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RESONANCE CHARGE EXCHANGE BETWEEN A MOLECULAR ION AND A DIATOMIC MOLECULE

V. I. BYLKIN, L. A. PALKINA, and B. M. SMIRNOV

Institute of High Temperatures, USSR Academy of Sciences

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A calculation is reported of the resonance charge-exchange cross section for a molecular ion on its own molecule. The exchange-interaction potential for given directions of the axes of the two particles is calculated by an asymptotic method, assuming that the distance between the particles is large in comparison with the size of the molecule. An allowance is made for the anisotropy of the electron distribution in the molecule, the exchange of valence electrons, and the correlation between the spin and the projection of the angular momenta of the electron and the atomic residue. The exchange-interaction potential is used to calculate the resonance charge-exchange cross section for moderate collision velocities when the axes of the molecular ion and the molecule remain effectively fixed during the collision time. Limiting cases are considered for the collision rates in the case of transition between vibrational levels, including the case of low velocities, when transitions between such vibrational states do not occur, and the case of high collision velocities, when transitions between vibrational levels satisfy the Franckck-Condon principle. A comparison is given between the calculations and experimental data on resonance charge-exchange cross sections for a molecular ion on its own molecule.

1. This paper is concerned with the calculation of the resonance charge-exchange cross section for a molecular ion on its own diatomic molecule. Gurnee and Magee[1] used a very approximate model to determine this cross section. This model does not include any of the features of the interaction and leaves one important parameter undetermined. The Gurnee-Magee approach is therefore not in accord with our present understanding of the process. Bates and Reid[2] have recently reported a satisfactory calculation of the resonance charge-exchange cross section for the molecular ion of hydrogen on the hydrogen molecule. The calculation of the exchange interaction was based in this paper on previous variational calculations of the wave function of molecular hydrogen and the molecular ion. This was subsequently used to find the resonance charge-exchange cross section. In the present paper we shall use the asymptotic method which was described in[3] and was found to be satisfactory in the case of charge exchange between an atomic ion and the corresponding atom. It is based on the assumption that the resonance charge-exchange cross section is large in comparison with the characteristic linear dimensions of the atom. This has enabled us to simplify the problem quite considerably and to perform the calculation not only for hydrogen but even for more complicated systems.

2. Since the process under consideration has a large cross section, the transitions take place at large distances between the particles as compared with the linear dimensions of the atoms. The interaction potential at such distances is small in comparison with the dissociation energy of the molecules, so that the degrees of freedom of each molecule can, as before, be subdivided into electronic, rotational, and translational. The collision energy of the atomic particles is not very low, so that the elastic-scattering cross section is small in comparison with the charge-exchange cross section. When this is so we can confine our attention to the straight-line approximation for the particle trajectories when we analyze the charge-exchange process. Moreover, the characteristic collision time is small in comparison with the characteristic time of rotation of the molecule, which is valid provided

$$\varepsilon \gg \varepsilon_{\text{tot}} \rho / a_0, \tag{1}$$

where ϵ is the energy of the colliding particles, ϵ_{rot} is the separation between the rotational levels, and ρ is the characteristic impact parameter which governs the charge-exchange cross section which, in turn, is of the order of $\sigma \sim \rho^2$. We shall use the atomic system of units in which $\hbar = m_{\text{el}} = e^2 = 1$. When the condition given by Eq. (1) is satisfied, the axis of the molecule will not rotate during the collision time.

Under the above conditions, electronic transitions proceed in the same way as in the case of charge exchange between an atomic ion and the corresponding atom.[3] The charge-exchange cross section is determined by the exchange interaction Δ between the ion and the molecule. Problems which arise as a result of this are connected with the allowance for the vibrational motion of the nuclei and the anisotropic distribution of the electrons in the molecule.

