Dissociation of molecular ions due to collisions with electrons in a plasma

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An experiment was carried out to study the dissociation of molecular ions caused by electrons in a plasma over the temperature range $T_e \approx 0.03$–2 eV. The magnitude and temperature dependence of the rate constant for the electron-induced dissociation of Xe_2^+ ions have been measured for the first time. This dissociation is more effective than dissociative recombination at electron temperatures $T_e > 1$ eV.

1. INTRODUCTION

Molecular ions play a key role in shaping the properties of plasmas at intermediate and high pressures and those of the active media of excimer and plasma lasers. The cross section for electron capture by a molecular ion reaches values on the order of 10^{-13} cm^2, so the appearance of such ions in a plasma is accompanied by a sharp increase in the rate of bulk charge neutralization. This circumstance is reflected in several effects, e.g., nonthermal contraction of discharges and selective filling of excited atomic states in a plasma which is not at equilibrium in terms of recombination. In a low-temperature plasma, molecular ions undergo dissociation in collisions with electrons or as a result of the capture of an electron into an autoionization state of the molecule. When the nuclei of such a molecule fly apart, atoms are formed in the ground and excited states:

$$A_2^+ + e \xrightarrow{\alpha} A_2^{**} \longrightarrow A_i^* + A. \qquad (1)$$

In addition to this capture of an electron into an autoionization state, the following dissociation may occur:

$$A_2^+ + e \xrightarrow{k_d} A^+ + A + e. \qquad (2)$$

The dissociative recombination (1) has been studied extensively, both experimentally and theoretically.[1,2] For electrons at thermal energies the recombination coefficient is $\alpha = \langle \sigma v \rangle \approx 10^{-6}$–$10^{-7}$ cm^3/s, and its temperature dependence is approximately $\alpha \propto T_e^{-0.5}$. The dissociation process (2) has received much less attention. Numerical calculations were carried out in Refs. 3 and 4 to find the cross section for dissociation of H_2^+ ions; the results agree with the results of beam experiments.[5,6] The cross sections for the dissociation of homonuclear molecular ions of inert gases were calculated in Ref. 7. It was shown there that at sufficiently high electron temperatures this process may be the dominant mechanism for the dissociation of molecular ions. For example, process (2) is more effective than process (1) at temperatures $T_e \approx 4$–5 eV for Ne_2^+, at temperatures 3–4 eV for Ar_2^+, at 2–3 eV for Kr_2^+, and at 1.5 eV for Xe_2^+. These estimates show that dissociation in collisions with electrons in the plasma of a gas discharge should play an important role in the balance of the density of molecular ions. There are no experimental data on the dissociation of molecular ions in plasmas.

In this paper we propose a method for studying the dissociation of molecular ions in plasmas. We have designed an experiment, straightforward in implementation and transparent in interpretation, in which the overall rate of dissociation of molecular ions, by either mechanism (1) or mechanism (2), is detected. The possibilities of the method are demonstrated in the particular case of a He–Xe plasma. This study has yielded data on the magnitude and temperature dependence of the rate constant for the dissociation of Xe_2^+ ions. The results of these measurements agree with the calculations of Ref. 7.

2. EXPERIMENTAL PROCEDURE AND CONDITIONS

The basic idea of the experiment is to measure the relative density of molecular ions as a function of the electron temperature in a decaying plasma. The plasma is produced by a periodic pulsed discharge in a glass tube filled with a He–Xe mixture to the partial pressures $p_{He} = 50$ torr and $p_{Xe} = 0.1$ torr. The length of the current pulse (several milliseconds) is sufficient to reach a steady-state discharge. The electron density in the plasma is $n_e \approx 3 \cdot 10^{10}$ cm^{-3}. Under these conditions the helium serves as a buffer gas, so the only positively charged particles are Xe^+ and Xe_2^+ ions.[8]

