

# Resonance charge exchange of diatomic molecular ions on molecules

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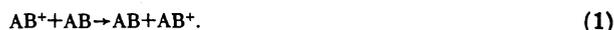
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The asymptotic theory of resonance charge exchange of a diatomic molecular ion on a molecule is presented. The asymptotic parameters of the valence electron in the diatomic molecule are found, and these parameters are used to determine the potential for exchange interaction of the molecular ion with the related diatomic molecule. The role of rotational transitions in the molecule and molecular ion in resonance charge exchange is clarified. Expressions are obtained for the cross section for resonance charge exchange. The theoretical cross sections are compared with experiment.

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1. In the present work we investigate the resonance charge exchange of a diatomic molecular ion on the related molecule:



The cross section for this process is expressed in terms of the potential for exchange interaction of the molecular ion and the molecule. In the case of resonance charge exchange of the  $H_2^+$  ion on the  $H_2$  molecule Bates and Reid<sup>1</sup> utilized calculations of the potential surface of the  $H_2^+ - H_2$  system, which are possible only for simple systems. Gurnee and Magee<sup>2</sup> and Flannery and co-workers<sup>3</sup> based their calculations of the cross sections for resonance charge exchange of other molecular ions ( $N_2^+$ ,  $O_2^+$ ,  $CO^+$ ,  $NO^+$ ) on model representations for the interaction potential, the accuracy of which was not established. For the present problem it would be natural to use asymptotic methods of calculation based on the fact that the cross section for the process significantly exceeds the size of the molecule. In this case the theory contains a small parameter which permits the accuracy of the result to be evaluated. Asymptotic approaches for the present problem were developed by Bylkin<sup>4</sup> but at that time reliable information was not available on the asymptotic behavior of the electron in the molecule. Use of the tables of molecular wave functions<sup>5</sup> which have appeared in recent years permits one to find simple mechanisms for the transitions under consideration, to obtain numerical values of resonance charge-exchange cross sections, and to analyze the nature of charge exchange at low collision velocities. In the present work we devote special attention to the role of rotational transitions in resonance charge exchange of molecular particles. These transitions are important in slow collisions of an ion with a molecule. Allowance for rotational transitions is difficult in terms of other approaches and therefore it has not been investigated previously.

2. In determination of the cross section for the process (1) we shall use the impact-parameter method<sup>1,4</sup> and shall take into account the fact that the transition of the electron in accordance with (1) occurs at rather large distances  $R$  between the centers of the colliding particles, such that the interaction between them is small in comparison with the characteristic electron energies. Here it is sufficient to take into account only

unexcited electronic states of the molecule and ion. In summary, we expand the wave function of the entire system in a set of normalized molecular functions  $\Phi_\alpha^{(1)}$ ,  $\Phi_\beta^{(2)}$ , defined at rather large distances  $R$  in comparison with the size of the molecules:<sup>1)</sup>

$$\begin{aligned} \psi(r, R, t) = & \sum_\alpha c_\alpha^{(1)}(t) \Phi_\alpha^{(1)}(r, R) \exp\{-iH_{\alpha\alpha}^{(1)} t\} \\ & + \sum_\beta c_\beta^{(2)}(t) \Phi_\beta^{(2)}(r, R) \exp\{-iH_{\beta\beta}^{(2)} t\}. \end{aligned} \quad (2)$$

Here  $r$  is the set of coordinates of the electrons (see Fig. 1), the subscripts 1 and 2 denote the electronic state of the system before and after the transition of the valence electron, and  $\alpha$  and  $\beta$  are the sets of vibrational-rotational quantum numbers. The matrix elements of the total Hamiltonian of the system  $\hat{\mathcal{H}}$  which occur in the arguments of the exponentials are defined as follows:

$$\begin{aligned} H_{\alpha\alpha}^{(1)} = & \langle \Phi_\alpha^{(1)} | \hat{\mathcal{H}} | \Phi_\alpha^{(1)} \rangle = E_\alpha^{(1)} + \langle \Phi_\alpha^{(1)} | \hat{V} | \Phi_\alpha^{(1)} \rangle, \\ H_{\beta\beta}^{(2)} = & E_\beta^{(2)} + \langle \Phi_\beta^{(2)} | \hat{V} | \Phi_\beta^{(2)} \rangle, \end{aligned}$$

