Detachment of a weakly bound electron from a negative ion in a collision with an excited molecule

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It is shown that the formulas of the classical theory for the cross section for ionization of highly excited atoms during collisions with excited particles are equivalent to the formulas obtained in the impulse approximation. The ionization cross section is expressed in terms of the cross section for scattering of an electron by the impinging particle. The method is extended to the negative-ion destruction reaction. The results of the calculation carried out within the framework of the approximation in question for electron detachment from the NO^- ion during collisions with CO_2 and H_2 molecules are found to be in good agreement with the experimental data.

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1. INTRODUCTION

The ionization of highly excited atoms during collisions with excited molecules has been theoretically studied before.[1-6] In these studies the authors used the approach first proposed by Fermi,[7] according to which in the reaction

$$A(n)+M(J_r)\to A^+ + M(J_r')+e, \quad J_r'<J_r, \tag{1}$$

where $A(n)$ is an atom in a highly excited Rydberg state, n, and M is a molecule in the angular momentum state J_r, the distance between the excited electron and the ion nucleus A^+ is so large that the incoming particle cannot interact simultaneously with the electron and the ion A^+. Since the electron-molecule collision time is significantly shorter than the period of the highly excited electron in the $A(n)$ atom, the electron is scattered almost instantaneously, and the fact that the electron is bound can be ignored. The last fact affects only the initial velocity distribution of the electron.

In Refs. 1 and 4 the cross section for the reaction (1) is computed on the basis of the impulse approximation,[8] while in Refs. 5 and 6 the calculation is carried out on the basis of the classical theory. In Refs. 2 and 3 the adopted method, which is similar to the approach used in Refs. 1 and 4, is extended to the reaction involving charge transfer from an excited atom to a polyatomic electronegative molecule:

$$A(n)+M\to A^+ + M^-. \tag{2}$$

The classical theory[5,6] is used in Refs. 9 and 10 to compute the cross sections for destruction, during collisions with excited particles, B^*, of negative ions for which the binding energy of the outer electron is small:

$$A^- + B^* \to A+B+e. \tag{3}$$

In the present paper we show that the formulas of the classical theory[5,6] for the cross sections for the reactions (1) and (3) are equivalent to the corresponding formulas of the impulse approximation.[1,4] For the case in which $I\ll J$, where I is the binding energy of the outer electron and J is the excitation energy of the incoming particle, the cross section for the reactions (1), (3) is expressed in terms of the cross section for scattering of an electron by the incoming excited particle. The reactions involving the destruction and production of NO^- ions during collisions with excited molecules are considered within the framework of the indicated approximations. Good agreement is obtained between the results of the present computations of destruction-rate constants for NO^- ions and the experimental data.

The NO^--ion destruction and production processes should be taken into consideration in, for example, the analysis of plasmochemical reactions in the active medium of gas-discharge CO_2 lasers,[11] the analysis of corona discharges in air,[12] the investigation of the electro-ionization method of production of the oxides of nitrogen.[13,14]

2. THE CLASSICAL AND IMPULSE APPROXIMATIONS

The classical approximation for the reaction (1) is considered in Ref. 5. In this case the approximation is valid, since transitions between a large number of the states of the atom occur during the ionization of the highly excited atom.

The ionization process itself can be regarded as the result of the scattering of the weakly bound electron by the impinging particle. The condition for the applicability of the approximation in question is that the characteristic distance between the weakly bound electron and the incoming particle at which the scattering occurs be significantly smaller than the distance of the electron to its own nucleus, i.e., the distance over which the strength of the potential of the interaction of the electron with its own ion in the atom changes appreciably.

According to Smirnov,[5] the probability per unit time of ionization of a highly excited atom colliding with an incoming excited particle in the reaction (1) is equal to

$$N_M\langle|\mathbf{v}-\mathbf{v}_M|\sigma_T\rangle,$$

where N_M and $\mathbf{v}_M$ are the density and velocity of the incoming particles, $\mathbf{v}$ is the velocity of the weakly bound electron, and σ_T is the cross section for deexcitation of the incoming particle by electron impact during which the weakly bound electron gains an energy sufficient for its liberation. The angular brackets denote averaging over the velocity distribution of the electron in