Let us consider the balance of the number density of molecular ions in the plasma. The primary source of these ions is the conversion of Xe^+ atomic ions in ternary collisions:

$$Xe^+ + Xe + He \rightarrow Xe_2^+ + He. \qquad (3)$$

The rate constant for this process is, in order of magnitude, $\beta \approx 10^{-31}$ cm^6/s. Considering ambipolar diffusion along with (1)–(3), we find

$$\frac{d[Xe_2^+]}{dt} = -\alpha_\Sigma n_e [Xe_2^+] + \beta [He][Xe][Xe^+] - \frac{[Xe_2^+]}{\tau_D},$$
$$\frac{d[Xe^+]}{dt} = -\beta [Xe][He][Xe^+] - \frac{[Xe^+]}{\tau_D'}, \qquad (4)$$
$$n_e = [Xe^+] + [Xe_2^+],$$

where τ_D and τ_D' are the time scales for the ambipolar diffusion of the Xe_2^+ and Xe^+ ions, and the square brackets mean the number density of the corresponding particles. The recombination of atomic ions can be ignored, since the process is inefficient. From (4) we find the following expression for the relative density of ions in a steady-state discharge:

$$\frac{[Xe_2^+]}{[Xe^+]}(T_e) = \frac{\beta [Xe][He]}{\alpha_\Sigma(T_e) n_e + 1/\tau_D(T_e)}. \qquad (5)$$

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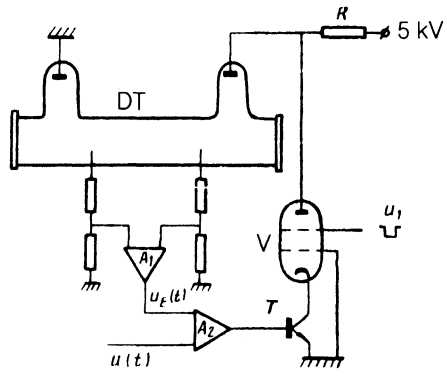

FIG. 1. Schematic diagram of the circuit for controlling the longitudinal electric field in a decaying plasma. *DT*—Discharge tube; *R*—ballast resistance. The other components are explained in the text proper.

It is important to note that under these conditions we have $[Xe_2^+]/[Xe^+] \ll 1$. This result follows directly from (5), as does the fact that at given densities [He], [Xe], and n_e the relative density of molecular ions is determined exclusively by the coefficients $\alpha + k_d$ and $1/\tau_D$, which in turn depend on the electron temperature. A change in T_e should thus give rise to a change in the ratio $[Xe_2^+]/[Xe^+]$. This circumstance could be utilized to measure $\alpha_\Sigma(T_e)$, since the time τ_D can easily be found from existing data on the Xe_2^+ diffusion coefficient in helium.

In practice, we solved the problem by the method of Ref. 9, which can be outlined as follows. The electron temperature in a discharge is known to be determined by the longitudinal electric field E and by the electron energy losses in collisions with plasma particles; i.e., we have $T_e = f(E/N)$, where N is the density of atoms. For a steady-state discharge we would have $T_e(E_{dis}/N) \approx 2$–2.5 eV. To vary the electron temperature over a wide range, an independent discharge with the desired value of E is established immediately after the pulse corresponding to the externally sustained discharge, in the plasma-decay stage. The experiment is illustrated by Figs. 1 and 2. Figure 1 explains the operation of the circuit which controls the field in the decaying plasma. During the negative pulse u_1, the tube V is cut off by the second grid, and the voltage which produces the self-sustaining discharge is applied to the plate of the discharge tube. For $t > t_1$, the tube conducts, and the voltage on the plate is set by the difference signal $\delta u = K[u_E(t) - u(t)]$, where K is the gain of differential amplifier A_2. A voltage $u_E(t)$ proportional to the longitudinal electric field is produced by the differential amplifier A_1, whose inputs receive signals from the electrical probes; $u(t)$ is the external signal. Clearly, in the limit $\delta u \to 0$, and with a sufficiently high gain of the chain A_1–A_2–T–V, a voltage will be maintained on the plate of the discharge tube such that the field $E(t)$ in the plasma will be proportional to the signal $u(t)$. This method makes it possible to produce decaying plasmas with various fields and to carry out experiments at electron temperatures ranging from $T_e(E=0) \approx 0.03$ eV to $T_e(E_{dis}/N) \approx 2$ eV.