If the collision time is long in comparison with the characteristic time of oscillation of the nuclei, transitions between the vibrational levels are adiabatically of low probability. This is valid when

$$\varepsilon \ll \sigma_{\text{ce}} \frac{1}{a_0^2} \frac{me^2}{\hbar^2}. \tag{2}$$

In this case, the transitions occur without change in the vibrational state of the ion and the molecule, and the charge-exchange cross section can be determined in the same way as the resonance charge-exchange cross section for the ion-atom system[4]

$$\sigma = \int_0^\infty 2\pi\rho\, d\rho \sin^2\delta = \frac{\pi R_0^2}{2}, \quad \delta = \int_{-\infty}^{+\infty} \frac{\Delta}{2}\, dt, \tag{3}$$

where R_0 is the impact parameter for which

$$\delta = 0.28.$$

The exchange-interaction potential for the ion-atom interaction is given by

$$\Delta = 2\langle \Psi_1 | \hat{H} | \Psi_2 \rangle, \tag{4}$$

where $\hat{H}$ is the Hamiltonian for the system of electrons, the wave function Ψ_1 corresponds to the case where the valence electron undergoing the transition is located in the first atomic residue, and Ψ_2 corresponds to the case when it is located in the second atomic residue. These two wave functions correspond to fixed directions of the axes of the molecules, and can be written as products of the electronic and nuclear vibrational wave functions. The exchange interaction can therefore be described by

$$\Delta = S_1 S_2 \Delta_{\text{el}}, \tag{5}$$

where S_1 and S_2 are the overlap integrals between the vibrational nuclear wave functions of the molecule and the ion for the first and second particles, respectively.

3. To find the exchange interaction Δ_{el} for a given configuration of the nuclei, which corresponds to the overlap of the electronic wave functions, we must represent the wave function of the system in the form of a combination of the wave functions for the molecular ion and for the electron undergoing the transition. This operation was carried out in[5] for interacting atomic particles and takes into account the contribution of the spin of the molecular ion and of the electron to the spin of the molecule, the spin of the molecular ion and the molecule to the resultant spin of the system, the composition of the orbital angular momenta of these particles, and the exchange of identical electrons.

As a result, the exchange-interaction potential for the ion-molecule system can be expressed in terms of the single-electron exchange interaction which corresponds to the case where the system contains only one valence electron. Under these conditions, the exchange interaction between the molecular ion and the molecule may be written in the form

$$\Delta_{\text{el}} = \frac{J + {}^1/_2}{2s+1} C N \Delta_1 \langle Y_{lm}(\mathbf{n}) | Y_{lm}(\mathbf{n}') \rangle. \tag{6}$$

The first factor represents the contribution of the spin of the electron and of the spins of the molecular ions (which are equal to s) to the total spin J of the system. This factor is, of course, the same as in the case of the interaction between the ion and the corresponding atom.[5]

The second factor, C, represents the correlation between the orbital angular momenta of the molecular ion, the valence electron, and the molecule. We have calculated this coefficient from the single-electron model of the molecule. Values of C found for special cases of the interaction by the method described in[6] are listed in the table. In the case of valence σ electrons the coefficient C is equal to unity. Next, the quantity N in Eq. (6) is the number of identical valence electrons whose transitions determine the exchange interaction, m is the difference between the components of the orbital angular momenta of the molecule and the molecular ion along the axis of the molecule, which is equal to the component of the angular momentum of the valence electron, l is the orbital angular momentum of the valence electron in the molecule, and n and n′ represent the directions of the axes of the molecule. The single-electron exchange interaction between the colliding particles in the case of a molecule and its singly-charged ion in the s state is given by[3]

$$\Delta_1 = A(\theta) A(\theta') e^{-1/\gamma - R\gamma} R^{2/\gamma - 1}, \tag{7}$$

where R is the distance between the interacting particles, θ is the angle between the axis of the molecule and the direction of the electron undergoing the transition, and γ can be expressed in terms of the binding energy of the electron in the molecule.

