

# Dissociation of homonuclear ions by electron impact

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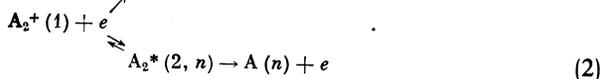
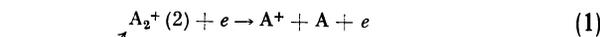
The dissociation of molecular ions in collisions with 1–10 eV electrons is considered. The dissociation cross sections are calculated for  $H_2^+$  and the excimer ions  $He_2^+$ ,  $Ne_2^+$ ,  $Ar_2^+$ ,  $Kr_2^+$ , and  $Xe_2^+$ . It is shown that, under the conditions prevailing in beam and plasma experiments, the dissociation process competes with dissociative recombination. It is established that inclusion of spin-orbit coupling in calculations of dissociation cross sections is essential and leads, in particular, to the appearance of two effective break-up channels for the heavy excimer ions.

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## 1. INTRODUCTION

The breakup of molecular ions in low-temperature plasma occurs mainly in the course of their dissociation recombination. Collisions with electrons can also lead to the dissociation of molecular ions. When the latter process predominates, positive plasma ions are largely atomic ions, and this gives rise to an important change in the rates of neutralization by charged particles. The competition between dissociative recombination and dissociation is therefore important for the kinetics of low temperature plasmas.

Dissociative recombination of ions has been extensively studied, both experimentally and theoretically (see, for example, the review given in Ref. 1). A relatively simple approach to the analytic description of this process is put forward in Ref. 2 (see also Refs. 3 and 4). Much less attention has been devoted to the dissociation process. Here, we note the numerical calculations on the dissociation of hydrogen molecular ions by electrons in Born approximation.<sup>5–7</sup> For energies  $\epsilon \gtrsim 20$  eV, these calculations result in good agreement with experimental data<sup>8,9</sup> obtained with crossed electron and ion beams. It has been shown<sup>10</sup> that the resonance dissociation of  $H_2^+$ , i.e., dissociation that proceeds through the formation of an autoionizing state, is less probable than dissociative recombination. We shall therefore analyze the competition between direct (nonresonance) dissociation (1) and the resonance process of dissociative recombinations (2) for collisions between electrons and homonuclear ions:



These two processes occur as a result of the transition  $A_2^+(1) \rightarrow A_2^+(2)$  of an internal electron in the molecular ion between states corresponding to different parities of the wave function. In dissociative recombination (2), the incident electron is captured to a level  $n$  with the formation of the autoionizing state  $S_2^*(2, n)$ . Dissociation of the heavy particles in processes (1) and (2) occurs during their motion in the repulsive state that corresponds to the excited state of the inner electron  $A_2^+(2)$ . In process (1), each excitation of the internal electron then leads to dissociation, in contrast to (2) for which the reverse process of autoionization of the elec-

tron after its capture is possible.

The dissociation cross sections of homonuclear ions is determined below for low electron energies  $\epsilon \lesssim 10$  eV. In contrast to Refs. 5–7, therefore, a more rigorous approach is to use the Coulomb-Born approximation because the acceleration of electrons in the Coulomb field of the ions must be taken into account at these energies. In the quasiclassical electron-energy range  $1/v \gtrsim 1$ , which we shall consider below, the dissociation cross sections turn out to be sufficiently high to enable us to assume that the corresponding impact parameters are greater than the characteristic distances between the nuclei. It is then reasonable to neglect all terms higher than the dipole term in the interaction between the inner electrons in the molecular ion and the incident electrons. We shall also use the quasiclassical method of averaging the dissociation cross sections over the spacings of the heavy particles for a given vibrational level  $\nu$  of the ion  $A_2^+(1)$ . The approximations just mentioned enable us to obtain analytic results (Section 2).

Specific calculations of dissociation cross sections for process (1) were performed for the homonuclear ions  $H_2^+$ ,  $He_2^+$ ,  $Ne_2^+$ ,  $Ar_2^+$ ,  $Kr_2^+$ , and  $Xe_2^+$ . The resulting cross sections were averaged over the populations of vibrational states corresponding to different experimental conditions. The spin-orbit coupling, which is taken into account by the simple "atom in molecule" approximation,<sup>11,12</sup> is important for the dissociation cross sections of the heavy ions  $Ar_2^+$ ,  $Kr_2^+$ , and  $Xe_2^+$  (see Section 3). The results of these calculations enable us to draw the following basic conclusions (Section 4).

1. The dissociation (1) of homonuclear ions can compete with dissociative recombination (2). Thus, under the conditions prevailing in beam experiments,<sup>8,9</sup> the dissociation of  $H_2^+$  predominates over the dissociative recombinations of these ions at electron energies in excess of 2 eV (see Fig. 2 below). Under equilibrium plasma conditions with low vibrational temperatures of the excimer ions  $T \sim 0.03 \div 0.05$  eV dissociation is more effective: for  $He_2^+$  at  $\epsilon \gtrsim 10$  eV; for  $Ne_2^+$  at  $\epsilon \gtrsim 4$ –eV; for  $Ar_2^+$  at  $\epsilon \gtrsim 3$ –4 eV; for  $Kr_2^+$  at  $\epsilon \gtrsim 2$ –3 eV, and for  $Xe_2^+$  at  $\epsilon \gtrsim 1.5$  eV (see Figs. 3 and 4 below).

2. The presence of spin-orbit splitting in heavy ions may ensure that the dissociation of  $A_2^+$  results in  $A^+$  mostly in

one of the two possible states  ${}^2P_{1/2}$  or  ${}^2P_{3/2}$ , depending on the electron energy (see Fig. 4).