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the atom. Dividing this expression by the incoming-particle flux, $N_M v_M$, and taking account of the fact that at thermal collision energies we practically always have $v \gg v_M$, we obtain the following formula for the cross section, σ, for the reaction (1):

$$\sigma = \langle v\sigma_T \rangle / v_M. \tag{4}$$

Let us, for definiteness, consider the reaction (1) in the impulse approximation,[1,8] although everything that follows is valid also for the reaction (3). The total Hamiltonian, H, of the colliding system for the reaction (1) in the center-of-mass system is equal to

$$H = T_R + H_A + H_M + U, \tag{5}$$

where T_R is the kinetic energy of the relative motion of the particles A and M, U is the potential of the interaction between them, and H_A and H_M are the Hamiltonians of these particles. The highly excited electron in the particle A can be considered to be almost free because of its large distance from the nucleus A^+. Therefore, the Hamiltonian H_A can be split into three parts:

$$H_A = T_e + H_{A^+} + V, \tag{6}$$

where T_e is the kinetic energy of the excited electron, H_{A^+} is the Hamiltonian of the ion A^+, and V is the potential of the interaction between the electron and the ion A^+. The potential U can be split into two parts: the potential, U_1, of the interaction between the electron and the particle M and the potential U_2 of the interaction between the particles A^+ and M.

In the reaction (1) the ionization occurs largely because of the interaction U_1, since the core ion A^+ does not participate in it. The potential U_2 can be neglected in comparison with the potential U_1, since the distance between the particles A^+ and M is large compared to the distance between the electron and the particle M during the period when the reaction (1) is taking place. Then the total Hamiltonian of the colliding system has the form

$$\begin{gathered} H = T_R + T_e + V(\mathbf{r}) + H_M + H_{A^+} + U_1(\rho), \\ T_R = -\nabla_R^2/2\mu, \qquad \mu = M_A M_M / (M_A + M_M), \end{gathered} \tag{7}$$

where $T_e = -\frac{1}{2}\Delta_r^2$; r and p are the radius vectors of the weakly bound electron relative to the particles A^+ and M; R is the radius vector of the particle M relative to A^+; M_A and M_M are the masses of the particles A and M. Here and below we use the atomic system of units and neglect the electron mass in comparison with the masses M_A and M_M.

The scattering amplitude $f(\theta)$ for the transition $\alpha\beta\gamma\mathbf{K} \to \alpha'\beta'\gamma'\mathbf{K}'$ is determined by the expression

$$f(\theta) = -\frac{\mu}{2\pi} \langle \psi_{\alpha'} \psi_{\beta'} \psi_{\gamma'} \exp(i\mathbf{K}'\mathbf{R}) | U_1 | \psi_{\alpha\beta\gamma\mathbf{K}} \rangle, \tag{8}$$

where ψ_α, ψ_β, and ψ_γ are the wave functions respectively of the weakly bound electron and the particles M and A^+; K is the wave vector of the relative motion of the particles M and A^+; θ is the angle between the vectors K and K′. The wave function $\psi_{\alpha\beta\gamma\mathbf{K}}$ is that eigenfunction of the Hamiltonian (7) which satisfies the asymptotic boundary condition for the scattering.

Let us go over from the coordinate space for the weakly bound electron into momentum space in accordance with the formulas

$$\psi_\alpha(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \int \exp(i\mathbf{qr}) G_\alpha(\mathbf{q})\, d\mathbf{q}, \tag{9}$$

$$G_\alpha(\mathbf{q}) = \frac{1}{(2\pi)^{3/2}} \int \exp(-i\mathbf{qr}) \psi_\alpha(\mathbf{r})\, d\mathbf{r}, \tag{10}$$

and expand the function $\psi_{\alpha\beta\gamma\mathbf{K}}$ in terms of the eigenfunctions, $\Phi_{\mathbf{q}\beta\gamma\mathbf{K}}$, of the Hamiltonian $H - V(\mathbf{r})$ that satisfy the boundary conditions for the scattering

$$\psi_{\alpha\beta\gamma\mathbf{K}} = \frac{1}{(2\pi)^{3/2}} \int \Phi_{\mathbf{q}\beta\gamma\mathbf{K}} G_\alpha(\mathbf{q})\, d\mathbf{q}. \tag{11}$$

This expansion corresponds to the impulse approximation.[8] Substituting the expressions (9) and (11) into (8), we obtain

$$\begin{aligned} f(\theta) = {} & -\frac{\mu}{(2\pi)^4} \int G_\alpha^*(\mathbf{q}) \\ & \times \langle \exp(i\mathbf{K}'\mathbf{R} + i\mathbf{q}'\mathbf{r}) \psi_{\beta'} \psi_{\gamma'} | U_1 | \Phi_{\mathbf{q}\beta\gamma\mathbf{K}} \rangle\, d\mathbf{q}\, d\mathbf{q}'. \end{aligned} \tag{12}$$

