Dissociative recombination of an electron and a molecular ion

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It is shown that the multichannel problem of the recombination of an electron and a molecular ion can be rigorously reduced to the determination of an optical potential for the elastic scattering of an electron by a molecular ion. A method, based on the formalism of many-particle theory, is proposed and makes it possible to construct the optical potential. As a result, formulas are derived for the reasonance part of the dissociative-recombination cross section with allowance for strong channel coupling. These formulas are used to calculate the cross section for dissociative recombination of an electron and a molecular-oxygen ion in various vibrational states. All the quantities in the formula for the cross section are determined by the present method, and are not adjustable parameters. The results are in satisfactory agreement with the experimental data.

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1. INTRODUCTION

Processes involving the scattering of electrons by molecules and molecular ions play a leading part in low-temperature plasma dynamics. Many papers have been published on these processes.[1] Nevertheless, many basic problems of the scattering of electrons by molecules remain unsolved. This is mainly the case for problems involving the effect of excited states of molecules and molecular ions on the cross sections for such processes as dissociative recombination, dissociative attachment, etc.

In this paper we consider one of the most important processes for plasma physics—dissociative recombination (DR)—and propose a method, based on the formalism of many-body theory, which makes it possible not only to interpret the available experimental data on DR cross sections correctly, but also to solve many fundamental problems of that phenomenon, including, in particular, the problem of the dependence of the DR cross section on the vibrational state of the ion. The results permit conclusions to be drawn concerning the part played by vibrationally excited ions in the dynamics of a low-temperature plasma.

Many authors have investigated the DR process.[2] The refinement of experimental tehcniques has now made it possible to investigate not only the DR rate constant, but also the DR cross section, which has a characteristic reasonance structure for some molecules (O_2, NO, and others).[3] In addition, there are experimental measurments of the dependence of the DR rate constant on the vibrational temperature of the ion (see, e.g., Ref. 4). Under various discharge conditions, however, especially at low pressures when the approximation of a vibrational temperature is not valid, i.e., when the vibrational levels do not have a Boltzmann distribution, it is necessary to know the dependence of the DR cross section on the number of the vibrational (electronic) state of the ion. There are no such experimental data in the literature, so a theoretical study is required.

The current approach to this problem[5] does not fully reflect the essence of the DR phenomenon: it does not take into account the resonance structure of the cross section.

Let us consider the DR process within the framework of the traditional model.[2] The incident electron first excites a target electron and undergoes a transition to the discrete spectrum. As a result, an autoionizing state of the molecule is formed which, as a rule, is a dissociative term, the nuclei remaining fixed at the electron-capture point R_c. After that the nuclei separate and dissociation takes place.

Thus, the DR process is by its nature a resonance process.[6] However, the study of DR, even within the limitations of the cited model, is a very complicated enterprise. The trouble is that there are many "suitable" autoionizing states and their density is rather high. As a result, in calculating DR cross sections one is faced with a multichannel problem.[7] The numerical methods now available for solving such problems[8] turn out actually to be applicable only to the simplest molecules such as H_2. In the case of molecules of practical interest (O_2, N_2, etc.) one usually has to neglect the interchannel correlations.[6] An alternative method for solving multichannel problems is to construct an optical potential[9]; in the general case this, too, is a rather laborious problem but, as will be shown below (see Sec. 3), it is quite solvable for molecules such as O_2, N_2, F_2, etc.

2. THE CROSS SECTION FOR DISSOCIATIVE RECOMBINATION

As was noted above, the DR process takes place in two stages. The incident electron is first captured in an autoionizing state which, as a rule, is a dissociative term of the molecule. If the lifetime of this state against electron emission is long enough, dissociation takes place. For the incident electron to undergo a transition to the discrete spectrum, it must lose some of its energy. Hence the capture of the incident electron must be accompanied by excitation (either electronic or vibrational) of the target molecule. The transfer of energy of the incident electron directly to the nuclei can take place only as a result of nonadiabatic effects. We shall show that such effects can be neglected in the case of DR. First, we note that the interaction between the motions of the nuclei and the electrons is weak (of the order of $(m/M)^{1/2}$, where m

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and M are the masses of the electron and the nuclei). Moreover, most of the dissociative terms of the molecule are not geneologically related to the ground state of the ion. In the case of the O_2^+ ion $3\sigma_g^2 1\pi_u^4 1\pi_g$, for example, the DR process goes via states with the configurations $3\sigma_g^2 1\pi_4^3 1\pi_g^3$, $3\sigma_g^1 1\pi_u^4 1\pi_g^3$, etc. In other words, to form a dissociative term of the molecule in the course of the DR process it would be necessary to restructure the electron shell of the ion, and this cannot be done on the basis of nonadiabatic transitions. Hence nonadiabatic effects can be neglected in the case of DR. We shall carry through the further analysis of the DR process within the limitations of the Born-Oppenheimer approximation, using the methods of the steady-state theory of scattering with redistribution.[9]