where  $E_\alpha^{(1)}$  and  $E_\beta^{(2)}$  are the values of the energy of the system of particles corresponding to an infinitely separated molecule and molecular ion, which are found in the specified quantum states; the angle brackets denote integration over the electron and nuclear coordinates; the operator  $\hat{V}$  characterizes the interaction of the molecule with the ion. By definition the wave functions  $\Phi_\alpha^{(1)}$  and  $\Phi_\beta^{(2)}$  describe situations in which the valence electron is concentrated mainly near the first or second residual molecule, experiencing a rather weak perturbation from the other molecular ion, i.e., they are defined in the limit of sufficiently large values of  $R$ .

Substituting the expansion (2) into the nonstationary Schrödinger equation  $i\partial\psi/\partial t = \hat{\mathcal{H}}\psi$  and using the condition of normalization of the wave functions  $\Phi$ , we obtain a system of equations for the transition probability amplitudes  $c_\alpha^{(1)}$  and  $c_\beta^{(2)}$ :

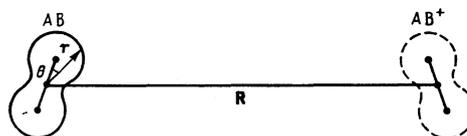


FIG. 1. Collision geometry in resonance charge exchange of a diatomic molecular ion on the molecule.

$$\begin{aligned}
i c_{\alpha}^{(1)} &= \sum_{\beta} c_{\beta}^{(2)} \langle \Phi_{\alpha}^{(1)} | \hat{\mathcal{H}} | \Phi_{\beta}^{(2)} \rangle - \langle \Phi_{\alpha}^{(1)} | \Phi_{\beta}^{(2)} \rangle \\
&\times \langle \Phi_{\beta}^{(2)} | \hat{\mathcal{H}} | \Phi_{\beta}^{(2)} \rangle \exp\{-i(H_{\beta\beta}^{(22)} - H_{\alpha\alpha}^{(11)})t\}, \\
i c_{\beta}^{(2)} &= \sum_{\alpha} c_{\alpha}^{(1)} \langle \Phi_{\beta}^{(2)} | \hat{\mathcal{H}} | \Phi_{\alpha}^{(1)} \rangle - \langle \Phi_{\beta}^{(2)} | \Phi_{\alpha}^{(1)} \rangle \\
&\times \langle \Phi_{\alpha}^{(1)} | \hat{\mathcal{H}} | \Phi_{\alpha}^{(1)} \rangle \exp\{-i(H_{\alpha\alpha}^{(11)} - H_{\beta\beta}^{(22)})t\},
\end{aligned} \quad (3)$$

from which for specified initial conditions  $c_{\alpha}^{(1)}(t \rightarrow -\infty) = 1$  and  $c_{\beta}^{(2)}(t \rightarrow -\infty) = 0$  we find a solution for  $c_{\beta}^{(2)}(t \rightarrow +\infty)$ , which determines the "partial" cross section for resonance charge exchange (1) from the channel  $\alpha$  to the channel  $\beta$  of the reaction,

$$\sigma_{\alpha\beta} = 2\pi \int_0^{\infty} |c_{\beta}^{(2)}(t \rightarrow \infty)|^2 \rho d\rho,$$

where  $\rho$  is the impact parameter of the collision. The combination of matrix elements occurring in the parentheses in the equations (3) includes the potential for exchange interaction of the electrons, which depends on the distance  $R$  and on the relative orientation of the axes of the molecule and the ion, which is averaged over the nuclear wave functions of the molecular particles. Systematic calculation of the probability of transition of the valence electron, and also allowance for vibrational-rotational transitions in the system, comprise the greatest difficulties in calculation of the cross section for reaction (1).

Analysis of various mechanisms for transitions between nuclear states of the particles in reaction (1) permits one to establish those regions of the collision energy  $E$  where it is possible to find analytic solutions of the system (3). In particular, we consider below the limiting case of low energies  $E$  where it becomes important to take into account transitions between rotational states of the charge-exchanging molecular particles. In this way it is possible to trace the behavior of the resonance charge exchange cross section over the entire energy region of practical interest for the collision of the particles in reaction (1).