## 2. BASIC FORMULAS

We shall determine the dissociation cross sections by using perturbation theory in the continuous spectrum. For a fixed distance  $R$  between the nuclei, the Hamiltonian for the set of electrons (written in the center-of-mass system of the heavy particles) has the following form (we are using the atomic system of units in which  $e = \hbar = m = 1$ ):

$$\hat{H} = -\frac{1}{2} \nabla_r^2 - \frac{Z}{|\mathbf{r} - \mathbf{R}/2|} - \frac{Z}{|\mathbf{r} + \mathbf{R}/2|} + \sum_{j=1}^N \frac{1}{|\mathbf{r} - \mathbf{r}_j|} + \hat{H}_{A_2^+}(\mathbf{r}_j, \mathbf{R}), \quad (3)$$

where  $\mathbf{r}$  and  $\mathbf{r}_j$  are the coordinates of the outer and inner electrons in  $A_2^+$  relative to its center of mass,  $\mathbf{R}$  is the radius vector connecting the heavy particles,  $Z$  is the nuclear charge, and  $\hat{H}_{A_2^+}$  is the Hamiltonian for the inner electrons in  $A_2^+$  (their number is  $N = 2Z - 1$ ).

In the dipole approximation, we have  $|\mathbf{r}| \gg |\mathbf{R}|$ ,  $|\mathbf{r}_j|$  and, using the relations

$$\frac{1}{|\mathbf{r} \pm \mathbf{R}/2|} = \frac{1}{r} \pm \frac{\mathbf{1} \cdot \mathbf{R}}{2r^3}, \quad \frac{1}{|\mathbf{r} - \mathbf{r}_j|} = \frac{1}{r} - \frac{\mathbf{r}_j \cdot \mathbf{r}}{r^3},$$

we can transform the Hamiltonian (3) to the simple form

$$\hat{H} = \hat{H}_e + \hat{H}_{A_2^+} + \hat{V}, \quad \hat{H}_e = \frac{1}{2} \nabla_r^2 - \frac{1}{r}, \quad \hat{V} = \left( \mathbf{r} \sum_{i=1}^N \mathbf{r}_i \right) / r^3, \quad (4)$$

where  $\hat{H}_e$  is the Hamiltonian for the outer electron in the Coulomb field of the single-charged ion, and  $\hat{V}$  is the operator representing the interaction between the outer electron and the dipole moments of the inner electrons.

We shall consider the operator  $\hat{V}$  as a perturbation of the zero-order Hamiltonian  $\hat{H}_e + \hat{H}_{A_2^+}$ . If the electron has the energy  $\varepsilon = k^2/2$  in the initial state ( $\mathbf{k}$  is the initial wave vector), while in the final state, its wave vector  $\mathbf{k}'$  lies in the range  $\mathbf{k}' + d\mathbf{k}'$ , then normalization of the initial electron Coulomb wave function  $k^{-1/2} \varphi_{\mathbf{k}}^+$  to unit current, and the normalization of the final wave function  $(2\pi)^{-3/2} \varphi_{\mathbf{k}'}^-$  to the delta-function of  $\mathbf{k}' - \mathbf{k}'_0$ , we obtain the following expression for the differential cross section for the process  $A_2^+(1) \rightarrow A_2^+(2)$  for a fixed separation between the nuclei:

$$d\sigma_{12}(\mathbf{k}, \mathbf{k}') = 2\pi |k^{-1/2} \varphi_{\mathbf{k}}^+(\mathbf{r})| \left| \langle \chi_1(\mathbf{r}_j, \mathbf{R}) \left| \frac{\mathbf{r}}{r^3} \sum_j \mathbf{r}_j \chi_2(\mathbf{r}_j, \mathbf{R}) \right. \right\rangle \times |\varphi_{\mathbf{k}'}^-(\mathbf{r})| |\delta(\varepsilon - \varepsilon' - \omega(R))| \frac{d\mathbf{k}'}{(2\pi)^3}. \quad (5)$$

The Coulomb wave functions  $\varphi_{\mathbf{k}}^+$  and  $\varphi_{\mathbf{k}'}^-$  in the continuous spectrum are superpositions of a plane and a diverging or converging spherical wave as  $r \rightarrow \infty$  (they are determined, for example, in Ref. 13). The functions  $\chi_1(\mathbf{r}_j, \mathbf{R})$  and  $\chi_2(\mathbf{r}_j, \mathbf{R})$  have opposite symmetries and are the eigenfunctions of the inner-electron Hamiltonian  $\hat{H}_{A_2^+}$ . Their eigenvalues are the energies corresponding to bound and repulsive terms;

$$U_1(R) = \langle \chi_1 | \hat{H}_{A_2^+} | \chi_2 \rangle, \quad U_2(R) = \langle \chi_2 | \hat{H}_{A_2^+} | \chi_2 \rangle.$$

The transition frequency  $\omega(R)$  corresponds to the energy

splitting of the terms for a given separation between the nuclei:  $\omega(R) = U_2(R) - U_1(R)$ . The total dissociation cross section is obtained by integrating (5) with respect to  $k'$ , and averaging over all the directions of the incident electron:

$$\sigma_{12}(k) = \frac{1}{2(2\pi)^3} \frac{k'}{k} |\langle \chi_1 | \sum_j \bar{\mathbf{r}}_j | \chi_2 \rangle|^2 \int \int dO_{\mathbf{k}} dO_{\mathbf{k}'} \times |\langle \varphi_{\mathbf{k}'}^+ | \frac{\mathbf{r} \mathbf{n}_{\mathbf{R}}}{r^3} | \varphi_{\mathbf{k}}^- \rangle|^2, \quad (6)$$