During the time interval $t_1 - t_2$, the ion composition of the plasma changes according to Eqs. (4). In this experiment, we have the following relations among time scales. The relaxation time of the electron temperature due to a change in the field satisfies $\tau_T < 10^{-6}$ s (the electrons effectively give up energy in elastic collisions with helium atoms). The conversion time is $\tau_\beta = 1/\beta[He][Xe] \approx 10^{-3}$ s. The ambipolar diffusion times at $T_e(E) < T_e(E_{dis})$ satisfy $\tau_D, \tau_D' > 10^{-3}$ s. The time scale for the dissociation of molecular ions is $\tau_\alpha = 1/(\alpha + k_d)n_e < 10^{-4}$ s under the condition $T_e(E) < T_e(E_{dis})$. The latter relation follows from the data of Ref. 10 on $\alpha(T_e)$. We thus see that if $\tau_\alpha < \Delta t = t_2 - t_1 \ll \tau_\beta$, τ_D holds then a quasi-equilibrium ratio of the densities of atomic and molecular ions in (5) is established by the end of this time interval. This quasi-equilibrium ratio corresponds to the value of $\alpha_\Sigma[T_e(E_{t_1-t_2})]$.

At the time t_2, a transition occurs to a plasma without a field (an afterglow). In this stage, it is a simple matter to monitor the density of molecular ions by spectroscopy. It is well known that the only source of excited Xe $7p$, $6p'$, $6p$ atoms in the afterglow of a discharge in either pure Xe (Ref. 10) or a He–Xe mixture[11] is the process (2). In other words, the intensities of the spectral lines of the corresponding tran-

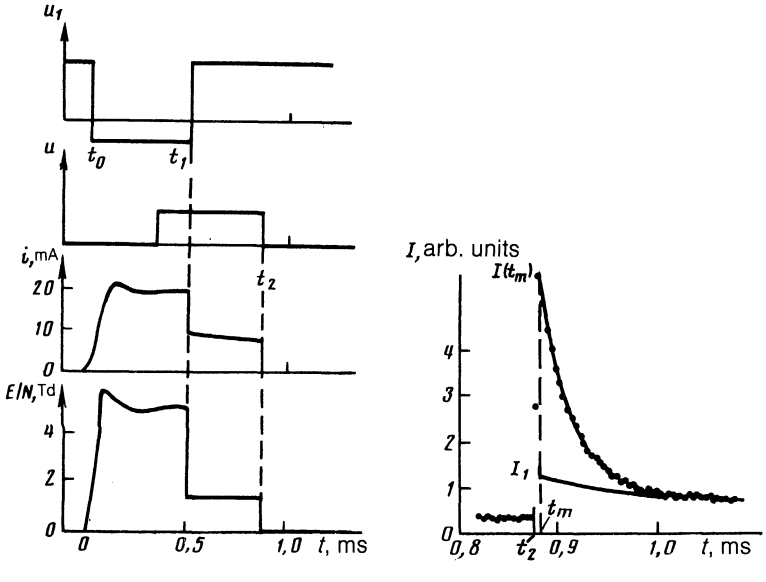

FIG. 2. Onset of the discharge ($t_0 - t_1$) and of the adjustable heating of the electrons in the decaying plasma ($t_1 - t_2$); $i(t)$—Discharge current; $E(t)$—longitudinal electric field; $I(t)$—intensity of the 4672 Å line of the Xe atom (the $7p$–$6s$ transition).

sitions are proportional to the recombination flux: $I \propto \alpha [Xe_2^+] n_e$. Figure 2 shows the time evolution $I(t)$ in the afterglow. We see that the transition to $E = 0$ is accompanied by (a) a sharp burst of emission from the plasma, as a result of relaxation of the temperature T_e from $T_e(E_{t_1 - t_2})$ to $T_e \approx 300$ K, and by (b) the formation of the characteristic recombination peak in the intensity $I(t)$ at $t = t_m$. In the region $t_2 < t < t_2 + 1/\alpha_0 n_e$, the density of molecular ions falls off,

$$[Xe_2^+](t) = [Xe_2^+](t_2) \exp(-\alpha_0 n_e t)$$

$$+ \frac{\beta [He][Xe]}{\alpha_0 n_e} [1 - \exp(-\alpha_0 n_e t)] \qquad (6)$$

$[\alpha_0 = \alpha_\Sigma (T_e = 300 \text{ K}) \approx \alpha(300 \text{ K})]$. In accordance with the relations among the time scales, this decay takes place at essentially constant values of the densities $[Xe^+]$ and n_e. For $t \gtrsim t + 1/\alpha_0 n_e$, the fast decay (with a recombination time $\tau_\alpha = 1/\alpha_0 n_e$) of the density $[Xe_2^+]$ gives way to a slow change (with a time scale $1/\tau = 1/\tau_\beta + 1/\tau_D \approx 1/\tau_\beta$) in $[Xe_2^+](t)$, as a result of a quasiequilibrium balance between the numbers of molecular and atomic ions. Ignoring the diffusive losses for simplicity, we find from (4) and (6)

$$\frac{[Xe_2^+](t_2)}{\beta [He][Xe][Xe^+]/\alpha_0 n_e} = \frac{\alpha_0}{\alpha_\Sigma (T_e(E_{t_1 - t_2}))} = \frac{I(t_m)}{I_1}. \qquad (7)$$