We shall assume that the electron-emission width Γ of an autoionizing state is not very large, i.e., that $\hbar/\Gamma > \Delta R/\bar{v}$, where ΔR is the distance from the electron-capture point R_c to the point R_{cr} where the ionic term crosses the term of the autoionizing state, and $\bar{v}$ is the mean separation velocity of the nuclei. This allows us to neglect electronic transitions in the dissociation of an autoionizing state, i.e., we shall assume that the nuclei separate long some definite term.

O'Malley[10] has presented the formal theory of electron scattering by a diatomic target molecule in the most general form. Following Ref. 10, we separate the complete wave function of the system into two parts, $Q\psi$ and $P\psi$, where Q and P are projection operators onto the scattering channel with (Q channels) and without (P channels) restructuring. There may actually be many Q channels; in that case we write $Q = \Sigma_j Q_j$. The operators P and Q have the following obvious properties:

$$PQ=QP=0, \quad P^2=P, \quad Q^2=Q, \quad P+Q=1.$$

The functions $P\psi$ and $Q\psi$ satisfy the following integral equations

$$P\psi=|\Phi_P\rangle+\hat{G}_P PHQQ\psi, \tag{1a}$$

$$Q\psi=\hat{G}_Q QHPP\psi, \tag{1b}$$

in which $\hat{G}_P$ and $\hat{G}_Q$ are the Green's operators for the P and Q channels,

$$\hat{G}_P=(E-PHP)^{-1}, \quad \hat{G}_Q=(E-QHQ)^{-1},$$

H is the complete Hamiltonian for the system, and $|\Phi_P\rangle$ is the asymptotic expression for $P\psi$.

Now let us determine the usual asymptotic conditions in the P and Q channels. In the P channel, the function $P\psi$ behaves asymptotically as

$$\Phi_P = \psi_P(r)\psi_e(r,R)\chi_v(R),$$

where $\psi_P(r)$ is a Coulomb wave, while $\psi_e(r,R)$ and $\chi_v(R)$ are the electronic and vibrational wave functions of the ion. We define the asymptotic behavior of the wave function in the Q channel so that it will correspond to two isolated atoms A and B, i.e.,

$$\Phi_Q=\psi_A\psi_B\chi_k(R),$$

where ψ_A and ψ_B are atomic wave functions and $\chi_k(R)$ is a plane wave.

In the case the channel V_P and V_Q have the form

$$V_P=\sum_m \frac{e^2}{|\mathbf{r}-\mathbf{r}_m|},$$

where the summation is over all the electrons in the ion, and $V_Q = E_Q(R)$ is the dissociative term of the molecule.

Let us assume that $\hat{G}_Q$ is do defined as to take all the Q-channel correlations into account (see Sec. 3). Then Eqs. (1) can be solved separately for each j-th channel Q_j. On substituting (1a) into (1b), we obtain

$$Q_j\psi=\hat{G}_{Q_j}Q_jHP|\Phi_P\rangle+\hat{G}_{Q_j}Q_jHP\hat{G}_P PHQ_jQ_j\psi. \tag{2}$$

Since (2) is a single-channel equation, it can be solved formally:

$$Q_j\psi=\frac{\hat{G}_{Q_j}Q_jHP|\Phi_P\rangle}{1-\hat{G}_{Q_j}Q_jHP\hat{G}_P PHQ_j}. \tag{3}$$

Then we obtain the following expression[9] for the t matrix for Q_j-channel scattering:

$$t_j=\langle\Phi_{Q_j}|V_{Q_j}|Q_j\psi\rangle$$

$$=\frac{\langle\Phi_{Q_j}|V_{Q_j}Q_jHP|\Phi_P\rangle}{E-E_j-\langle\Phi_{Q_j}|Q_jHP\hat{G}_P PHQ_j|\Phi_{Q_j}\rangle}, \tag{4}$$

where E_j is the energy of the j-th autoionizing state.