where  $\mathbf{n}_{\mathbf{R}} = \mathbf{R}/R$  is the unit vector along the axis of the ion  $A_2^+$ . The result given by (6) should be independent of the direction of the vector  $\mathbf{n}_{\mathbf{R}}$  in space, so that, after the integration with respect to  $O_{\mathbf{k}}$  and  $O_{\mathbf{k}'}$  is performed, we find that, by directing the  $z$  axis along  $\mathbf{n}_{\mathbf{R}}$  and recalling that

$$\int \int dO_{\mathbf{k}} dO_{\mathbf{k}'} \left| \left\langle \varphi_{\mathbf{k}'}^+ \left| \frac{z}{r^3} \right| \varphi_{\mathbf{k}}^- \right\rangle \right|^2 = \frac{1}{3} \int \int dO_{\mathbf{k}} dO_{\mathbf{k}'} \times \left| \left\langle \varphi_{\mathbf{k}'}^+ \left| \frac{\mathbf{r}}{r^3} \right| \varphi_{\mathbf{k}}^- \right\rangle \right|^2,$$

we obtain the following expression for the total dissociation cross section for given separation between the nuclei:

$$\sigma_{12}(k, R) = \frac{2\pi^2}{3} D_{12}^2(R) \mathcal{E}_{e, e'}^2, \quad D_{12}(R) = \left| \left\langle \chi_1(\mathbf{r}_j, R) \left| \sum_j \mathbf{r}_j \right| \chi_2(\mathbf{r}_j, R) \right\rangle \right|, \quad (7)$$

where  $D_{12}$  is the matrix element of the dipole moment of the inner-electron transition  $A_2^+(1) \rightarrow A_2^+(2)$ . The quantity  $\mathcal{E}_{e, e'}^2$  has been investigated in detail in the theory of bremsstrahlung by electrons in the Coulomb field (see, for example, Ref. 14), and is given by

$$\mathcal{E}_{e, e'}^2 = \frac{1}{2(2\pi)^4} \frac{k'}{k} \int \int \left| \left\langle \varphi_{\mathbf{k}'}^+ \left| \frac{\mathbf{r}}{r^3} \right| \varphi_{\mathbf{k}}^- \right\rangle \right|^2 dO_{\mathbf{k}} dO_{\mathbf{k}'} = g_{\Gamma}(e, e') \frac{4\pi}{\sqrt{3}k^2}. \quad (8)$$

In the quasiclassical range of electron energies in which we are interested here and for which  $\eta = k^{-1} \gg 1$ , we can use the classical limit of the Gaunt factor:

$$g_{\text{cl}}(\nu) = \sqrt[3]{\pi} \sqrt[3]{3} i\nu H_{i\nu}^{(1)}(i\nu) H_{i\nu}^{(1)*}(i\nu) = \begin{cases} \frac{\sqrt{3}}{\pi} \ln \frac{1.123}{\nu} + 1.99\nu^0, \\ 1 + \frac{0.222}{\nu^{1/2}} \end{cases}, \quad (9)$$

where  $\nu = 1/2\eta(\omega/\varepsilon) = \omega/\omega_{\text{cl}}$  is the classical frequency ( $\omega_{\text{cl}} = k^3$ ). The above simple approximation to the classical Gaunt factor, given by (9), is convenient in practical calculations.

We shall now find the dissociation cross section of the ion  $A_2^+$  in a given vibrational state  $\nu$  with the quasiclassical wave function for the nuclear motion:

$$\psi_v = \frac{2}{T_v^{1/2}} \frac{1}{V^{1/2}(R)} \cos \left( \int_{a_1}^R \mu V(R) dR - \pi/4 \right),$$

$$V(R) = [2(E_v - U_1(R)) / \mu]^{1/2}$$

where  $V(R)$  is the relative velocity of the nuclei,  $\mu = M_A + /2$  is the reduced mass,  $E_v$  is the energy in the vibrational state  $v$ , measured from the dissociation limit, and  $T_v$  is the period of the vibrational motion in the state  $v$ . Averaging the cross section (7) over the probability  $|\psi_v|^2 dR$  for heavy particles separated by the distance  $R$  and using (8), we obtain

$$\begin{aligned} \sigma_v(k) &= \frac{8\pi^2}{3\sqrt{3}} \frac{1}{k^2} \frac{2}{T_v} \int_{R^*}^{b_v} g_r(\varepsilon, \omega(R)) \frac{D^2(R)}{v(R)} dR \\ &= \frac{2\pi^2}{3\sqrt{3}} \frac{b_v^2}{k^2} g_r(\varepsilon, \omega(b_v)) \varphi(k, v). \end{aligned} \quad (10)$$

The integral in (10) is evaluated from  $R^*$  up to the right-hand turning point  $b_v$ . We then have  $R^* = R_\varepsilon$  for  $R_\varepsilon > a_v$  and  $R^* = a_v$  or  $a_v \geq R_\varepsilon$ , where  $R_\varepsilon$  is the nuclear separation corresponding to the threshold excitation at given energy, which is set by the condition  $\varepsilon = \omega(R_\varepsilon)$ , and  $a_v$  is the left-hand turning point. In (10), we have introduced the dimensionless threshold function

$$\varphi(\varepsilon, v) = \frac{2}{T_v} \frac{4}{b_v^2} \int_{R^*}^{b_v} g_r(\varepsilon, \omega(R)) \frac{D^2(R)}{v(R)} dR, \quad (11)$$

where the integral is evaluated from  $\max(R_\varepsilon, a_v)$  to  $b_v$ . For low-lying vibrational states,  $v \sim 1$ , we can ignore the slow variation in the function  $g_r D^2$  within the interval  $(a_v, b_v)$ , and take its value corresponding to the equilibrium nuclear separation  $R = R_\varepsilon$  outside the integral. Using the Morse potential to describe the bound term

