VELOCITY DISTRIBUTION OF ELECTRONICALLY-EXCITED MOLECULES IN NONEQUILIBRIUM PLASMA.

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ABSTRACT

In the present work the velocity distribution of the $N_2(C^3\Pi)$ molecules excited in the exothermic collisions of $N_2(X^1\Sigma)$ with metastable N_2 molecules and Ar atoms is investigated. Form of this distribution is found by regularization methods from the shapes of the 2^+ system of N_2 spectral lines. Effect of translational relaxation of the electronically-excited molecules is discussed.

1. INTRODUCTION

In low pressure plasma the lifetimes of the electronically-excited molecules are typically smaller or comparable with the thermalization times for internal and translational motions. That is why the peculiarities of the vibrational, rotational and translational energy distributions essentially depend on the excitation mechanisms. If the processes of excitation are exothermic collisions with atoms or molecules, the electronically-excited molecules will have nonequilibrium rotational and translational movements. In earlier works the nonequilibrium rotational distribution $N_2(C^3\Pi)$ was investigated [1-3]. In this communication the velocity distribution formation of $N_2(C^3\Pi)$ in the exothermic collisions of $N_2(X^1\Sigma)$ with the metastable N_2 molecules and Ar atoms are under investigation.

2. EXPERIMENTAL , CALCULATION PROCEDURE.

The nonequilibrium movement of $N_2(C^3\Pi)$ molecules results in anomalous broadening of the second positive system (2^+) spectral lines [4]. The line shapes are studied with the pressure scanned Fabry-Perot interferometer crossed with the grating monochromator. The interferometer base must be chosen with account of both the needs of sufficiont resolution and free spectral range for single line resolution in the developed molecular spectra. The R_1-branch lines of the (0,0) band of the second positive system are investigated in glow discharges in the cylindrical tube and hollow cathode with water and liquid nitrogen cooling. The pressures of the mixtures N_2-He, N_2-Ar, N_2-Ar-CO_2-H_2 are 0.05-5 Torr; the discharge current 20-30 mA.

The relation between the intensity distribution in the line contour $\varphi_\alpha(\nu)$ and the isotropic velocity distribution function $P(v)$ is as follows:

$$\int_{\mu}^{\infty}\frac{P(v)}{v}dv=\varphi_{\alpha}(\nu),\qquad \mu=\frac{|\nu-\nu_0|}{\nu_0}\cdot c. \tag{1}$$

The interferometer function $a(\nu)$ deconvolution procedure leads to equation:

$$\int_{-\infty}^{\infty}a(\nu-\nu')\varphi(\nu')d\nu'=f(\nu)=f_0(\nu)+\varepsilon(\nu), \tag{2}$$

where $f(\nu)$, $\varphi(\nu)$ are measured and real lineshapes; $\varepsilon(\nu)$ is the noise. Equation (2) was solved by regularization methods: a) statistical regularization method; b) Fourier modification of the Tichonov's method; c) Kryanev's method (see [5]). The composition of different methods was performed for a wide range of modeling tasks. The method b) proves to be mostly acceptable, and the effective numerical algorithm was developed. To determine the velocity distribution function from equation (1) we have also used the regularization methods. Function $a(\nu)$ was determined by using the laser lines and from the measurements of the lines with known profiles as well.

3. RESULTS.

The anomalous broadening of spectral lines of the second positive system of N_2 is observed under excitation in reactions:

$$N_2(X^1\Sigma)+Ar(3p^54s)\rightarrow N_2(C^3\Pi)+Ar(3p^6\,{}^1S_0)+\Delta E_1, \tag{3}$$

$$N_2(X^1\Sigma)+N_2(E^3\Sigma)\rightarrow N_2(C^3\Pi)+N_2(X^1\Sigma)+\Delta E_2. \tag{4}$$

The studies show that the linewidths are different for different rotational states (even for the same electronically-vibrational band), so there exist a specific velocity "sorting" of the excited particles. Fig. 1 presents some examples of line shapes for $R_1(3)$ and $R_1(26)$ at different pressures of N_2-He(1:10) and N_2-Ar(1:9). Contour of $R_1(3)$ is normal Gaussian, which corresponds to Doppler broadening with gas temperature of ≃ 150 °K. The $R_1(26)$ contours are non-Gaussian with the width formally corresponding to Doppler broadening at 2000-3000°K. Fig. 2 illustrates the velocities distributions of N_2 $(C^3\Pi, v'=0, K'=26)$ for N_2-He(1:10)and