Going over from the variables R, r to R, ρ, we have

$$\begin{aligned} & \langle \exp(i\mathbf{K}'\mathbf{R} + i\mathbf{q}'\mathbf{r}) \psi_{\beta'} \psi_{\gamma'} | U_1(\rho) | \Phi_{\mathbf{q}\beta\gamma\mathbf{K}} \rangle \\ & = (2\pi)^3 \langle \exp(i\mathbf{q}'\rho) \psi_{\beta'} \psi_{\gamma'} | U_1(\rho) | \Phi_{\mathbf{q}\beta\gamma} \rangle \delta(\mathbf{K} + \mathbf{q} - \mathbf{K}' - \mathbf{q}'), \end{aligned} \tag{13}$$

where

$$\Phi_{\mathbf{q}\beta\gamma\mathbf{K}} = \Phi_{\mathbf{q}\beta\gamma} \exp(-i\mathbf{KR} + i\mathbf{qR}).$$

The transformation (13) is valid for $q \gg K/\mu$, which is fulfilled at thermal energies of the colliding particles if the principal quantum number of the weakly bound electron $n \lesssim 100$.[1] Substituting (13) into (12), we obtain

$$\begin{aligned} f(\theta) & = -\frac{\mu}{2\pi} \int G_{\alpha'}^*(\mathbf{q}') G_\alpha(\mathbf{q}) \langle \exp(i\mathbf{q}'\rho) \psi_{\beta'} \psi_{\gamma'} | U_1(\rho) | \Phi_{\mathbf{q}\beta\gamma} \rangle\, d\mathbf{q} \\ & = \mu \langle \psi_{\gamma'} | \psi_\gamma \rangle \int G_{\alpha'}^*(\mathbf{q}') G_\alpha(\mathbf{q}) f_e(\varphi)\, d\mathbf{q}, \end{aligned} \tag{14}$$

where $f_e(\varphi)$ is the amplitude for deexcitation of the incoming excited particle by electron impact and φ is the angle between the vectors q and q′. Here

$$\mathbf{q}' = \mathbf{q} + \mathbf{K} - \mathbf{K}'. \tag{15}$$

In our case

$$G_{\alpha'}(\mathbf{q}') = \delta(\mathbf{q}' + \mathbf{K}' - \mathbf{q} - \mathbf{K}), \tag{16}$$

$$f(\theta) = \mu \langle \psi_{\gamma'} | \psi_\gamma \rangle f_e(\varphi) G_\alpha(\mathbf{q}). \tag{17}$$

It follows from (15) that

$$d(\cos\theta) = \frac{qq'}{KK'} d(\cos\varphi). \tag{18}$$

For the cross section for the reaction (1) we obtain from (17) and (18) the expression

$$\sigma(q') = 2\pi \frac{K'}{K} \int |f(\theta)|^2 d(\cos\theta) = \mu^2 |\langle \psi_{\gamma'} | \psi_\gamma \rangle|^2 \frac{q^2}{K^2} |G_\alpha(\mathbf{q})|^2 \sigma_T(\mathbf{q}); \tag{19}$$

$\sigma_T(\mathbf{q})$ is the cross section for deexcitation by electron impact of the incoming excited particle. The right-hand side of the formula (19) should be multiplied by v_M/v, since in the case under consideration the flux of the weakly bound electrons impinging on the particle M is determined by the velocity v_M, and not by v, which corresponds to the effective decrease of the cross section σ_T by a factor of v/v_M. Taking this into account, and integrating the cross section $\sigma(\mathbf{q}')$ over all possible values of q′, we obtain up to the factor $|\langle\psi_{\gamma'}|\psi_\gamma\rangle|^2$ the formula, (4), derived in the classical theory:

$$\sigma = \int \sigma(\mathbf{q}')\, d\mathbf{q}' = |\langle \psi_{\gamma'} | \psi_\gamma \rangle|^2 \langle v\sigma_T(v) \rangle v_M^{-1}. \tag{20}$$

If the particle A is a molecule, then $|\langle\psi_{\gamma'}|\psi_\gamma\rangle|^2$ is the Franck-Condon coefficient for a transition between the corresponding vibrational levels of A and A^+; if the particle A is an atom, then the factor is equal to unity.

The assumption underlying the impulse approximation is that[8] the collision between the electron and the incoming particle should be a fast one, i.e., that $a/v \ll T_e$, where a is the characteristic dimension of the incoming particle and T_e is the characteristic period of the motion of the electron in the initial state. Since $vT_e \sim R$, the distance of the electron from its own nucleus A^+, the condition of applicability of the impulse approximation can be written in the form

$$a \ll R, \tag{21}$$

which coincides with the condition for the validity of the classical theory.