$$U_1(R) = E_0 \left[ \exp \left( -2\alpha \frac{R - R_\varepsilon}{R_\varepsilon} \right) - 2 \exp \left( -\alpha \frac{R - R_\varepsilon}{R_\varepsilon} \right) \right] \quad (12)$$

and evaluating the integral in (11), we obtain

$$\begin{aligned} \sigma_v(k) &= \frac{8\pi^2}{3\sqrt{3}} \frac{D^2(R_\varepsilon)}{k^2} g_r(\varepsilon, \omega(R_\varepsilon)) \varphi_0(\varepsilon, v), \quad v_{max} \gg v \gg 1, \quad (13a) \\ \varphi_0(\varepsilon, v) &= \frac{1}{2} + \frac{1}{\pi} \arctg \frac{1 - |\beta_v| \mp [1 + u(R^*)]^{1/2}}{[|\beta_v| (-|\beta_v| - u(R^*))]^{1/2}} \\ &(0 \leq \varphi_0 \leq 1), \end{aligned} \quad (13b)$$

where  $u(R) = U_1(R)/E_0$ ,  $B_v = E_v/E_0$ . The negative sign in (13b) correspond to energies  $\varepsilon = k^2/2$ , where  $R^*$  lies on the right-hand branch ( $b_v > R^* = R_\varepsilon > R_\varepsilon$ ), and the positive sign is taken for higher energies  $\varepsilon$  for which  $a_v \leq R^* = \max\{a_v, R_\varepsilon\} < R_\varepsilon$ .

From the point of view of the kinetics of formation or breakup of molecular ions, it is interesting to consider, in addition to the low values of  $v$ , the dissociation cross section for higher vibrational states  $v \gg 1$ , for which (13) is no longer valid. The threshold behavior of the function  $\varphi(\varepsilon, v)$  for  $v \gg 1$  [see (11)] can, nevertheless, be described with the aid of (13b). This is so because the main contribution to the integral in (11) is provided by the right-hand turning point  $R = b_v$ , so that the function  $g_r D^2$  at this point can be taken outside the integral sign [ $R_\varepsilon$  in (13a) must then be replaced with  $b_v$ ].

Numerical calculations based on (11) [using the approximation  $D(R) = R/2$  (see below)] show that there is good agreement with the function  $\varphi_0(\varepsilon, v)$  in the threshold region  $\varepsilon \gtrsim \omega(b_v)$ , and give the value  $\approx 1/2$  for  $\varepsilon = \omega(R_\varepsilon)$ , i.e.,  $u(\varepsilon) = -1$ . We can use this to obtain a more accurate analytic approximation for the case  $v \gg 1$ :

$$\sigma_v(k) = \frac{8\pi^2}{3\sqrt{3}} \frac{D^2(b_v)}{k^2} g_r(\varepsilon, \omega(b_v)) \varphi_1(k, v), \quad v \gg 1, \quad (14a)$$

where  $\varphi_1 = 1/2$  for  $R_\varepsilon \leq R_\varepsilon$ , whereas for  $b_v \geq R_\varepsilon \gg R_\varepsilon$ , we have

$$\varphi_1(\varepsilon, v) = \frac{1}{4} \frac{|\beta_v| [1 - |\beta_v u|]^{1/2}}{[1 - |\beta_v|]^{1/2} - 1 + |\beta_v|}, \quad (14b)$$

where  $\varphi_1(\varepsilon, v)$  has the threshold behavior that is identical with that of  $\varphi_0(\varepsilon, v)$ , and also gives the correct value for  $R_\varepsilon = R_\varepsilon$ .

The total dissociation cross section, averaged over the relative populations of the vibration-rotation levels, is given by

$$\sigma_d(\varepsilon) = \sum_{vJ} \sigma_{vJ}(\varepsilon) \exp(-E_{vJ}/T) / g_{rot}(T) g_{vib}(T). \quad (15a)$$

In the approximation of a harmonic oscillator and a rigid rotator, i.e.,  $E_{vJ} = \omega_e(v + 1/2) + B_e J(J + 1)$ , the partition functions  $g_{vib}$  and  $g_{rot}$  by the following expressions (see, for example, Ref. 15):

$$\begin{aligned} g_{vib} &= \exp \left( -\frac{\omega_e}{2T} \right) \left[ 1 - \exp \left( -\frac{\omega_e}{T} \right) \right]^{-1}; \\ g_{rot} &= \sum_J (2J+1) e^{-B_e J(J+1)/T} \approx \frac{T}{B_e}. \end{aligned} \quad (15b)$$

For the heavy excimer ions  $Ne_2^+$ ,  $Ar_2^+$ ,  $Kr_2^+$ ,  $Xe_2^+$  with low vibrational energies ( $\varepsilon_e = 0.065, 0.036, 0.022$ , and  $0.014$  eV, respectively), it is more convenient in the case of the Boltzman distribution with temperature  $T \gtrsim \omega_e$  to use averaging over the probability

$$\frac{N_A^+ N_A}{N_{A_2^+}} 4\pi R^2 dR \exp \left( -\frac{U(R)}{T} \right)$$

of finding the atoms  $A^+$  and  $A$  separated by the distance  $R$  in the molecule  $A_2^+$  (we assume, naturally, that  $N_{A_2^+} \gg N_{A^+}$ ). In the case of equilibrium dissociation, we have

$$\frac{N_A^+ N_A}{N_{A_2^+}} = \frac{1}{8} \left( \frac{M_A T}{\pi} \right)^{3/2} \frac{B_e}{T} \frac{1 - \exp(-\omega_e/T)}{\exp(-\omega_e/2T)} \exp \left( -\frac{E_0}{T} \right),$$

where  $B_e$  is the rotational constant,  $M_A$  is the mass of atom  $A$ , and we have used the expressions given by (15b) for the partition functions  $g_{vib}$  and  $g_{rot}$ .

