MECHANISM OF VIBRATIONAL RELAXATION IN THE NONEQUILIBRIUM PLASMA OF A VACUUM ARC

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It is known that the excitation of a weakly ionized molecular gas at electron energies characteristic for nonequilibrium discharge ~1 eV takes place in the following sequence. First, the energy of the electric field is transmitted to the electrons, then the larger part of the energy of the discharge is used in excitation of the vibrational levels of the molecules, and finally, the vibrational excitation can be transmitted to the translational degrees of freedom, i.e., to heat. Despite of the fact that the balance of vibrational energy has a fundamental importance for the self-sustaining gas discharge, the presence of vibrationally excited molecules in the plasma has essential influence on the rate of practically all elementary processes in which molecules participate. Therefore the interest is timely, and the attention given to the studies of peculiarities of vibrational kinetics in nonequilibrium gases and plasma is understandable.

The present work is devoted to the study of peculiarities of vibrational relaxation in gas-metallic plasma of a stationary vacuum arc plasma. The increased interest shown for this type of discharge in recent years is related basically to practical needs: commutation of electric current in vacuum [1], creation of powerful ionic beams [2], and preparation of surfaces with accelerated streams of plasma [3-5]. In the process of study, a number of interesting properties of the vacuum arc are clarified, in particular, the presence of concentrated streams of neutral particles and multicharged ions of the cathode material in the arc plasma [3-5]. Naturally, these streams should essentially influence the whole picture of physicochemical processes in the discharge including the balance of vibrational energy.

Experiment. The experimental apparatus used in the present work is schematically depicted in Fig. 1. The vacuum discharge was created in the cylindrical chamber (3) of radius R = 25 cm serving as anode. The streams of plasma generated by the titanium cathode (1) propagated along the chamber and could deposit on the base (4). Gaseous nitrogen was introduced in the chamber at pressures $p = 1.33 \cdot 10^{-2}$-$6.65 \cdot 10^{-1}$ Pa, the arc current was i = 80-140 A, and the voltage between the anode and cathode was $U \simeq 20$ V. The radiation from the plasma was received through quartz windows (5) from the region 20-25 cm away from the working end of the cathode and focused on the slit of the monochromator with photoelectric registration of spectra (6). In the chamber, the probes (2) were inserted via special hermetic ports.

The distribution of nitrogen molecules on vibrational levels of the electronic ground state $N_2(X^1\Sigma_g^+)$ was obtained from the measurement of the intensities of the electronic-vibrational bands of the second positive (2+) system of nitrogen (the transition $N_2(C^3\Pi_u, v' \rightarrow B^3\Pi_g, v'')$ [6]. The validity of the assumption of this method was subjected to special experimental verification. As a result of the fact that in the experimental conditions the distribution of the nitrogen molecules on vibrational levels of the electronic excited state $N_2(C^3\Pi_U)$ was close to the Boltzmann distribution (at least up to level $v' = 3$), we used the concept of vibrational temperature of the state $N_2(C^3\Pi_u) - T_V^C$. After the determination of T_V^C, we computed the vibrational temperature of the electronic ground state $N_2(X^1\Sigma_g^+) - T_V^X$. This procedure was based on the fact [7, 8] that the rate constant of excitation by electron impact in the process $N_2(X^1\Sigma_g^+, v^0 \rightarrow C^3\Pi_u, v')$ is proportional to the Franck–Condon factors and to a factor accounting for the value of the distribution function of the electrons over the energy variable for the excitation threshold energies. In concrete calculations we used the data from the probe measurements and the values of Franck–Condon factors obtained in [9] for the RKR potential.