Thus, the classical and impulse approximations for the cross section for the reactions (1) and (3) lead to the same formulas, and the conditions for their applicability coincide.

3. DESTRUCTION OF THE NO⁻ ION

Let us consider the reaction (3) if for the particle A the energy of affinity to the electron is small compared to the characteristic atomic energies. We can then use the impulse approximation. A typical example of such an ion is the NO^- ion, in which the binding energy of the outer electron $I \sim 0.2 - 0.034$ eV,[5] and the difference in energy of the vibrational quanta of the NO and NO^- molecules is of the order of 0.05 eV, which characterizes the coupling of the outer electron in NO^- to the nuclear vibrations. Then

$$R \sim \hbar/(2mI)^{1/2} \sim 10\ \text{Å}$$

and the condition, (21), for the validity of the impulse approximation is fulfilled.

The rate constant of the reaction

$$NO^- + M^* \to NO + e + M \tag{22}$$

in the impulse approximation is, according to (20), equal to

$$k = \langle v_M \sigma \rangle_M = G_{00} \langle v \sigma_T \rangle; \tag{23}$$

$\langle\ \rangle_m$ denotes averaging over the relative velocities of the heavy particles, G_{00} is the Franck-Condon coefficient for a transition between the ground vibrational states of NO and NO^-. The rate constant of the reaction (22) turns out to be independent of the gas temperature T.

The weakly-bound-electron velocity distribution function, which is used in the averaging in the formula (23), is appreciably different from zero in the region of low electron energies, ε, where the cross section, σ_T, for deexcitation of the impinging excited particle by electron impact and the cross section, σ_b, of the inverse reaction are equal[15]:

$$\sigma_b = C(J-\varepsilon)^{1/2}, \quad \sigma_T = \frac{g_0}{g_b}\left(\frac{2}{m}\right)^{1/2} \frac{JC}{v}, \tag{24}$$

where g_0 and g_b are the statistical weights of the ground and excited states of the impinging particle and C is a constant. The formulas (24) are valid for $\varepsilon \ll J$, and since for a weakly bound electron $\varepsilon \sim I$, they can be used when $I \ll J$.

Substituting (24) into (23), we have

$$k = G_{00} \frac{g_0}{g_b}\left(\frac{2}{m}\right)^{1/2} JC. \tag{25}$$

Thus, the rate constant of the reactions (1) and (3) is expressible in terms of the constant C, which characterizes the cross section for electron scattering by the incoming excited particle in the near-threshold region.

The total rate constant of the reactions (1) and (3) is obtained by summing over all the excited levels of the incoming particle. If the distribution over its levels is an equilibrium distribution, then

$$k_\Sigma(T) = G_{00} g_0 \left(\frac{2}{m}\right)^{1/2} {\sum_i}' J_i C_i \exp\left(-\frac{J_i}{T}\right) \left[\sum_i g_i \exp\left(-\frac{J_i}{T}\right)\right]^{-1}. \tag{26}$$

The prime denotes summation over the levels, i, for which $J_i > I$.

In Fig. 1 we compare the rate constants of the reactions

$$NO^- + CO_2 \to NO + e + CO_2, \tag{27}$$

$$NO^- + H_2 \to NO + e + H_2, \tag{28}$$

computed from the formula (26), with the experimentally measured rates.[16,17] The constants C_i were determined from the experimentally measured electron-energy dependence of the cross sections for excitation by electron impact of the first excited level of the deformation mode of CO_2 vibrations[18] with a threshold of 0.083 eV and the second and third H_2[19] rotational levels H_2[19] with thresholds of 0.045 eV and 0.075 eV. The error in the constants C_i is ~30%. The coefficient G_{00} was found from the formula for harmonic oscillators:

$$G_{00} = 2\frac{(\omega_1\omega_2)^{1/2}}{\omega_1+\omega_2} \exp\left[-(r_1 - r_2)^2 \Big/ \frac{\hbar}{\mu_1}\left(\frac{1}{\omega_1}+\frac{1}{\omega_2}\right)\right], \tag{29}$$

where $\hbar\omega_1$, $\hbar\omega_2$, r_1, and r_2 are the vibrational quanta and the equilibrium distances of the NO and NO^- molecules

