particular, if $K'=18$, we find that $2\varepsilon_1^0(K'=18)+\varepsilon_K'(K'=18)=2700$ cm^{-1}. Finally, the energy of the required state is found to be $E_{e,v}^0=95\,800\pm700$ cm^{-1}. This is in agreement with the energy of the $E^3\Sigma$ state ($E=95\,772$ cm^{-1}—see Ref. 28) and even if we allow for the experimental errors, it is still less than the energies of the states $C'^3\Pi$ ($E=97\,580$ cm^{-1}— see Ref. 28) and $D^3\Sigma$ ($E=103\,576$ cm^{-1}—Ref. 28). Thus, the formation of the $N_2^{hot}(C^3\Pi)$ hot molecules is due to the $E^3\Sigma$ state.

V. CONCLUSIONS

Our experimental investigation of the velocity distributions of electron-excited molecules is clearly the first of its kind. The observed anomalous Doppler broadening of the molecular lines in a nonequilibrium plasma, the dependences of this effect on the energy of the bound state (sorting in accordance with velocity), and the ranges of conditions under which the effect appears are all important for the optical pyrometry of plasmas as well as in investigations of nonequilibrium flow and of the upper layers of the atmosphere. Our study was carried out on the lines of the 2^+ system of N_2, which is the best known and most widely used in plasma diagnostics.

A detailed analysis of the molecular velocity distributions, rigorous allowance and separation of the relaxation processes, including processes with energy exchange between different degrees of freedom, should clearly be carried out on the basis of the Boltzmann equation. This has not been possible within the framework of our investigation. Therefore, use has been made of simplified model representations which do not utilize all the information carried by the experimental results. Consequently, the discussion has been confined only to the most probable energies of the molecules because the nature of the distributions have been considered on a purely qualitative basis. However, our analysis has revealed new opportunities, particularly those for the identification of the molecular excitation mechanisms and determination of rates of relaxation processes.

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1) The values of E_R and ΔE generally differ by $\delta E_{v,K}$, representing the vibrational–rotational energy of the ground electronic state $\Delta E = E_R - \delta E_{v,K}$. In this case we have $\Delta E = E_R$.

2) The profiles of the lines representing transitions in hot molecules with $K' < 18$ were not investigated systematically by us.

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