4. The next problem is to determine the asymptotic coefficient A which is introduced so that the radial wave function for the valence electron at a large distance r from the molecule is normalized to unity and is of the form

$$\varphi(r)_{r\to\infty} = A(\theta) r^{1/\gamma - 1} e^{-r\gamma}. \tag{8}$$

For the hydrogen molecule this coefficient was found by comparing the valence-electron density at large distances, obtained from a given asymptotic function, with the result of a variational calculation

$$\rho(\mathbf{r}_2) = \int |\Phi(r_1, r_2)|^2 d\mathbf{r}_1 = \frac{A^2(\theta)}{4\pi} r_2^{2/\gamma - 2} e^{-2r_2\gamma}, \tag{9}$$

where the subscripts 1 and 2 refer to electrons in the molecule. To find $\rho(\mathbf{r}_2)$ we have used the sufficiently accurate wave function given by James and Coolidge[7] with 13 variable parameters:

Parameters governing the resonance charge-exchange cross section (in atomic units) and the charge-exchange cross section at 1 eV collision energy in the laboratory system

Molecule	Ion	γ	N	C	$A_{at} = A_1 + A_2/2$	Equilibrium distance between nuclei		Overlap integral S	Charge exchange cross section in units of 10^{-15} cm² at 1 eV
						α_{mol}	α_{ion}		
$H_2(^1\Sigma)$	$H_2^+(^2\Sigma)$	1,07	2	1	2	1.4	2.05	0.314	2.5
$N_2(^1\Sigma)$	$N_2^+(^2\Sigma)$	1,07	2	1	1.5	2,11	2,07	0.945	5.4
$O_2(^3\Sigma)$	$O_2^+(^2\Pi)$	0,95	1	1/2	1.1	2,28	2.12	0.48	2.4
$NO(^2\Pi)$	$NO^+(^1\Sigma)$	0,825	1	1	1.3	2,17	2.01	0.407	5.1
$CO(^1\Sigma)$	$CO^+(^2\Sigma)$	1,015	2	1	1.1	2.13	2.11	0.988	5.8
$OH(^2\Pi)$	$OH^+(^3\Sigma)$	0,983	1	1	1.5	1.84	1.94	0,926	2.9

$$\Phi = \frac{1}{2\pi} e^{-0{,}75(\eta_1+\eta_2)} \{4{,}45 + 1.19(\xi_1^2 + \xi_2^2) - 0.916\xi_1\xi_2 - 0.827(\eta_1 + \eta_2)$$
$$- 0{.}121(\eta_1\xi_2^2 + \eta_2\xi_1^2) + 124\xi_1\xi_2(\eta_1 + \eta_2) - 0.171(\eta_1\xi_1^2 + \eta_2\xi_2^2)$$
$$+ 0{,}083(\eta_1^2 + \eta_2^2) + 0{,}701\lambda + 0.07\lambda(\xi_1^2 + \xi_2^2) - 0.0228\xi_1\xi_2\lambda$$
$$- 0.0398(\eta_1 + \eta_2)\lambda - 0.0238\lambda^2\},$$
$$\lambda^2 = \eta_1^2 + \eta_2^2 + \xi_1^2 + \xi_2^2 - 2 - 2\eta_1\eta_2\xi_1\xi_2 -$$
$$- 2[(\eta_1^2 - 1)(\eta_2^2 - 1)(1 - \xi_1^2)(1 - \xi_2^2)]^{1/2} \cos(\varphi_1 - \varphi_2), \quad (10)$$

where $\eta_1, \eta_2, \xi_1, \xi_2, \varphi_1$, and φ_2 are the elliptic coordinates of the electrons.

Since the molecule has rotational symmetry, we can average Eq. (10) with respect to $\varphi = \varphi_1 - \varphi_2$ and, since $\eta_2 \gg \eta_1$, we have

$$\overline{\lambda} \approx \eta_2 - \eta_1\xi_1\xi_2, \quad \overline{\lambda}^2 = \eta_1^2 + \eta_2^2 + \xi_1^2 + \xi_2^2 - 2 - 2\eta_1\eta_2\xi_1\xi_2.$$