We write E_j^0 for the energy of the j-th autoionizing state without allowance for Q-channel correlations (the Hartree-Fock energy); then

$$M_j=E_j-E_j^0+\langle\Phi_{Q_j}|Q_jHP\hat{G}_P PHQ_j|\Phi_{Q_j}\rangle$$

is the mass operator for the autoionizing state and the expression for the t matrix takes the form

$$t_j=\frac{\langle\Phi_{Q_j}|V_{Q_j}Q_jHP|\Phi_P\rangle}{E-E_j^0-M_j}. \tag{4a}$$

The imaginary part of M_j determines the half-width $\Gamma_j/2$ of the j-th autoionizing state. Thus, the problem reduces to that of accurately determining M_j.

We shall treat the ground state of the ion as the vacuum. This permits us to deal with the single-particle Green's function G_Q alone. In that case

$$t_j=\frac{\langle\Phi_{Q_j}|(\varepsilon_j^0+M_j)Q_jHP|\Phi_P\rangle}{\varepsilon-\varepsilon_j^0-M_j}, \tag{5}$$

where ε_j^0 is the electron-capture resonance energy and ε is the energy of the incident electron.

It has been shown[11] that the motion of the nuclei in the dissociation process can be treated quasiclassically. In that case one can calculate the complex phase shift incident to Q-channel scattering. If the dissociative terms of the molecule have a considerable slope U_j (in our case $U_j \sim 20$ eV$/a_0$), the quasiclassical nuclear wave function can be approximated[10] by a delta function: $\chi_k = U_j^{1/2}\delta(R-R_c)$. In that case we obtain the following approximate expression for the t matrix:

$$t_j(R_c)\approx\frac{(\varepsilon_j^0(R_c)+M_j(R_c))\langle\psi_{Q_j}|V_P|\psi_P\rangle\chi_v(R_c)\rho}{U_j^{1/2}(\varepsilon-\varepsilon_j^0(R_c)-M_j(R_c))}, \tag{5a}$$

where

$$\rho = \exp\left(-\int_{R_{cr}}^{R_c} \frac{\Gamma_j}{2\hbar v}\, dR\right)$$

is the survival factor, ψ_{Q_j} is the Q_j-channel electronic wave function, and v is the separation velocity of the nuclei.

Now we can easily obtain an expression for the DR cross section:

$$\sigma(R_c) \approx \sum_j \frac{\hbar^2(2l+1)}{\pi m \varepsilon U_j} \frac{|\varepsilon_j^0(R_c)+M_j(R_c)|^2\Gamma_j^0|\chi_v(R_c)|^2\rho^2}{[\varepsilon-\varepsilon_j^0(R_c)-\operatorname{Re} M_j(R_c)]^2+\Gamma_j^2/4}, \tag{6}$$

where

$$\Gamma_j^0 = 2\pi|\langle\psi_{Q_j}|V_P|\psi_P\rangle|^2.$$

Equation (6) must be averaged over R_c.

We note that for some molecules, e.g., for oxygen, we have

$$\sigma(R_c) \approx C(E)\,|\chi_v(R_c)|^2.$$

Actually, at resonance we have $\rho \approx 1$ and $\Gamma_j \sim (\varepsilon_j^0)^\alpha$, where $\alpha \approx 1/2$; hence

$$\sigma(R_c) \sim (\varepsilon_j^{0^{1/2}}/U_j)\,|\chi_v(R_c)|^2.$$

Using the data of Ref. 12, we find that for the oxygen molecule, the R_c dependence of ε_j^0/U_j is considerably weaker than that of $|\chi_v|^2$. On averaging (6) over R_c, therefore, we obtain an expression similar to the Breit-Wigner formula, so the DR cross section will have a characteristic resonance structure. When ε_j^0/U_j depends strongly on R_c there will be no resonance structure (in this case the width of the peaks will actually be determined by the expression $\Delta R\, U_j \sim 10$ eV). In the other words, for the DR cross section to have a resonance structure it is necessary that the nuclear wave function of the ion be "narrow".[2]

The summation in Eq. (6) is taken over the partial cross sections, not over the corresponding probability amplitudes. This is associated with the fact that the half-width of an autoionizing state is defined as the imaginary part of the electron mass operator, it being assumed that the correlations between all of the autoionizing states are taken into account in constructing the mass operator. Now we turn to the solution of this problem.

3. THE GREEN'S FUNCTION FOR AN AUTOIONIZATION STATE

Let us consider the capture of an electron into a bound state. We shall regard the ground state of the ion as the vacuum. Then the excitation of an electron of the target molecule will be equivalent to the production of a particle-hole pair. Thus, an autoionizing state formed by two electrons and a hole is produced as a result of the capture. If the nuclei of the atoms remain stationary, after a certain time one of the electrons will recombine with the hole and the other electron will undergo a transition to the continuous spectrum. This process is described by the first diagram of the series in Fig. 1a and the diagram of Fig. 1b. Since there are many autoionizing states, their possible correlations must be taken into account. If the exchange effects are small, this can be done by summing the series of Fig. 1a. Summing this series makes it possible to construct an optical potential (an electron mass operator) with allowance for correlations between all the autoionizing states produced by two electrons and a hole.