If we use these results to evaluate the average of (7) over the nuclear spacings, we obtain the following expression for the total cross section.

$$\begin{aligned} \sigma_{12}(\varepsilon) &= \frac{2\pi^{3/2} M_A^{3/2} B_e T^{3/2}}{3\sqrt{3}} \frac{1 - \exp(-\omega_e/T)}{\varepsilon \exp(-\omega_e/2T)} \\ &\int_{R^*}^{\infty} g_r(\varepsilon, \omega(R)) R^2 D^2 e^{-E(R)/T} dR, \end{aligned} \quad (16a)$$

where  $E(R) = E_0 + U(R)$  is the term energy measured from the bottom of the potential well. We note that, when  $T \gtrsim \omega_e$ ,

the "classical" method of averaging used in (16) is equivalent to performing the quasiclassical averaging with the aid of (10) and (15a) (see Appendix).

At low temperatures,  $\omega_e/2 \ll T \ll E_0$ , for which the main contribution to the cross section is provided by spacings near the bottom of the well, i.e., the harmonic-oscillator approximation suffices, we obtain the following simpler formula from (16a):

$$\sigma_{12}(\varepsilon) = \frac{\pi^2 M_A B_e T}{3\sqrt{3} \varepsilon \alpha E_0^{3/2}} \frac{1 - \exp(-\omega_e/T)}{\exp(-\omega_e/2T)} g_{\Gamma}(\varepsilon, \omega(R_e)) R_e^3 D^2(R_e) \times \left\{ 1 \mp \operatorname{erf} \left( \alpha \left( \frac{E_0}{T} \right)^{1/2} \frac{R_e - R_e}{R_e} \right) \right\}, \quad (16b)$$

where the negative sign corresponds to energies for which  $R_e > R_e$  and the positive sign corresponds to  $R_e < R_e$ ;  $\operatorname{erf}(x)$  is the probability integral.

### 3. TRANSITION DIPOLE MOMENT, INCLUDING SPIN-ORBIT COUPLING

For large separation,  $R \gg 1$ , between the nuclei, the asymptotic wave functions  $\chi_1$  and  $\chi_2$  of the homonuclear ion  $A_2^+$  readily yield  $D_{12}(R) = R/2$  (see, for example, Ref. 16). However, numerical calculations performed for  $H_2^+$  have shown<sup>17</sup> that the  $R/2$  approximation is satisfactory up to separations close to the bottom of the well (the uncertainty is about 5%). For the excimer ions, the dependence of the transition dipole moment on the nuclear separation exhibits features connected with the presence of spin-orbit coupling. In the  $LS$ -coupling approximation, i.e., when the spin-orbit interaction is ignored, the ion  $A_2^+$  has four terms: the ground term  $^2\Sigma_u$  and the repulsive excited terms  $^2\Pi_g$ ,  $^2\Pi_u$ ,  $^2\Sigma_g$  (in order of increasing energy). Two transitions are allowed, namely,  $^2\Sigma_u \rightarrow ^2\Sigma_g$  and  $^2\Pi_g \rightarrow ^2\Pi_u$  for which the matrix elements  $D_{12}(R)$  are in good agreement with  $R/2$  when  $R \gtrsim R_e$ . When  $R = R_e$ , the error in the  $R/2$  approximation is at a maximum in the range  $R \gtrsim R_e$  in which we are interested and amounts to 3% for  $Ne_2^+$ , 10% for  $Ar_2^+$ , 18% for  $Kr_2^+$ , and 24% for  $Xe_2^+$ .<sup>12</sup> The  $LS$ -coupling approximation is justified when the nuclei approach one another to distances  $R$  for which the spin-orbit interaction can be neglected in comparison with the exchange interaction. For excimer ions  $He_2^+$  and  $Ne_2^+$ , this is valid in practically the entire Frack-Condon range of nuclear spacings because the spin-orbit splitting is then small  $\Delta_{so} = 6.3 \times 10^{-3}$  eV for  $Ne^+$  and  $\Delta_{so} = 0.177; 0.666; \text{ and } 1.31$  eV for  $Ar^+, Kr^+, Xe^+$  when the dissociation energies  $E_0$  of the ions  $Ne_2^+, Ar_2^+, Kr_2^+$ , and  $Xe_2^+$  are, respectively, 1.2, 1.15, 1.03, and 0.79 eV). For  $Ar_2^+$  and the heavier ions,  $LS$ -coupling breaks down even at small separations ( $R \approx 6.5a_0 \approx 1.4R_e$  for  $Ar_2^+$ ,  $R \approx 5.5a_0 \approx R_e$  for  $Kr_2^+$ , and so on). The molecular wave functions in the  $|J\Omega\rangle$ -representation of the ground  $|I(1/2)_u\rangle$  and the excited  $|II(1/2)_g\rangle$  states (to which dipole transitions are possible) for intermediate-type coupling can be expanded in terms of the  $LSD$  coupling functions, as follows ( $A\Sigma$ -representation,  $\Omega = A + \Sigma$ ; see, for example, Ref. 14):

$$|I(1/2)_u\rangle = a|^2\Sigma_u^+\alpha\rangle + b|^2\Pi_u^+\beta\rangle, \quad |I(3/2)_g\rangle = |^2\Pi_g\alpha\rangle,$$