Bearing this in mind, we find that the density distribution for the second electron is

$$\rho(\mathbf{r}_2) = \int \Phi^2 \frac{a^3}{8}(\eta_1^2 - \xi_1^2)\, d\eta_1\, d\xi_1\, d\varphi_1 = 0{,}0546 e^{-1{,}5\eta_2}[11.55 - 1.877\eta_2$$
$$+ 0{,}162\eta_2^2 - 0.0076\eta_2^3 + 0{,}0003\eta_2^4 + 5{,}75\xi_2^2 + 0.929\xi_2^4 + 0.0042\xi_2^6$$
$$- 1.284\eta_2\xi_2^2 + 0{,}0945\eta_2^2\xi_2^2 + 0.0087\eta_2^2\xi_2^4 - 0.1867\eta_2\xi_2^4 - 0{,}0031\eta_2^3\xi_2^2]. \quad (11)$$

$$\eta_2 = (r_{b_2} + r_{c_2}) / a, \quad \xi_2 = (r_{b_2} - r_{c_2}) / a,$$

where a is the equilibrium distance between the nuclei b and c in the molecule. Since for $r \to \infty$ we have $r_{b_2} \approx r + \frac{1}{2} a \cos\theta$ and $r_{c_2} \approx r - \frac{1}{2} a \cos\theta$, it follows that at large distances $\eta_2 \approx 2r/R$ and $\xi_2 \approx \cos\theta$ (r is the distance from midpoint of the axis of the molecule to the electron).

By making Eq. (9) continuous for each fixed angle in the range of distances where A(r) varies slowly, we obtain

$$A(\theta) = 2.4\, \mathrm{ch}(0.75 \cos\theta) = 2.4\, \mathrm{ch}(\tfrac{1}{2}\gamma a \cos\theta). \quad (12)$$

In the case of arbitrary molecules, the asymptotic coefficient $A(\theta)$ will be found from a model in which the wave function of a valence electron in the molecule is

$$\psi = \frac{1}{\sqrt{1+K}} \left[\psi_{\mathrm{at}}\left(\mathbf{r} + \frac{\mathbf{a}}{2}\right) + \psi_{\mathrm{at}}\left(\mathbf{r} - \frac{\mathbf{a}}{2}\right)\right]. \quad (13)$$

In this expression, Ψ_{at} represents the atomic wave functions and K is the overlap integral. It is clear that this model assumes weak interaction between the atoms. Moreover, we shall use the ionization potential of the molecule as the electron binding energy. If most of the dependence of the wave function on distance is exponential, this yields

$$A(\theta) = \frac{A_{\mathrm{at}}}{\sqrt{1+K}}\, \mathrm{ch}\left(\frac{\gamma a}{2}\cos\theta\right). \quad (14)$$

In view of the accuracy with which Δ is calculated, we shall take for the overlap integral the expression obtained by using hydrogen-like functions. This gives

$$A(\theta) = \frac{A_{\mathrm{at}}\sqrt{2}\, \mathrm{ch}(\tfrac{1}{2}\gamma a \cos\theta)}{[1 + e^{-\gamma a}(1 + a\gamma + \tfrac{1}{3}a^2\gamma^2)]^{1/2}}. \quad (15)$$

In particular, in the case of hydrogen,

$$A = 2.16\, \mathrm{ch}(0.75 \cos\theta), \quad (16)$$

which is not very different from the expression obtained as a result of the variation of the wave function with 13 parameters.

The exchange-interaction potential between the ion and the molecule in the case of a valence s electron is thus given by

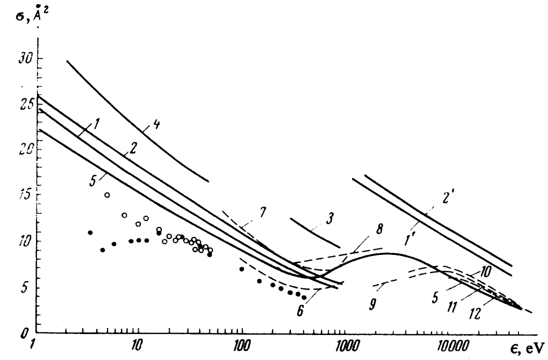

FIG. 1. Resonance charge-exchange cross section for $H_2^+ + H_2$. Solid line represents theoretical calculations. Broken line and points show experimental data. Curves 1 and 2–present work, based on Eq. (16) and variational calculation; curves 1′ and 2′ corresponds to S = 1; 3–[1]; 4–[8]; 5–[2], ○–[9], ●–[10]; 6–[11]; 7–[12]; 8–[13]; 9–[14]; 10–[15]; 11–[16]; 12–[17].