Using well-known rules to recover the analytic form of the diagrams, we obtain[13]

$$iM_1 = -\sum_{\Delta q}\int\frac{d\Delta\varepsilon}{2\pi}\, iG_0(q-\Delta q,\ \varepsilon-\Delta\varepsilon)\sum_p\int\frac{d\beta}{2\pi}(i)^2G_0(p,\beta)$$

$$\times G_0(p+\Delta q,\ \beta+\Delta\varepsilon)(-i)^2V_c^2(p,q,\Delta q), \tag{7}$$

$$iM_2 = \sum_{\Delta q}\int\frac{d\Delta\varepsilon}{2\pi}\, iG_0(q-\Delta q,\ \varepsilon-\Delta\varepsilon)$$

$$\times\sum_{p_1,p_2}\int\frac{d\beta_1\, d\beta_2}{(2\pi)^2}(i)^4G_0(p_1,\beta_1)$$

$$\times G_0(p_2,\beta_2)G_0(p_1+\Delta q,\beta_1+\Delta\varepsilon)G_0(p_2+\Delta q,\beta_2+\Delta\varepsilon)(-i)^3$$

$$\times V_c(p_1,q,\Delta q)V_d(p_1,p_2,\Delta q)V_c(p_2,q,\Delta q), \tag{8}$$

where V_c and V_d are matrix elements for the interelectron interaction potential between wave functions of the continuous and discrete spectra, respectively.

It can be shown (see the Appendix) that the matrix elements $V_c(p, q, \Delta q)$ and $V_d(p_1, p_2, \Delta q)$ depend only on the changes Δq of the quantum numbers. In that case formula (8) takes the form

$$iM_2 = \sum_{\Delta q}\int\frac{d\Delta\varepsilon}{2\pi}\, iG_0(q-\Delta q,\varepsilon-\Delta\varepsilon)\gamma_1(\Delta\varepsilon,\Delta q)\Pi_0(\Delta\varepsilon,\Delta q), \tag{9}$$

where γ_1 and Π_0 are defined by the formulas

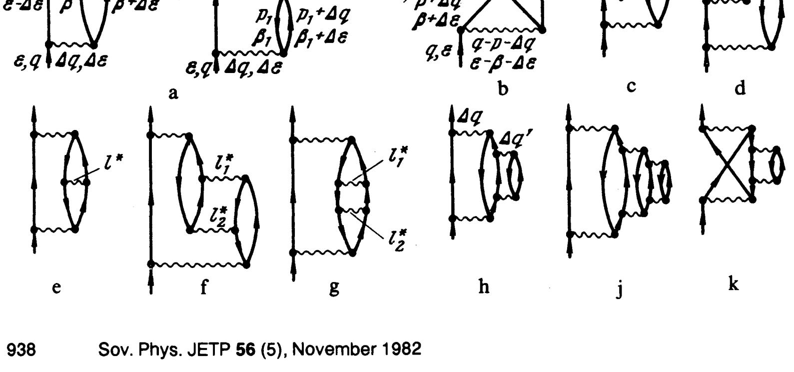

FIG. 1. Mass-operator diagrams. The lines with arrowheads pointing up (down) are particle (hole) propagators described by the free Green's function $G_0 = (\varepsilon - \varepsilon_q + i\delta_q)^{-1}$, where q is the set of quantum numbers characterizing the state of the particle (hole), ε_q is the energy of the state, and ε is an energy parameter. The wavy lines represent Coulomb interaction between electrons. The affixes $\Delta\varepsilon$, Δq, and l^* indicate energy transfer, changes in the quantum numbers, and the multipolarity of the interaction, respectively.

$$i\gamma_1 = -\sum_p \int \frac{d\beta}{2\pi} G_0(p,\beta) G_0(p+\Delta q, \beta+\Delta\varepsilon) V_c^2(\Delta q), \quad (10)$$

and

$$i\Pi_0 = \sum_p \int \frac{d\beta}{2\pi} G_0(p,\beta) G_0(p+\Delta q, \beta+\Delta\varepsilon) iV_d(\Delta q). \quad (11)$$