$$|I(1/2)_g\rangle = c|^2\Sigma_g^+\alpha\rangle + d|^2\Pi_g^+\beta\rangle,$$

$$|II(1/2)_g\rangle = d|^2\Sigma_g^+\alpha\rangle - c|^2\Pi_g^+\beta\rangle,$$

where  $\alpha, \beta$  are the spin wave functions. Hence, it is clear that the  $I(1/2)_u \rightarrow I(3/2)_g$  transition remains practically forbidden because the  $^2\Sigma_u \rightarrow ^2\Pi_g$  transitions is weak (see Ref. 12) and the  $|^2\Pi_u\beta\rangle \rightarrow |^2\Pi_g\alpha\rangle$  transition is connected with a change in the spin component. In the  $R/2$  approximation for the  $I(1/2)_u \rightarrow I(1/2)_g$  and  $I(1/2)_u \rightarrow II(1/2)_g$  transitions, we have

$$D_{II} = \langle I(1/2)_u | z | I(1/2)_g \rangle = 1/2 R (ac + bd),$$

$$D_{I,II} = \langle I(1/2)_u | z | II(1/2)_g \rangle = 1/2 R (ad - bc).$$

In the region in which  $LS$ -coupling is valid, so that  $b = c = 0, a = d = 1$ , we have  $D_{I,II} = R/2$ , and  $D_{II} = 0$ , as expected. In the opposite limit of  $jj$ -coupling, i.e., large nuclear separation [for which the coefficients  $a, b, c, d$  are identical with the Clebsch-Gordan coefficients connecting the wave functions in the  $J\Omega$  representation, i.e.,  $a = c = 02/3)^{1/2}, b = d = 1/3]$ , we have  $D_{II} = R/2$  and  $D_{I,II} = 0$ . It is clear, even from the asymptotic behavior of the matrix elements  $D_{II}$  and  $D_{I,II}$ , that, for separations for which the exchange interaction is comparable with the spin-orbit interaction, the  $R/2$  approximation is unsatisfactory.

The potential curves for the  $J\Omega$  representation and the dipole moment matrix elements were calculated in Ref. 12 (see Fig. 1 and Table I) for the range of separations corresponding to intermediate coupling. This calculation was based on the sufficiently reliable, semiempirical "atom in molecule" approximation<sup>11</sup> in which the magnitude of the spin-orbit interaction is assumed to be independent of the nuclear separation. The "atom in molecule" approximation is based on experimental data on spin-orbit splitting in atomic ions. It is clear from the table that the increase in the nuclear separation is accompanied by a gradual transition from values  $D_{I,II} = R/2 \gg D_{II}$  to  $D_{II} R/2 \gg D_{I,II}$ , which is in accordance with the foregoing.

Thus, inclusion of the spin-orbit interaction leads to

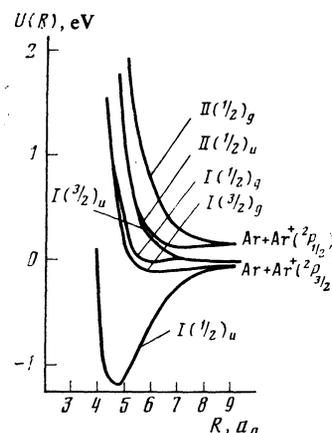


FIG. 1. Typical potential curves for an excimer ion (the example of  $Ar_2^+$ ), including the spin orbit interaction in accordance with Ref. 12.

TABLE I. Dipole moment matrix elements for the transitions  $I(1/2)_u \rightarrow I(1/2)_g$  and  $I(1/2)_u \rightarrow II(1/2)_g$  in  $Ne_2^+$ ,  $Ar_2^+$ ,  $Kr_2^+$  and  $Xe_2^+$ .

$R, a_0$	$Ne_2^+, R_e = 3.3$		$Ar_2^+, R_e = 4.75$		$Kr_2^+, R_e = 5.25$		$Xe_2^+, R_e = 5.75$	
	I - I	I - II	I - I	I - II	I - I	I - II	I - I	I - II
3.5	0.075	1.7	—	—	—	—	—	—
4	0.154	1.94	0.0687	1.63	—	—	—	—
5	0.646	2.37	0.207	2.23	0.462	1.91	0.497	1.42
6	2.07	2.11	0.641	2.74	1.26	2.26	1.28	1.9
7	3.33	0.92	1.84	2.83	2.62	1.89	2.44	1.7
8	3.95	0.301	3.54	1.67	3.68	0.994	3.46	1.08

two possible dissociation channels:  $I \rightarrow I$  and  $I \rightarrow II$ , where the  $I(1/2)_u \rightarrow II(1/2)_g$  transition provides a contribution for small nuclear spacings, and the  $I(1/2)_u \rightarrow I(1/2)_g$  transition contributes for large spacings. For the heavier excimer ions  $A_2^+$ , the  $I \rightarrow I$  channel should assume increasing importance, since this transition becomes allowed for nuclear spacings approaching the equilibrium value (at least for  $Kr_2^+$  and  $Xe_2^+$ ).

#### 4. RESULTS OF CALCULATIONS AND DISCUSSION

(a) The dissociation cross sections of  $H_2^+$  in different vibrational states  $v = 0$  to 8, calculated from (10), are shown in Fig. 2. We note that the difference between the analytic formulas (13) and (14), on the one hand, and (10), on the other, does not exceed 20–30%. The comparison given in Fig. 2 between the calculated<sup>2</sup> dissociative recombination cross sections of  $H_2^+$  for given states  $v$  shows that the dissociation cross sections become rapidly predominant above the threshold dissociation energies  $\epsilon = \omega(b_v)$  for this particular level.