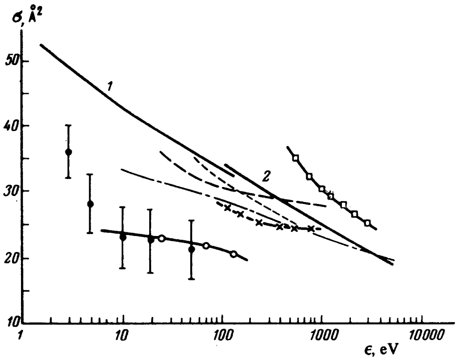

FIG. 2. Resonance charge-exchange cross section for $N_2^+ + N_2$. Curves 1, 2 (present work) are compared with experimental results; 2–corresponds to S = 1, □–[18], ○–[19], ---- [20], ---- [21], ×–[22], -·-- [23], ●–[8].

$$\Delta = S^2 \frac{J + \tfrac{1}{2}}{2s + 1} A(\theta) A(\theta') N R^{2/\gamma - 1} e^{-R\gamma - 1/\gamma} \quad (17)$$

whereas for a valence p electron

$$\Delta = S^2 \frac{J + \tfrac{1}{2}}{2s + 1} A(\theta) A(\theta') C N R^{2/\gamma - 1 - |m|} e^{-R\gamma - 1/\gamma} 3 \frac{(1 + |m|)!}{(1 - |m|)!} \frac{1}{(2\gamma)^{|m|}} \cos\vartheta. \quad (18)$$

In this expression, ϑ is the angle between the axes of the molecules and S is the overlap integral between the vibrational wave functions. Substituting these expressions into the formula for the charge-exchange cross section, and averaging over the directions of the molecular axes θ and θ', we obtain the following expression for the resonance charge-exchange cross section:

$$\sigma = \frac{\pi R_0^2}{2}, \quad 0{,}28v = \sqrt{\frac{\pi R_0}{2\gamma}}\, \Delta(R_0) \Big|_{\cos\theta = \cos\theta' = 1/2}. \quad (19)$$

Comparison with experimental results for hydrogen, nitrogen, and oxygen is given in Figs. 1-3, and the calculated results for other cases are given in the table.

The above case corresponds to low collision energies, as defined by Eq. (2), when transitions involving

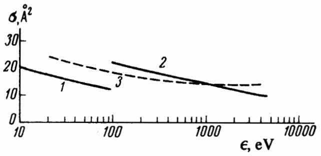

FIG. 3. Resonance charge-exchange cross section for $O_2^+ + O_2$. Curves 1 and 2 (present work) are compared with the experimental curve 3–[23], curve 2 corresponds to S = 1.

a change in the vibrational states are adiabatically of low probability. In the opposite limiting case, when transitions to different vibrational levels occur quite freely, the transition probability is independent of the vibrational states and the transition cross section is given by the previous formulas but with the overlap integral between the nuclear functions replaced with unity. The intermediate situation in the case of hydrogen was considered by Bates and Reid.[2] If the overlap integral between the nuclear functions is close to unity, the results for limiting cases are identical, and the theory developed here is valid throughout the range of collision energies.

Figures 1–3 show the resonance charge-exchange cross sections for $H_2^+ - H_2$, $N_2^+ - N_2$, and $O_2^+ - O_2$, calculated from Eqs. (3), (17), and (18), and the experimental results. The table lists the resonance charge-exchange cross sections for a number of pairs at 1 eV. In addition to the above experimental data there are also measurements of the resonance charge-exchange cross sections for NO^+ on NO which yield 1.3×10^{-15} cm² and 10^{-15} cm² at 100 and 1000 eV, respectively. The calculated cross sections obtained on the assumption that the vibrational states of the ion and of the molecule do not change during charge exchange lead to much higher values at these energies, namely 2.4×10^{-15} and 1.4×10^{-15} cm², respectively.

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