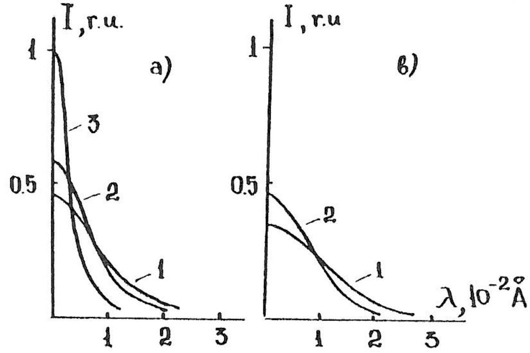

Fig. 1. The line shapes of (0,0) band 2^+ system of N_2. The discharge current 20 mA, liquid nitrogen cooling. a) N_2-He(1:10): (1)-R_1(26) line shape at mixture pressure P=0.5 Torr; (2)-R_1(26), P=3 Torr; (3)-R_1(3), P=0.5 Torr. b) N_2-Ar(1:9): (1)-R_1(26), P=0.1 Torr; (2)-R_1(26), P=3 Torr.

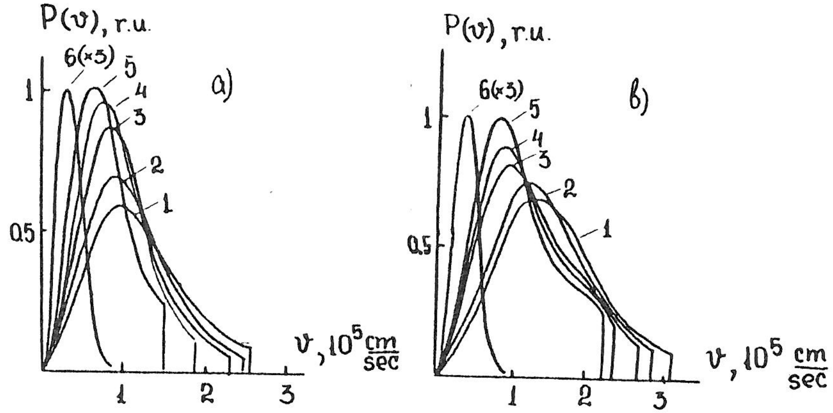

Fig. 2. The velocity distributions of $N_2(C^3$, =0, =26). The discharge current 20 mA, liquid nitrogen cooling. All curves are normalized to the same area. a) N_2-He(1:10): (1)-P=0.5 Torr; (2)-P=1 Torr; (3)-P=2 Torr; (4)-P=3 Torr; (5)-P=5 Torr; (6)-Maxwellian velocity distribution of N_2 at T=150°K. b) 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 velocity distribution of N_2 at T=150°K.

N_2-Ar(1:9) mixtures at various pressures. The breaks of the distributions at high v limit the region of the reliable measurements of the line wings with the signal-to-noise ratio >1. The Maxwellian distribution for T=150°K is also shown on Fig.2. All the curves are normalized to the same area. An increase of pressure leads to the narrowing of distributions, and to the decrease of the most probable velocities. The velocity distribution depend on two factors. Firstly, on the sourse function $P^0(v)$ which describes the initial distribution and, secondly, on the translation relaxation processes. The function $P^0(v)$ was calculated by using the Whipple theory [6], and taking additionally into account the real initial rotational and vibrational distributions of the colliding molecules.

We analysed some peculiarities of translation relaxation process of electronically-excited molecules. It was proposed that:

1 - the colliding molecules as well as hard spheres;

2 - the $P(v)$ functions relax approximately like Maxwellian distributions with the same most probable velocities;

3 - throughout relaxation process of electronically-excited molecules $N_2(C^3\Pi)$ the bulk of noble gas (He or Ar) is not heated.

Under such conditions the relaxation equation can be written in the following form:

$$-\frac{d\bar{E}_{N_2}}{dt}=4n_M\cdot\sigma_{N_2,M}\cdot\frac{8}{3}\frac{m_{N_2}\cdot m_M}{(m_{N_2}+m_M)^2}\cdot(3\pi m_{N_2})^{1/2}\left(\frac{m_{N_2}}{m_M}\bar{E}_M+\bar{E}_{N_2}\right)(\bar{E}_{N_2}-\bar{E}_M), \qquad (5)$$

where $\overline{E}_{N_2}$ and $\overline{E}_M$ are the mean translation energies of $N_2(C^3\Pi)$ and the noble gas (He or Ar); n_M - is concentration of noble gas atoms; $\sigma_{N_2,M}$ - is cross section of collision; m_{N_2} and m_M - are the masses of N_2 molecules and noble gas (He or Ar) atoms; if $\overline{E}_{N_2} \cong \overline{E}_M$, the equation (5) will turn into well-known Landau-Teller equation:

$$-\frac{d\overline{E}_{N_2}}{dt} = \frac{1}{\tau_r}\cdot\left(\overline{E}_{N_2} - \overline{E}_M\right), \qquad (6)$$

$$\tau_r^{-1} = 4n_M\cdot\sigma_{N_2,M}\cdot\frac{8}{3}\frac{m_{N_2}\cdot m_M}{(m_{N_2}+m_M)^2}\cdot\left(\frac{\overline{E}_M}{3\pi m_{N_2}}\right)^{1/2}\cdot\left(\frac{m_{N_2}}{m_M}+1\right)^{1/2}.$$