3. As has already been mentioned, the asymptotic theory of charge exchange utilizes the fact that the transition of the electron from one molecular core to the other occurs at large distances between the centers of the colliding particles. Here, in the electron-coordinate region responsible for the main contribution to the potential for their exchange interaction and located far from the ionic core, the wave function of the valence electron can be represented in the form

$$\psi(r, \theta, \varphi) = A(\theta) r^{1/2} e^{-\gamma r} e^{im\varphi}, \quad (4)$$

where  $r$  is the distance from the selected center of the molecular particle (below we shall assume that this center coincides with the electrical center of the molecule),  $\theta$  is the angle between the radius vector of the electron and the axis of the molecule,  $\varphi$  is the azimuthal angle (see Fig. 1),  $-\gamma^2/2$  is the binding energy of the valence electron in the molecule, and  $m$  is the projection of the electron angular momentum on the axis of the molecule. In contrast to the case of charge exchange of atomic particles, we have included in the asymptotic coefficient  $A(\theta)$  the angular dependence of the electron wave function. The remaining dependence, in

TABLE I. Asymptotic coefficients \* of homonuclear molecules and their ions.

Molecule	$\gamma$	$\gamma R_e$	$a$	$b$	$c$	$\alpha$	$\beta$
H <sub>2</sub>	1.065	1.53	2.26±0.01	0.35±0.01	0.09±0.02	0	0
C <sub>2</sub>	0.935	2.20	2.05±0.06	0.48±0.09	0.32±0.16	1	0
C <sub>2</sub> <sup>-</sup>	0.510	1.22	0.66±0.04	2.10±0.31	0.84±0.32	0	0
N <sub>2</sub>	1.070	2.22	1.52±0.04	1.20±0.01	-0.03±0.01	0	0
O <sub>2</sub>	0.941	2.15	2.53±0.01	0.65±0.02	0.01±0.01	1	1
O <sub>2</sub> <sup>-</sup>	0.180	0.46	1.51±0.07	2.52±0.07	0.37±0.15	1	1
F <sub>2</sub>	1.074	3.05	2.72±0.06	0.39±0.08	0.38±0.15		

$$*) A(\theta) = [a \operatorname{ch}(\gamma R_e \cos \theta) (1 + c \cos^2 \theta) \sin^{\alpha} \theta \cos^{\beta} \theta]$$

addition to  $A(\theta)$ , of the electron wave function on the coordinates was found by solution of the Schrödinger equation for an electron in the Coulomb field of the molecular core.

In Tables I-III we have given the values of the asymptotic coefficient  $A(\theta)$  for a number of molecules, which were found by matching the wave function in the form (4) with the Hartree-Fock one-electron wave functions of the valence electrons, which have been represented in analytical form in Refs. 5. The procedure for matching these wave functions was carried out for a given angle  $\theta$  in the region of distances to the center of the molecule  $2a < r < 4a$ , where  $a$  is a dimension of the order of the equilibrium internuclear distance in the molecule. In the coordinate region considered, the self-consistent one-electron wave function in the molecule<sup>5</sup> is best approximated by the function (4). The limits of variation of the quantity  $A(\theta)$ , obtained by comparison of wave functions in this coordinate region, have been included in the error of the asymptotic method presented. In the angular dependence  $A(\theta)$  we have separated the part characterizing the electron state, and the remaining part is represented in the form of an appropriate expansion in trigonometric functions.

4. By representing the wave function of the valence electron in the form (4), i.e., as a one-centered function with a separated angular dependence, it is possible to reduce the problem of determining the potential for exchange interaction of the electrons in the system to the atomic case. Here the specific features of charge exchange of the molecular particles appear in the angular dependence of the electron wave function and the transitions between the nuclear states of the particles.

In the zeroth Born-Oppenheimer approximation we represent the wave functions of the system  $\Phi_{\alpha}^{(1)}, \Phi_{\beta}^{(2)}$  in the form of the product of the electronic and nuclear wave functions, and we represent the total Hamiltonian of the system in the form of the sum

$$\hat{\mathcal{H}} = \hat{H}_{el} + \hat{H}_{nu},$$

TABLE II. Asymptotic coefficients \* of heteronuclear molecules.