In the experiments reported in Refs. 8 and 18, the  $H_2^+$  beams were produced by ionizing hydrogen molecules with fast electrons. The distribution over vibrational states is then proportional to the Franck-Condon factors between the ground vibrational state of the molecule and the vibrational states of the ion. The precise distribution over the vibrational states was measured in experiments<sup>19</sup> on the photodissociation of the molecular ion  $H_2^+$ , and is used here to average the dissociation cross section in accordance with (15a). Comparison of the result with experimental dissociative recom-

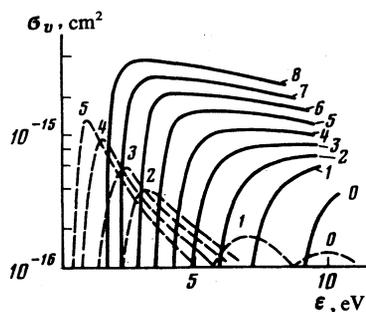


FIG. 2. Dissociation cross sections [the solid curves are calculated from (10)] and cross sections for dissociative recombination [the dashed curves are based on Ref. 2] for  $H_2^+$  with given vibrational quantum number  $v$  (indicated by the numbers shown against the curves).

bination cross sections<sup>18</sup> shows that preferential dissociation occurred in these experiments for electron energies  $\epsilon \gtrsim 2.2$  eV (see Fig. 3).

(b) The dissociation cross sections of the excimer ions  $H_2^+$ ,  $Ne_2^+$ ,  $Ar_2^+$ ,  $Kr_2^+$ , and  $Xe_2^+$  were averaged with the aid of (15a) and (16a) by using the Boltzmann distribution over the vibrational levels. These cross sections increase rapidly with increasing vibrational temperature in the region of the dissociation threshold, since dissociation then becomes possible at lower electron energies that correspond to term-splitting at the right-hand turning point of the vibrationally-excited levels. Vibrational temperatures of the order of the temperature of the heavy particles, i.e.,  $T \simeq 0.03$ – $0.05$  eV, are of the greatest interest for plasma experiments. For the  $He_2^+$  ions, the temperature is  $T < \omega_e/2 \sim 0.1$  eV, so that the dominant contribution to the dissociation cross section is provided by the  $v = 0$  ground state, and it is convenient to use (15a) in the averaging procedure. For the heavier ion  $Ne_2^+$ ,  $Ar_2^+$  and so on, we have  $T \gtrsim \omega_e/2$ , so that the “classical” averaging procedure based on (16) was employed.

Figures 3 and 4 show the calculated dissociation cross sections of the excimer ions. Detailed comparison with the dissociative recombination cross sections (rates) are complicated in this case because the dependence of these cross sec-

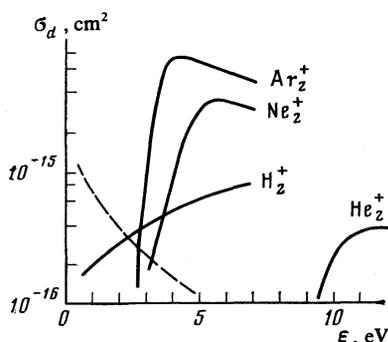


FIG. 3. Cross sections for the dissociation of  $He_2^+$ ,  $Ne_2^+$  and  $Ar_2^+$  due to the excitation of the transition  ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$  (which is important for these ions) or  $I(1/2)_u \rightarrow II(1/2)_g$  (in the  $jj$ -coupling notation). The cross sections were calculated from (15a) and (16a) for the vibrational temperature  $T = 0.03$  eV. Comparison of the dissociation cross sections of  $H_2^+$  averaged over the nonequilibrium distribution of vibrational-level populations (corresponding to the conditions prevailing in the beam experiments reported in Refs. 8 and 18) with experimental data from Ref. 18 on the total dissociative recombination cross section for these ions (dashed curve).

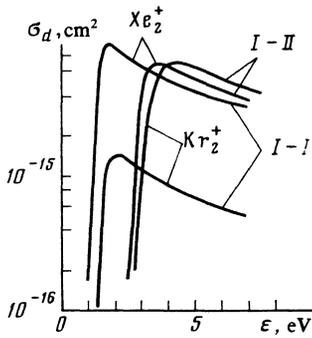


FIG. 4. Dissociation cross section of the heavy excimer ions  $Kr_2^+$  and  $Xe_2^+$  due to the excitation of  $I(1/2)_u \rightarrow II(1/2)_g$ ,  $I(1/2)_u \rightarrow I(1/2)_g$  transitions, calculated from (16a) for the vibrational  $T = 0.03$  eV.

tions on the degree of vibrational excitation of molecular ions has not been adequately explored (see, for example, Refs. 1 and 20). Estimates suggest that, in equilibrium situations (i.e., when vibrational relaxation succeeds in establishing the distribution over the levels  $v$ ) with reasonable vibrational temperatures  $T \leq 0.03 - 0.1$  eV, the dissociation process begins to compete only at high electron energies:  $\epsilon \gtrsim 10$  eV for  $He_2^+$ ,  $\epsilon \gtrsim 4 - 5$  eV for  $Ne_2^+$ ,  $\epsilon \gtrsim 3 - 4$  for  $Ar_2^+$ ,  $\epsilon \gtrsim 2 - eV$ , for  $Kr_2^+$ ,  $\epsilon \gtrsim 1.5$  eV for  $Xe_2^+$  (see Figs. 3 and 4 and data on the rates of dissociative recombination<sup>1</sup>).