The entire series depicted in Fig. 1a reduces to the expression

$$M = \sum_{\Delta q} \int \frac{d\Delta\varepsilon}{2\pi} G_0(q-\Delta q, \varepsilon-\Delta\varepsilon) \gamma_1(\Delta\varepsilon, \Delta q) \times [1 - \Pi_0(\Delta\varepsilon, \Delta q)]^{-1}. \quad (12)$$

In the general case the exchange effects cannot be neglected. The diagrams that take account of exchange between electrons can be separated into two groups (within the limitations of the model employed). The first group consists of diagrams like those depicted in Fig. 1b–d. They describe corrections to the first terms of the series in Fig. 1(a), i.e., corrections to $\gamma_1(\Delta\varepsilon, \Delta q)$. The second group (Fig. 1e–g) describes corrections to the polarization operator $\Pi_0(\Delta\varepsilon, \Delta q)$. To allow for the contribution to the mass operator from correlations between states formed by three electrons and two holes, four electrons and three holes, etc., one must take into account diagrams like those depicted in Fig. 1h–k. These diagrams essentially describe corrections associated with the polarization of the medium to states of the discrete spectrum.

Let us estimate the contribution from the various diagrams depicted in Fig. 1 to the mass operator. The internal lines of these diagrams correspond to states of the valence electrons; for the molecules under consideration, these are $3\sigma_g$, $3\sigma_u$, $1\pi_g$, and $1\pi_u$ electrons. For definiteness we shall consider the valence shell of the oxygen molecule. The ground state has the configuration $3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^2\ (X^3\Sigma_g^+)$. According to the definition given above, the vacumm is defined by the configuration $3\sigma_g^2\ 1\pi_u^4\ 1\pi_g\ (X^2\Pi_g)$. The main contribution to the matrix element for the electron-interaction potential comes from terms of zero multipolarity, $l^* = 0$ (see the Appendix). Starting from this, we easily find that the diagram of Fig. 1b is approximately six times smaller than the second-order diagram of Fig. 1a. This is due to the fact that both wavy lines on the first diagram of Fig. 1a correspond to the same matrix element $V_c(\Delta q)$. In the diagram on Fig. 1b the wavy lines correspond $V_c(\Delta q)$ and $V_c(q - p - \Delta q)$. Certain conditions must be imposed on q and p if these matrix elements are to correspond to an interaction of multipolarity zero. Since an $l^* = 0$ interaction corresponds to a change $\Delta\lambda = 0$ in the projection of the orbital angular momentum and a change $\Delta\varkappa = 1$ in the parity, it is necessary that $\lambda - \Delta\lambda = \lambda_1$ and $|\varkappa - \Delta\varkappa - \varkappa_1| = 1$. For the electrons under consideration, the projection of the orbital angular momentum may assume three values, $\lambda = 0, \pm 1$, and the parity may assume two values, $\varkappa = 0, 1$. Since $\Delta\lambda$ and $\Delta\varkappa$ are summed over [formula (7)] there occur 18 terms with $l^* = 0$ in the expression for the second-order diagrams in Fig. 1a. There are only three such terms in the diagram of Fig. 1b. Hence the second-order exchange diagram amounts to ~1/6 of the second-order direct interaction diagram. The same can be said of the diagrams of Fig. 1h and j. Thus, the diagram of Fig. 1h amounts to ~1/6 of the fourth-order diagram occurring in the series of Fig. 1a. The diagram of Fig. 1j amounts to ~1/18 of the sixth-order diagram of Fig. 1a.

Let us return to the exchange diagrams of Figs. 1c–g. Since the valence-electron shell of the O_2 molecule is more than half filled, the wavy lines l_i on these diagrams correspond to a dipole interaction. As a result, on repeating the above discussions we find that the contribution from the diagrams depicted on Fig. 1c and e amounts to ~1/12 of the third-order diagram of Fig. 1a (the dipole-interaction matrix element is approximately half as large as the matrix element for the interaction with $l^* = 0$). Similarly, the diagrams on Fig. 1d,f, and g amount to ~1/36 of the diagrams of the corresponding order on Fig. 1a. Summarising what has been said, we may assume that it is sufficient to consider the contribution to $\gamma_1(\Delta\varepsilon, \Delta q)$ from the diagrams of Fig. 1b and h in order for the calculation to be accurate within ~10%. In the diagram of Fig. 1h it is necessary to take fully into account the correction to the internal lines due to polarization of the medium, i.e., the wavy line $\Delta q'$ corresponds to