Calculation of Population Densities of Vibrational Levels. In order to theoretically describe the results obtained, we considered the following processes of excitation and relaxation of vibrational quanta of nitrogen molecules in the electronic ground state:

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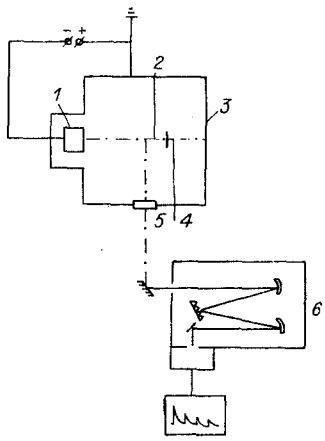

Fig. 1

– excitation and deexcitation of vibrations by electrons and fast titanium ions;

– vibrational–translational V–T exchange in collisions with other nitrogen molecules and titanium atoms;

– vibrational–vibrational V–V exchange of nitrogen molecules with each other (with subsequent V–T relaxation on the upper vibrational levels);

– vibration quenching on the walls of the chamber.

Because in conditions of vacuum arc discharge the energies of the titanium ions were very large (achieving tens of electronvolts and more [5]) and in accordance with the principle of detailed balance they could neither excite the nitrogen molecules nor quench them. At the same time, reactions involving titanium atoms and nitrogen molecules at thermal energies lead to effective deexcitation of vibrations.

Since for the nitrogen molecules the radiative transitions in the ground electronic state are forbidden, then taking account of the recomputed excitation and relaxation processes, the balance of quanta for the first vibrational level is written in the form

$$W_e N_0 = W'_e N_1 + W_{VT} N_1 + W_{VV} N_1 + W_D N_1 + k^a_{VT} N_a N_1, \qquad (1)$$

where W_e and W_e' are the rates of excitation and deexcitation of vibrations by electrons; W_{VT} and W_{VV} are the rates of the V–T and V–V exchanges in collisions of nitrogen molecules with each other; W_D is the deexcitation rate of vibrations due to collisions with the chamber walls; $k^a_{VT} N_a$ is the relaxation rate of vibration of nitrogen molecules in collisions with titanium atoms: written explicitly, k^a_{VT} is the rate constant of relaxation, and N_a is the concentration of titanium atoms.

If we introduce the notion of temperature of population of the first vibrational level of the nitrogen molecule in its ground electronic state $T_1^X = -\frac{\Delta E}{k} \ln\left(\frac{N_1}{N_0}\right)$, then after some simple transformations using (1), we can get

$$T_1^X = -\frac{\Delta E}{k}\left\{\ln\left(\frac{W_e}{W'_e + W_{VT} + W_{VV} + W_D + k^a_{VT} N_a}\right)\right\}^{-1}. \qquad (2)$$

For the nitrogen molecule the dependence on the parameter E/N (E is the intensity of electric field, N is density of molecules) is known for practically all rate constants of the processes included in (2) except for $k^a_{VT} N_a$, which is, henceforth, the free parameter in the given balance equation. From this, in particular, follows that every term in (2) depends indirectly through E/N on the pressure of the gas in the chamber. The strongest dependence on the discharge current intensity is observed, naturally, for those terms in Eq. (2) which are related to the excitation and deexcitation of vibrations by electrons. For other terms in (2), the dependence on the current intensity is expressed indirectly, as a rule, through the dependence of the rate constants on the gas temperature.

In order to determine T_1^X from (2) information about the electronic component of the plasma is required. In the present work the average energies and concentrations of electrons were measured experimentally by the method of Langmuir probes and subsequent determination of the slope of the characteristics on a semilogarithmic graph and its discontinuity at the