Here τ_r - is relaxation time. The solution of equation (5) is written down as follows:

$$\overline{E}_{N_2}(t) = E_M\left(1+\frac{m_{N_2}}{m_M}\right)\cdot\frac{[C\cdot\exp(t/\tau_r)+1]^2}{[C\cdot\exp(t/\tau_r-1]^2} - \frac{m_{N_2}}{m_M}\cdot\overline{E}_M, \qquad (7)$$

where C - constant defined from the conditions. Dependence of the mean energy $\overline{E}_{N_2}(t)$ on time at $\overline{E}_{N_2}(t=0)=2250$°K, $\overline{E}_M = 150$°K is presented on Fig. 3. It is shown the relaxation process is very fast. At $t=0.5\,\tau_r$ the mean energy decreases by a factor of e; and at $t=3\tau_r$ $\overline{E}_{N_2}$ is approximately equal to $\overline{E}_M$.

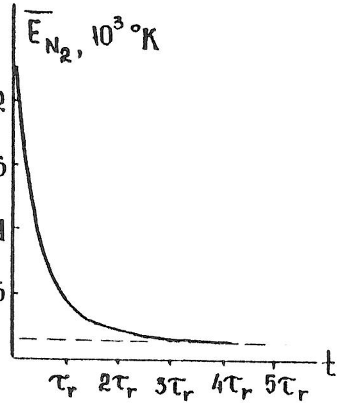

Fig. 3. The dependence of the mean translation energy of N_2 on time at $\overline{E}_{N_2}(t=0)=2250$°K, $\overline{E}_M=150$°K.

Fig. 4 presents dependences of the most probable energies of $N_2(C^3\Pi)$ on concentrations of He (a) and Ar (b). The points correspond to experimental values and the lines correspond to theoretical calculations. The best agreement takes place when the cross sections are equal to $\sigma_{N_2,He} = (5.8\pm0.5)\cdot10^{-15}\,cm^2$ and $\sigma_{N_2,Ar} = (4.1\pm1.5)\cdot10^{-15}\,cm^2$. Quite good agreement of experimental and theoretical dependences give proof of suggested simple relaxation model of electronically-excited molecules.

Using the energy storage in the vibrational, rotational and translational states one can find the energy excess ΔE of exothermal reaction of excitation and identify the reaction channel. Thus, the results of this work that the main excitation mechanism of $N_2(C^3\Pi, v'=0, K'=26)$ molecules lies in the collisions of $N_2(X^1\Sigma)$ with $Ar(^3P_2)$ for N_2-Ar mixture and $N_2(E^3\Sigma, v'=0)$ energy state for N_2-He ones. In the case of N_2-He mixture (or in pure N_2) the parent nitrogen state has the energy $E=96270\pm700\ cm^{-1}$. This definitely indicates that this is the $N_2(E^3\Sigma, v'=0)$ state (the energy of the $N_2(E^3\Sigma, v'=0)$ is equal $E_1=95772\ cm^{-1}$ [7]), but not the state $N_2(C'^3\Pi)(E_2=97580\ cm^{-1})$ or $N_2(D^3\Sigma)$ $(E_3=103576\ cm^{-1})$ (see [8]).

So, the first investigation of the nonequilibrium velocity distributions of the excited molecules give the new possibilities in studying the relaxation processes and the identification of particle excitation mechanisms.

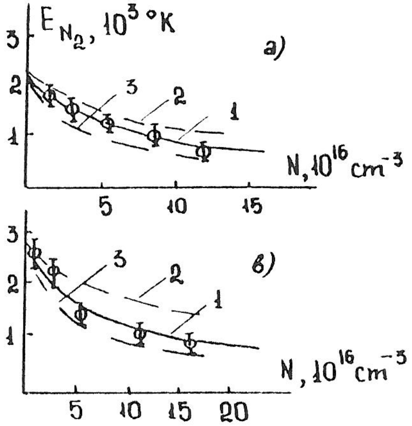

Fig. 4. The dependences of the most probable energies of N_2 ($C^3\Pi$, $v'=0$, $k'=26$) on density of He (a) and Ar (b). Points - experimental values, lines - theoretical calculations. a)(1) $\sigma = 5.8 \cdot 10^{-15}$; (2) $\sigma = 3 \cdot 10^{-15}$; (3) $\sigma = 12 \cdot 10^{-15}$; b) $\sigma = 4.1 \cdot 10^{-15}$; (2) $\sigma = 2 \cdot 10^{-15}$; (3) $\sigma = 8 \cdot 10^{-15}$. (all in cm^2).

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