$$V_d[1 - \Pi_0(\Delta\varepsilon', \Delta q')]^{-1}.$$

The imaginary part of the mass operator corresponds to the total half width of all the autoionizing states formed in the elastic scattering of an electron by a molecular ion. If we are interested in some specific state, that case would correspond to certain specific values of the quantum numbers of the particle-hole pair. On integrating over the energy in formulas (7) and (10)–(12) we obtain an expression for the imaginary part of the mass operator:

$$\operatorname{Im} M = \sum_{\Delta q} [\operatorname{Im}\gamma_1(1 - \operatorname{Re}\Pi_0) + \operatorname{Im}\Pi_0 \operatorname{Re}\gamma_1] |1 - \Pi_0|^{-2}, \quad (13)$$

where

$$\operatorname{Im}\gamma_1 = \pi \sum_p V_c^2(\Delta q) \delta(|\varepsilon_p - \varepsilon_{p+\Delta q}| - \varepsilon_r),$$

$$\operatorname{Re}\gamma_1 = \sum_p V_c^2(\Delta q) P \frac{2(\varepsilon_p - \varepsilon_{p+\Delta q})}{(\varepsilon_p - \varepsilon_{p+\Delta q})^2 - \varepsilon_r^2},$$

$$\operatorname{Im}\Pi_0 = \pi \sum_p V_d(\Delta q) \delta(|\varepsilon_p - \varepsilon_{p+\Delta q}| - \varepsilon_r),$$

$$\operatorname{Re}\Pi_0 = \sum_p V_d(\Delta q) P \frac{2(\varepsilon_p - \varepsilon_{p+\Delta q})}{(\varepsilon_p - \varepsilon_{p+\Delta q})^2 - \varepsilon_r^2}.$$

Here ε_r is the electron-capture resonance energy, and P indicates that the sum is to be taken as a principal value.

Only the first diagram of the series depicted in Fig. 1a is included in the expressions for Im γ_1 and Re γ_1. This was done only because the expressions for the corresponding diagrams of Fig. 1b and h are very cumbersome. Thus, the proposed method makes it possible to obtain relatively simple expressions for the mass operator and the half widths of the autoionizing states.

It is of interest to consider the limiting case $\Delta\varepsilon \to \infty$. In this case Im Π_0 turns out to be zero. Then the imaginary part

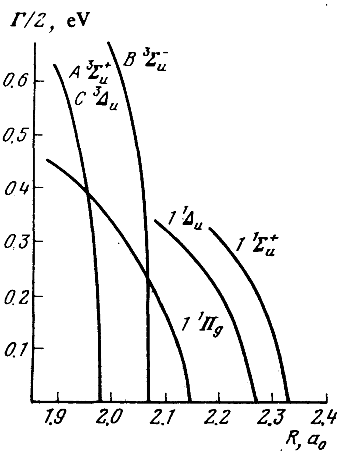

FIG. 2. Half widths of some autoionizing states of the O_2 molecule.

of the mass operator corresponds simply to Im γ_1. As a result, formula (13) reduces to the expression usually used for the half width of an autoionizing state[14]:

$$\Gamma/2=\sum_{\Delta q,p} V_c^2(\Delta q)\,\delta(|\varepsilon_p-\varepsilon_{p+\Delta q}|-\varepsilon_r). \qquad (14)$$

4. RESULTS

Below we present the results of calculations of the DR cross section for an electron and an O_2^+ $(X\,^2\Pi_g)$ ion as an example.

Figure 2 shows the dependences of the half-widths of several autoionizing states of the O_2 molecule on the internuclear distance. Formula (13) was used for the calculations, γ_1 being determined with allowance for the diagrams of Fig. 1b and h. It should first be noted that the half-widths of the autoionizing states depend strongly on the internuclear distance. The half-widths turn out to be rather large; this confirms the necessity of allowing for correlations between the autoionizing states. We note for comparison that the half-widths calculated with formula (14) for small values of ε_r turn out to be smaller by factors of 1.5–2.

Figure 3 shows the results of calculations of the resonance part of the DR cross section for an electron and an O_2^+ ion in the zeroth, first, and second vibrational states. The DR cross section averaged over the vibrational distribution function corresponding to the conditions of Ref. 3 is presented in Fig. 4 for comparison with experiment. The beam of O_2^+ ions at a pressure of $\sim 10^{-10}$ Torr was used in that experiment. The ions were produced by ionizing O_2 molecules by 14- or 33-eV electrons. In the first case the O_2^+ ions were produced only in the electronic ground state $(X\,^2\Pi_g)$ and were distributed over the vibrational states in accordance with the Franck-Condon factors. (Of course there was no vibrational relaxation at such low pressures.) In the second case it is more difficult to determine the distribution of the ions formed over the vibrational states. This is due to the fact that when an O_2 molecule is ionized by 33-eV electrons the resulting O_2^+ ion may be in any of several excited electronic states. As a result, in the general case various vibrational states may be populated by electron transitions.