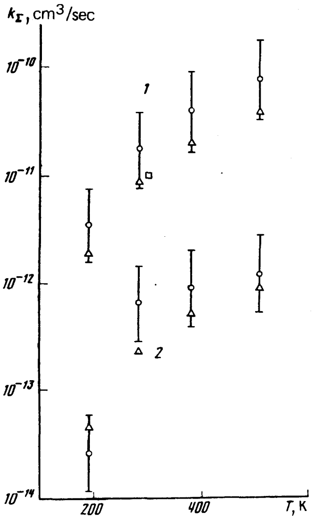

FIG. 1. Dependence of the rate constant for destruction of NO^--ions in collisions with CO_2 (1) and H_2 (2) molecules on the gas temperature: ○) the present computation, △) experiment by McFarland *et al.*,[16] □) experiment by Parkes and Sugden.[17]

and μ_1 is the reduced NO mass. For the computation we used the spectroscopic constants of NO^- obtained experimentally by Siegel *et al.*[20]: $\hbar\omega_2 = 1470 \pm 200\ cm^{-1}$, $r_2 = 1.258 \pm 0.010$ Å. Because of the exponential dependence on the spectroscopic constants, the coefficient G_{00} gives the greatest error in the present computation—70%. Since the errors in the experimental data[16,17] on the rate constants of the reactions (27), (28) range from 10 to 50%, the results of the computation with the formula (26) differ from the experimental data[16,17] by amounts lying within the limits of their errors. The small deviation observed for the rate constant of the reaction (28) at sufficiently low temperatures is due to the fact that at these temperatures the dominant contribution to the reaction (28) is made by the H_2 molecule excited to the second rotational level. Its excitation energy only slightly exceeds the energy of electron affinity to the NO molecule, and therefore the formulas (24) are less accurate. In view of this, here to compute the ratio constant of the reaction (22) we should use the formula (23), and not (26). But for this purpose it is necessary to know the velocity distribution function of the weakly bound electron in NO^-. It can be found with the aid of the collective model of the atom, using the fact that the outer electron is located far from the inner-shell electrons. This, however, leads to some complication of the problem.

The binding energy of the outer electron in NO^- is known with limited accuracy,[5] but this should not affect the results of the present calculations, since only the number of terms of the sum in the formula (26) depends on the magnitude of the binding energy, and the variation of the binding energy within the limits of the results of the published experiments on its determination does not change the number of terms in the formula (26) for the reactions (27) and (28).

When the gas temperature is raised, higher excited levels of the H_2 and CO_2 molecules, which are not taken into consideration in the present computation, get occupied. Their inclusion allows the use of the formula (26) for higher temperatures too, as well as for nonequilibrium conditions, when the distribution of the molecules over the excited levels is not a Boltzmann distribution. In this case it is necessary to replace the Boltzmann distribution in the formula (26) by the real distribution. Such conditions are realized in, for example, a gas discharge.

From the formula (26) we can determine the rate constants of the reaction (3) as well for other excited particles, M, if the cross section for their excitation by electron impact is known. The constant of the inverse process, in which an electron, flying past a NO molecule, collides with another molecule, gives up part of its energy to the molecule's vibrational or rotational degrees of freedom, and gets captured by the NO molecule, can be determined from the cross section of the reaction (3) from the principle of detailed balance.[21]

As indicated in the Introduction, the processes of production and destruction of NO^- ions should be taken into consideration in a number of practical applications. The constant for three-body attachment of electrons to NO on molecules $\sim 10^{-29} - 10^{-30}\ cm^6/sec$,[16] which is comparable with, or greater than, the constants for three-body attachment of electrons to other molecules.[5] Because of the large constant for the inverse process ($\sim 10^{-11} - 10^{-12}\ cm^3/sec$, Ref. 16), the equilibrium NO^--ion concentration is usually small. But the NO^- ion may turn out to be the intermediate link in the formation of other more stable ions on account of the charge-transfer process, since, for example, the rate constants for charge transfer by the NO^- ion to the molecules O_2 and NO_2 are equal to $5 \times 10^{-10}\ cm^3/sec$ and $7.4 \times 10^{-10}\ cm^3/sec$,[16] which are considerably greater than the rate constant for NO^--ion destruction through detachment of an electron from it. Therefore, the NO^- ion, in spite of its small equilibrium concentration, can make an appreciable contribution to the kinetics of the ionization-recombination process in a low-temperature plasma.

It should be noted that, from the experimental data on the rate constants for NO^- ion destruction by molecules, we can determine with the aid of the formula (26) the constants, C_i, characterizing the cross section for excitation of the incoming molecules by electron impact.

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