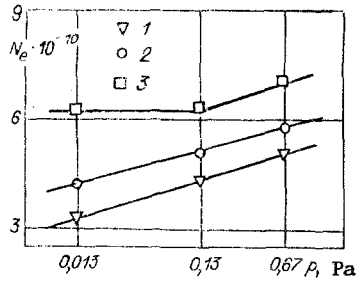

Fig. 2

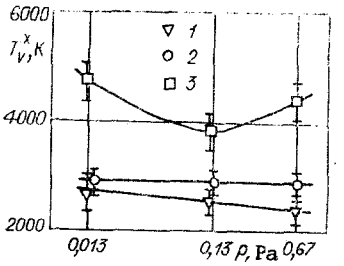

Fig. 3

point of the space potential [10], respectively. We note that the measurements of the distribution function of electrons in energy, performed by us with the aid of radiotechnical differentiation [10], showed that up to the energy $\varepsilon_e \approx 6$ eV the distribution function is Maxwellian. This offers the possibility to use the Maxwell function to describe the energy distribution of electrons in calculating the excitation of vibrational levels of nitrogen molecules in the ground state because in excitation of vibrational levels of the state $N_2(X^1\Sigma_g^+)$, the electrons with average energy $\bar{\varepsilon}$ = 2-3 eV [11, 12] are most effective. The average energies of experimentally obtained electron distributions were $\bar{\varepsilon}_e$ = 2-2.5 eV. The dependences of electron concentration on the discharge conditions are given in Fig. 2 (symbols 1-3 correspond to currents 80, 100, and 140 A, respectively). The electric field intensity $E \approx 0.1$ V/cm practically did not depend on the change of discharge conditions.

The rate of vibrational deexcitation on the chamber walls was computed from the standard formula

$$W_D = \beta D/\Lambda^2, \qquad (3)$$

where the vibrational accommodation coefficient of the nitrogen molecules on the chamber walls was $\beta = (1\text{-}3)\cdot 10^{-3}$ [13]; the diffusion coefficient D was determined from the data in [14]; the diffusion length Λ was calculated for the concrete geometry of the discharge chamber. In experimental conditions the constant of V–T relaxation by neutral nitrogen molecules was $k_{VT}^0 \approx 10^{-17}$ cm^3/cm [15], and the rate constant for excitation of the first vibrational level of the nitrogen molecule by electron impact $k_e \approx 2\cdot 10^{-9}$ cm^3/cm [11]. The rate constant for deexcitation of vibrations by electron impact k_e' was found by using the value of k_e from the principle of detailed balance. The dissipation channel of vibrational quanta via the V–V exchange was taken into account in analogy with [12, 16, 17]. We note that in conditions of the present experiment the V–T and V–V exchange of nitrogen molecules with each other did not play a remarkable role in the balance of vibrational quanta due to low density of molecules in the chamber.

Comparison of Calculation with Experiment. The unknown parameter in formula (2) is the product $k_{VT}^a N_a$, i.e., the rate of V–T relaxation of vibrationally excited nitrogen molecules by titanium atoms. It can be estimated from comparison of experimental and calculated dependence of vibrational temperatures of nitrogen molecules on the pressure and the discharge current. As an example in Fig. 3, we show the dependence of T_V^X on the pressure (points 1-3 correspond to currents 80, 100, and 140 A, respectively). As a result of comparison in Figs. 4a, b we see the dependences of the product $k_{VT}^a N_a$ on the pressure and the discharge current produced by using Fig. 3 and the data on the electronic component of the plasma (in Fig. 4b the points 1-3 correspond to pressures $1.33\cdot 10^{-2}$, $1.33\cdot 10^{-1}$, and $6.65\cdot 10^{-1}$ Pa).