The intensities $I(t_m)$ and I_1 are shown in Fig. 2. It can be seen from (7) that one can use spectroscopic measurements in the afterglow to find the temperature dependence of the rate of dissociation of molecular ions. To determine the absolute value of the constant $(\alpha + k_d)(T_e)$ we measured α_0. We found it from the time scale, $\tau = 1/\alpha_0 n_e$, of the fast recombination decay of the intensity $I(t > t_2)$. In the experiments, the light was collected from the narrow central part of the discharge, in the direction parallel to the discharge axis. The light was detected by multichannel photon counting.

It follows from this discussion that the magnitude and temperature dependence of the overall rate $(\alpha_\Sigma = \alpha + k_d)$ of the dissociation of molecular ions, due to either dissociative recombination or dissociation in collisions with electrons in the plasma, can be determined from an experiment involving heating of the electrons of a decaying plasma and spectroscopic measurements of the relative density of molecular ions.

3. EXPERIMENTAL RESULTS

Figure 3 shows the results of an analysis of the experimental data. In the interval $T_e \approx 0.03$–0.8 eV, the value found for α_Σ agrees well with the coefficient for the dissociative recombination of Xe_2^+ ions which was measured in Ref. 10 by a method involving microwave heating of the electrons of a decaying xenon plasma. Under the conditions of Ref. 10, the time scale τ_β of the conversion of atomic ions in the process $Xe^+ + 2Xe \rightarrow Xe_2^+ + Xe$ was significantly shorter than the recombination time τ_α; i.e., the condition $[Xe_2^+] \approx n_e \gg [Xe^+]$ held. For this reason, the dissociation process could not be observed.

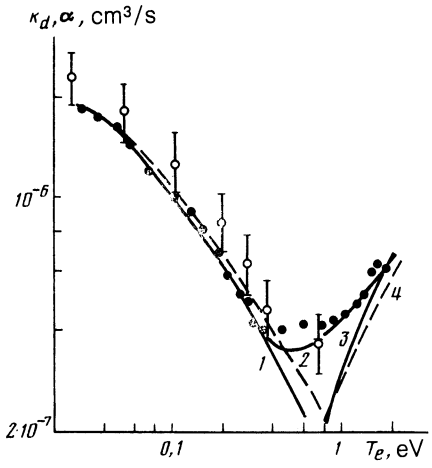

FIG. 3. ○, ●—Rate constants for the dissociation of Xe_2^+ ions by electrons according to Ref. 10 and the present study, respectively; 1–4—recombination coefficient (1, 2) and dissociation rate constant (3, 4) for the real electron energy distribution (1, 3) and for a Maxwellian one (2, 4).

We have neither measurements nor calculations of the recombination coefficients for molecular ions at temperatures $T_e \gtrsim 0.8$ eV. Distinguishing between processes (1) and (2) for $T_e \gtrsim 0.8$ eV thus requires *a priori* information on the behavior of α and k_d as a function of the electron temperature. Marchenko[7] has published some theoretical dissociation cross sections $\sigma_d^{\text{theo}}(\varepsilon)$. The following procedure was used with regard to $\alpha(T_e)$. The analysis by Eletskiĭ and Smirnov[1] shows that the existing experimental data on the temperature dependence $\alpha(T_e)$ for various ions can be interpreted on the basis of a semiclassical description by means of the Breit–Wigner formula for the cross section for the process in the approximation of a single autoionization state:

$$\sigma(\varepsilon, R) = \frac{\pi \hbar^2}{2m\varepsilon} \frac{\Gamma^2}{[\varepsilon - E_a(R)]^2 + \Gamma^2/4}, \qquad (8)$$