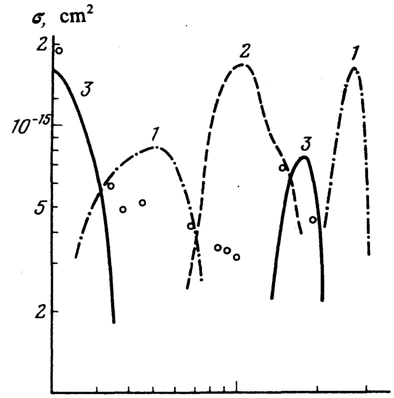

FIG. 3. Resonance parts of the DR cross sections for an electron and an O_2^+ ion in the zeroth (1), first (2), and second (3) vibrational states.

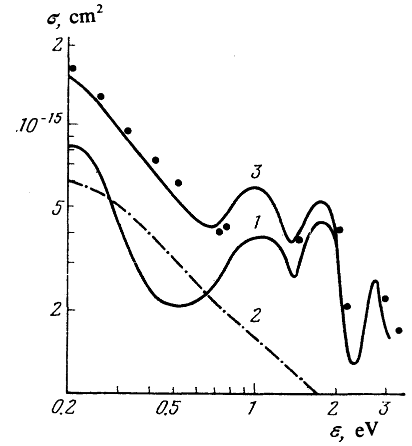

FIG. 4. Averaged total DR cross section for an electron and an O_2^+ ion: 1—resonance part of the cross section [Eq. (6)], 2—potential part of the cross section (calculated using the approach of Ref. 15), 3—sum of the resonance and potential parts. The experimental points are from Ref. 3.

Comparison of the calculation results with experiment reveals satisfactory agreement. The discrepancies between the experimental data and the magnitude of the resonance part of the cross section in the low-energy region disappears when the potential-scattering cross section, determined by the method of Ref. 15, is taken into account. As the calculations show,[4] the potential-scattering cross section is virtually independent of the vibrational state of the ion. The agreement of the half-width of the central peak with the experimental data shows that the proposed method yields acceptable results. It is interesting to compare the DR cross section of the O_2^+ ion in the second vibrational state with the experimental data for the case in which the O_2 molecules were ionized by 33-eV electrons. The agreement of these results permits us to suppose that in this case it was mainly the second vibrational level of the O_2^+ ion that was populated.

Thus, the proposed method makes it possible to calculate the cross sections for various processes taking place in the scattering of electrons by molecules with fair reliability. The main advantage of the method is its simplicity, which makes it possible to dispense with complicated computer calculations.

It is interesting to analyze the effect of the results obtained here on the DR coefficient K, which is usually defined as the product σv_e averaged over the electron velocity distribution (v_e is the electron velocity).

If the ion is in the vibrational ground state, the DR cross section will have the form of a curve, falling as $\sim 1/\varepsilon$, with widely spaced resonance peaks superimposed on it. As a result, the DR coefficient turns out to be dependent on the electron temperature: $K \sim T_e^{\alpha}$, where $\alpha \sim 0.5$ (Ref. 2). Vibrational excitation of the ion results in the presence of more resonance peaks more closely spaced (see Figs. 3 and 4); a consequence of this is a change in the effective dependence of the DR cross section on the electron energy. If it happens that $\sigma \sim \varepsilon^{-1/2}$, K will be constant, i.e., the DR coefficient will be independent of T_e. With further excitation of the ion, the $\sigma(\varepsilon)$ curve becomes even less steep, and this leads to the appearance of regions of T_e values in which the DR coefficient K increases with increasing T_e. When using experimental data on K as a function of T_e in specific calculations of the dynamics of a low-temperature plasma, therefore, one must make sure that the distribution of the ions over the vibrational states corresponds to the conditions of those experiments.