(c) Dissociation of the excimer ions is affected by the presence of the spin-orbit interaction. This ensures that appreciable dissociation occurs for the heavy ions  $Kr_2^+$  and  $Xe_2^+$  even at low electron energies  $\epsilon \sim 1.5$  eV (see Fig. 4) as a result of the excitation of the  $I(1/2)_u \rightarrow I(1/2)_g$  transition, which is allowed in these ions, as indicated in Sec. 3 (the spacing of the terms  $I(1/2)_u$  and  $I(1/2)_g$  is much smaller than of the terms  $I(1/2)_u$  and  $II(1/2)_g$ ; see Fig. 1). We note that the dissociation of  $Kr_2^+$  by electron impact may result in the effective formation of the  $Kr_2^+$  ion in two possible states, namely,  $^2P_{1/2}$  and  $^2P_{3/2}$ , where the formation of the metastable state  $^2P_{1/2}$  corresponds to the transition  $I(1/2)_u \rightarrow II(1/2)_g$  by inner electrons in the excimer ion which is excited only at sufficiently high energies  $\epsilon \gtrsim 4$  eV (see Fig. 4). We note that the fraction of ions in the  $^2P_{3/2}$  is no more than 10%. At lower electron energies ( $\epsilon \approx 2$  eV), the  $Kr_2^+$  ion dissociates in the  $^2P_{3/2}$  ground state (the fraction of ions in the  $^2P_{1/2}$  state is less than 1%). This provides us, for example, with the possibility of producing a beam of atomic ions with a given resultant angular momentum  $\hat{j} = \hat{l} + \hat{s}$  by exploiting the dissociation of the molecular ions  $Kr_2^+$  by electrons.

(d) The dissociation process can be much more effective in strongly nonequilibrium situations, for example, fast processes in shock tubes, in discharges with high degree of ionization and high electron energies (non-Maxwellian distributions play a significant role here), beam experiments, and so on. High vibrational states of the molecular ions are then populated, so that interaction with electrons should result in preferential dissociation, i.e., a change in the ion species (from  $A_2^+$  to  $A^+$ ) and, corresponding, in the rate of recombination of the charged particles. Precisely this situation appears to have been observed in experiments on the dissociative recombination of  $Ne_2^+$  and  $Ar_2^+$  in shock tubes.<sup>21,22</sup>

However, it does not seem possible to draw an unambiguous conclusion about the mechanism responsible for the dissociation process (i.e., whether it was due to electron or heavy-particle impact, as suggested in Ref. 23) because of the absence of information on the distribution over the vibrational states. We note, however, the ideas put forward in Ref. 24 (p. 308), which are equivalent to the proposition that dissociation by heavy particles is unlikely since the thermodynamic equilibrium between the densities of atomic and molecular ions cannot be established for the fast process occurring in shock tubes.

The author is indebted to I. S. Lakoba, O. B. Firsov, and M. I. Chibisov for discussions of the above results.

## APPENDIX

We shall prove that averaging procedures based on (15a) and (16a) are equivalent for  $T \gtrsim \hbar\omega_e$ . To do this, we replace the summation in (15a) over the quantum numbers  $v$  and  $J$  by integration:

$$\sigma_d(\epsilon, T) = \frac{4\pi^2}{3\sqrt{3}} \frac{1}{\epsilon} \frac{1}{g_{\text{rot}}(T)g_{\text{vib}}(T)} \int \int_{v,J} (2J+1) e^{-E_{vJ}/T} \times \int_{R_e}^{b_v} g_r(\epsilon, \omega) \frac{D^2}{V(R)} dR dJ dv. \quad (\text{A.1})$$

The integral with respect to  $v$  and  $J$  is evaluated for

$$E_{vJ} = \omega_e(v + 1/2) + B_e J(J+1) \geq E_0 + U(R_e).$$

We now introduce the continuous variable  $E = E_{vJ} - (E_0 + U(R))$  (for given  $R$ ), and reverse the order of integration in (A.1). We thus obtain

$$\sigma_d(\epsilon, T) = \frac{4\pi^2}{3\sqrt{3}} \frac{1}{\epsilon g_{\text{rot}}(T)g_{\text{vib}}(T)} \int_{R_e}^{\infty} g_r(\epsilon, \omega) D^2 \exp\left(-\frac{E_0 + U(R)}{T}\right) \times dR \int_0^{\infty} \frac{dJ dv (2J+1) e^{-E/T}}{V_E(R) (T_v/2)},$$

$$V_E(R) = \left[ \frac{2}{\mu} (E_{vJ} - E_0 - U(R)) \right]^{1/2} = \left( \frac{2}{\mu} E \right)^{1/2}. \quad (\text{A.2})$$

If we restrict the radial motion in the continuous spectrum to a sufficiently large  $\Delta R = V_E T_v / 2$  and recall the quantization conditions for radial  $\mu V_{E\perp} \Delta R = 2\pi v \hbar$  and azimuthal  $\mu v_{E\parallel} R = J \hbar$  motions, we can evaluate the integral with respect to  $v$  and  $J$  in (A.2), i.e., we obtain

$$\frac{1}{\Delta R} \int_0^{\infty} \exp\left(-\frac{\mu v_{E\perp}^2}{2T} - \frac{\mu v_{E\parallel}^2}{2T}\right) dv dJ = \pi R^2 \left(\frac{\mu T}{\pi \hbar^2}\right)^{3/2}.$$

This can be used to show that the average dissociation cross section is given by

$$\sigma_d(\epsilon, T) = \frac{2\pi^{3/2}}{3\sqrt{3}} \frac{1}{\epsilon} \frac{(M_A T)^{3/2}}{g_{\text{rot}}(T)g_{\text{vib}}(T)} \times \int_{R_e}^{\infty} g_r(\epsilon, \omega) D^2(R) \exp\left(-\frac{E_0 + U(R)}{T}\right) R^2 dR. \quad (\text{A.3})$$

Finally, if we substitute the expression for the partition functions (15b) in (A.3), we obtain a formula that is identical with

the classical average (16a). We note that, when  $T < \hbar\omega_e$ , these averaging procedures are not completely equivalent because classical averaging gives the maximum probability of finding the particle at the bottom of the potential well, whereas the quasiclassical approximation gives the corresponding probability near the turning point.

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