where ε is the energy of the electron, Γ is the width of the term to which the electron is captured, and E_a is the difference between the energy of autoionization state Xe_2^* and the energy of the molecular ion, with a distance R between the nuclei. In this approximation the recombination coefficient $\alpha(T_e)$ is found by taking an average of (8), with allowance for the distribution of the nuclei in the molecular ion with respect to the relative distance between their separation and with respect to the electron energy distribution. No claim can be made, of course, that such a procedure could lead to a correct description of the process, since the process is a multichannel process. Nevertheless, this procedure does seem reasonable for extrapolating the dependence $\alpha(T_e)$ to high electron temperatures. In the calculations, we assumed that the parameters Γ and $E_a(R)$ were independent of R, and the average was taken over the distribution function found through a numerical solution of the Boltzmann equation with allowance for electron acceleration in the field, elastic collisions with He atoms, inelastic collisions with Xe atoms in the ground and Xe 6*s* metastable states, and the interelectron interaction. The parameters E_a and Γ were found

through a least-squares fit of the experimental electron-temperature dependence $\alpha(T_e)$ in the region $T_e < 0.4$ eV, where dissociation is improbable. The experimental data were then approximated by the sum $\alpha(T_e) + k_d(T_e)$, again by the method of least squares. The adjustable parameter here was the absolute value of the cross section[7] for process (3). The results of these calculations are shown in Fig. 3. Note the good agreement between the absolute value of σ_d corresponding to the value found for the constant k_d and that calculated in Ref. 7: $\sigma_d^{\text{exp}} = 0.7\sigma_d^{\text{theo}}$. Also shown in Fig. 3 is the dissociation rate constant for the case of a Maxwellian distribution function. We see that in the range considered here, $kT_e = (2/3)\bar{\varepsilon}$, the particular distribution function has no great effect on the dissociation rate. The data obtained on the dissociation rate constant $k_d(T_e)$ can thus be used to analyze this process in various plasma entities.

4. ROLE PLAYED BY THE DISSOCIATION OF MOLECULAR IONS IN THE PLASMAS OF INERT-GAS MIXTURES USED AS LASER ACTIVE MEDIA

As an application of the results of this study, we will evaluate the role played by this dissociation under the conditions prevailing in the plasmas of high-pressure inert-gas mixtures used as the active media of lasers. Such mixtures have recently attracted much interest because of several advantages.[11,12] The best lasing characteristics have been achieved on transitions of the Xe atom in an Ar–Xe plasma during combined pumping by an electron beam and an electric discharge. The dissociative recombination of Xe_2^+ ions and electrons has been discussed in several places (e.g., Refs. 12 and 13) as a mechanism for pumping the working level. The typical parameter values of the plasma of the active medium are $n_e \approx 10^{14}$–10^{15} cm^{-3}, $P_{\text{Ar}} \approx 1000$ torr, $p_{\text{Xe}} \approx 10^{-2} p_{\text{Ar}}$ and an average electron energy of a few electron volts. Comparing the rates at which the Xe_2^+ molecular ions are formed and destroyed (for an Ar–Xe mixture the conversion rate constant is $\beta \approx 5 \cdot 10^{-31}$ cm^6/s), we find β [Ar][Xe] $\ll n_e k_d$. As can be seen from Fig. 3, the dissociation is the primary mechanism for the dissociation of Xe_2^+ ions by electrons. The density of Xe_2^+ molecular ions in a plasma of this type is thus an order of magnitude lower than it has been assumed to be in the active media based on mixtures of inert gases which have usually been discussed.

5. CONCLUSION

This study has yielded the first experimental data on the dissociation of the molecular ions Xe_2^+ in collisions with electrons in a plasma, through a study of the electron-temperature dependence of the density of molecular ions in an externally sustained discharge in a He–Xe mixture. According to the results, this process is the dominant mechanism for the dissociation of Xe_2^+ ions in plasmas with electron temperatures $T_e > 1$ eV. In view of the good agreement between the experimental and theoretical results in the case of Xe_2^+ ions, which is the case most difficult to deal with theoretically (because the spin-orbit interaction must be taken into account), one might suggest that the cross sections proposed in Ref. 7 can be used to evaluate the efficiency of the process in the plasmas of other inert gases also.

We wish to stress that this dissociation process should be considerably more effective in a highly nonequilibrium plasma, e.g., in the plasma produced by an intense electron beam or a brief pulsed discharge. The dissociation cross section at a given electron energy increases with increasing vibrational excitation of the ions, and molecular ions form primarily through conversion in highly excited vibrational states, with a binding energy on the order of the thermal energy of the particles. A systematic solution of the problem of the kinetics of molecular ions should thus include an analysis of the evolution of the populations of the vibrational levels of these ions, with allowance for dissociation in collisions with plasma electrons.

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