The accommodation coefficient of the nitrogen molecules on the chamber walls β depends strongly on many parameters of the gas discharge (condition of the chamber's surface, temperature of the gas, etc.) and is usually known with substantial uncertainty [13]. For instance, in [13] coefficients are given for steel $\beta^{(1)} = (1\text{-}3)\cdot 10^{-3}$ and $\beta^{(2)} = 2.6\cdot 10^{-3}$ for stainless steel. These values of β are used in calculations of $k_{VT}^a N_a$. Hence, in Fig. 4b the solid lines show the values of $k_{VT}^a N_a$ obtained using $\beta^{(2)} = 2.6\cdot 10^{-3}$, while the dashed and dotted lines show data computed for $\beta^{(1)} = 10^{-3}$ and $3\cdot 10^{-3}$, respectively. The other symbols in Fig. 4 are analogous to the symbols of Fig. 3. It is clear that the indeterminacy of the β parameter does not fundamentally change $k_{VT}^a N_a$. Moreover, analysis of the influence of the variation of the other terms in (2) on the accuracy of $k_{VT}^a N_a$ was performed. Because the constants of excitation and deexcitation of the vibrations of nitrogen molecules by electron impact are known from literature with good accuracy [11, 12, 16], their variation had a small influence (clearly smaller than the indetermancy in the β parameter) on the sensitivity of the determination of $k_{VT}^a N_a$. What concerns the constants of V–T and V–V relaxation, their variation had also a weak effect on the accuracy of $k_{VT}^a N_a$ because, as we noted before, the V–T

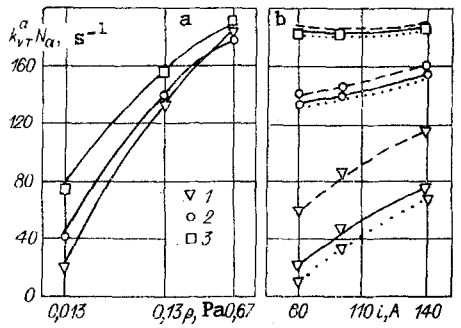

Fig. 4

and V–V exchange processes played no significant role in the balance of vibrational quanta.

It is interesting to perform a quantitative comparison of rates of various processes of vibrational relaxation of nitrogen molecules in vacuum arc plasma. The calculations show that the rates of the corresponding processes vary in the intervals $W_{VT} = 10^{-5}$-10^{-3} sec^{-1}, $W_{VV} = 10^{-6}$-10^{-4} sec^{-1}, and $W_D = 1$-100 sec^{-1}; $k^a_{VT}N_a$, as Fig. 4 shows, is 10-200 sec^{-1} i.e., together with heterogeneous processes, the main channels of vibrational relaxation of nitrogen molecules are the processes involving titanium atoms.

In this manner as a result of the performed investigation, it was shown that in conditions of the plasma of a vacuum arc the main role in the balance of vibrational energy is played by excitation by direct electron impact and relaxation by collisions with titanium atoms and the walls of the discharge chamber.

In conclusion on the basis of the obtained results, one can carry out an estimate of the absolute concentrations of titanium atoms in the plasma. At present the constants of quenching of the vibrations of nitrogen molecules by titanium atoms k^a_{VT} are unknown. The most complete data on quenching of molecular vibrations by atoms exists for alkali metals [18]. In particular, the rate constant for the V–T relaxation of molecules by alkali metal atoms at thermal collision energies is $\approx 10^{-10}$ cm^3/sec, i.e., is of gas-kinetic order of magnitude and is energy-independent for a wide range of collision energies [18]. If in the first approximation one is to assume that this result is valid for titanium atoms, then one can draw a conclusion from Fig. 4 about the behavior of N_a as a function of the discharge conditions.

Firstly, the dependence of N_a on the arc current agrees with analogous dependences obtained by measuring the transport of the cathode material by neutral particles (atoms and droplets) [19], namely: the concentration of neutral atoms increases monotonically with increasing current [19]. Secondly, there is a possibility of estimating absolute concentrations of the titanium atoms in the vacuum arc. If one is to assume, like for the alkali metals, that $k^a_{VT} \simeq 10^{-10}$ cm^3/sec, then from Fig. 3 it follows that the concentration of titanium atoms in discharge should not exceed $N_a \simeq 10^{12}$ cm^{-3}. These values, obviously, should be taken as upper bounds, since in the calculations the possibility of the quenching of the vibrations of nitrogen molecules by the drops of the cathode material was not taken into account.

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