In concluding, let us examine the effect of the errors that inevitably arise in calculations of electron wave functions and molecular terms on the results of the present work. We note first of all the published results of calculations of dissociative terms are available only for a small number of molecules (of the molecules of practical interest, only the oxygen molecule has actually been well investigated). For calculations of the DR cross section using formula (6), information on single-electron wave functions and energies and on the dissociative terms of the molecule are required. Let us analyze the effect of errors in the determination of these three components on the results of calculations of DR cross sections. Errors in determining the first two factors affect only the magnitude of Γ_j. Since the wave functions occur only in the corresponding intergrals, the relative error in Γ_j will be approximately equal to the relative error in determining the wave functions. The situation is worse as regards inaccuracies in determining the single-electron energies and the dissociative terms of the molecule. Since the values of these energies determine the positions of the resonance peaks, even a slight error in determining the dissociative terms can greatly distort the resonance structure of the DR cross section. As an example, we note that shifting the $1^1\Delta_u$ term by only $\Delta R \approx 0.04 a_0$ (this quantity lies within the mean-error limits of the calculations[12]) changes the resonance energy from 2.8 to 1.3 eV. Summarizing what was said above, we can conclude that in the present method simplifying assumptions are permissible only as regards the matrix elements and the functions that occur in them. The electron energies and the positions of the dissociative terms must be determined with the greatest possible accuracy.

APPENDIX

The matrix element of the Coulomb potential for the interaction between electrons

Here we present a scheme for determining the dependence on the electron quantum numbers of the matrix element of the electron-electron interaction potential. The wave functions of the valence electrons are taken in the form of an expansion[16]:

$$\psi_{\varkappa,\lambda}=\sum_{l} C_l[\varphi_{l,\lambda}(\mathbf{r}_A)\pm(-1)^{\lambda}\varphi_{l,\lambda}(\mathbf{r}_B)], \qquad \text{(A.1)}$$

where l, λ, and $\varkappa$ represent the orbital angular momentum of the electron, its projection onto the molecular axis, and the parity of the state, respectively. In the case considered here (molecules of the O_2 type) we may drop all terms of the expansion (A.1) except those with $l = 0$ and $l = 1$.[17] The atomic wave functions $\varphi_{l,\lambda}$ are determined in the form of expansions in series of Slater orbitals.[18] The arguments of the exponentials for the $2s$ and $2p$ electrons are sometimes chosen equal in spectroscopic calculations.[19]

The matrix element of the electron interaction potential $V(R)$ breaks up into integrals of four types: single-centered integrals (J_1), hybrid integrals (J_2), exchange integrals (J_3), and Coulomb integrals (J_4).[17] For the case under consideration it can easily be shown that if the quadrupole interaction be neglected we shall have $V(R) = 2(J_1 - J_4)$. Since the radial parts of the wave functions for $2s$ and $2p$ electrons are similar, the radial parts of the J_1 integrals turn out to be roughly equal for various transitions (with an error of $\sim 7\%$). The same thing obtains for the radial parts of the J_4 integrals. This only provides the dependence of $V(R)$ on $\Delta\varkappa$. To determine the dependence of $V(R)$ on $\Delta\lambda$ the atomic wave functions must be reduced to a common center. This can be done with the aid of the following relations[20]:

$$|\mathbf{r}-\mathbf{R}|\,Y_{1,\lambda}(\widehat{r-R})=\sum_{\substack{l_1,l_2\\ l_1+l_2=1}} r^{l_1}R^{l_2}(-1)^{l_2}Y_{l_1\lambda}(\hat{r})\langle l_1 l_2 \lambda 0|1\lambda\rangle \times\left[\frac{3!}{(2l_1+1)!\,(2l_2)!}\right]^{1/2}, \qquad \text{(A.2)}$$

and

$$\exp(-\zeta|\mathbf{r}-\mathbf{R}|)=-\frac{d}{d\zeta}\sum_{l_1}(Rr)^{1/2}I_{l_1}(\zeta r)K_{l_1}(\zeta R) \times(2l_1+1)P_{l_1}(\cos\hat{r}). \qquad \text{(A.3)}$$

Here I_{l_1} and K_{l_1} are modified Bessel functions. Since the main contribution to the matrix element comes from the integration region close to the axis joining the nuclei (small values of the angle $\hat{r}$) we may retain only the $l_1 = 0$ term (the first order in $1/R$) in (A.3). In that case the wave function $\psi_{\varkappa,\lambda}$ reduces to the form

$$\psi_{\varkappa,\lambda}=\sum_{l=0,1}\Lambda_{l,\varkappa}(r,R)\,Y_{l,\lambda}(\hat{r})$$

so $V(R)$ will depend only on $\Delta\lambda$, i.e., $V(R) = V(\Delta\lambda, \Delta\varkappa)$.

Now we shall estimate the contribution to $V(R)$ from the quadrupole interaction. It is determined by the magnitude of the Clebsch-Gordan coefficients and amounts toi $\sim 4\%$. Hence $V(R) = V(\Delta\lambda, \Delta\varkappa)$ with an accuracy of $\sim 10\%$.

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