Molecule	$\gamma$	$R_e$	$\gamma R_e$	$a$	$b$	$c$	$\alpha$
NF	0.951	2.489	2.367	1.59±0.06	0.87±0.08	-0.63±0.31	1
CO	1.015	2.132	2.164	2.04±0.08	0.16±0.04	-0.41±0.20	0
NO	0.842	2.1747	1.829	0.51±0.04	0.20±0.05	-0.21±0.16	1

$$*) A(\theta) = \left[ \frac{a \operatorname{ch}(\gamma R_e \cos \theta)}{1 + b \cos \theta} (1 + c \cos^2 \theta) \right] \sin^{\alpha} \theta \cos^{\beta} \theta$$

TABLE III. Asymptotic coefficients \* of hydrides and their ions.

Molecule	$R_e$	$\gamma$	$\alpha$	$b$
OH	1.8342	0.985	1.88±0.05	0.21±0.03
OH <sup>-</sup>	1.781	0.365	0.78±0.09	0.28±0.09
NH	1.9614	0.984	1.83±0.09	0.21±0.08
NH <sup>-</sup>	1.923	0.167	0.32±0.06	0.08±0.06
CH	2.1214	0.895	1.68±0.09	0.14±0.04
CH <sup>-</sup>	2.086	0.233	0.61±0.10	0.16±0.09
PH	2.708	0.833	2.20±0.06	0.10±0.04
SH	2.551	0.874	2.15±0.02	0.07±0.02
HF	1.7328	1.077	1.42±0.08	0.17±0.06

\*  $A(\theta) = (\alpha + b \exp(\gamma R_e \cos \theta)) \sin \theta$

where  $\hat{H}_{el}$  is the electron Hamiltonian and  $H_{nu}$  is the nuclear Hamiltonian. Since the characteristic energies of the electrons significantly exceed the characteristic energies of the nuclear transitions, we can set  $\mathcal{H} \approx \hat{H}_{el}$ . With these assumptions the potential for exchange interaction of the molecular particles, which by definition is equal to

$$\Delta = 2(\langle \Phi_\alpha^{(1)} | \hat{\mathcal{H}} | \Phi_\beta^{(2)} \rangle - \langle \Phi_\alpha^{(1)} | \Phi_\beta^{(2)} \rangle \langle \Phi_\beta^{(2)} | \hat{\mathcal{H}} | \Phi_\alpha^{(1)} \rangle) \quad (5)$$

[see Eq. (3)], is written in the form

$$\Delta = \langle \chi_\alpha | \Delta_{el} | \chi_\beta \rangle,$$

where  $\Delta_{el}$  is the electron exchange interaction potential, which depends on the configuration of the nuclei, and  $\chi_\alpha$  and  $\chi_\beta$  are the nuclear wave functions of the molecular particles respectively before and after the transition of the valence electron.

Using a genealogical scheme of constructing the electronic wave function of the molecule from the wave functions of the valence electron and the wave functions of the electrons of the molecular ion, and also the rule for addition of the spins of the molecule  $S$  and of the molecular ion  $S'$  to obtain the total spin  $J$  of the system, we can reduce the quantity  $\Delta_{el}$  to the potential of the one-electron exchange interaction  $\Delta_m$  (Ref. 4):

$$\Delta_{el} = \frac{J+1/2}{2S'+1} \Delta_m;$$

here  $m$  is the quantum number of the projection of the orbital angular momentum of the electron on the axis of the molecule. Since in the asymptotic theory of resonance charge exchange the potential of the one-electron exchange interaction is determined by the overlap of the wave functions of the electrons in a narrow region of coordinates far from both molecular cores, where the value of the asymptotic coefficient  $A(\theta)$  can be assumed constant, then by analogy with the case of transition of an electron from an atom to an atomic ion, the desired quantity  $\Delta_m$  will be equal to<sup>4</sup>

$$\Delta_m = \text{Re}^{-1/\gamma} \psi_1(R/2) \psi_2(-R/2),$$

where  $R$  is the distance between the centers of the charge-exchanging molecular particles and  $\psi_{1,2}(R/2)$  is the value of the electron wave function in the corresponding molecule at the center of this distance interval. With use of expression (4) the exchange potential  $\Delta_{el}$  takes the final form

$$\Delta_{el} = \frac{J+1/2}{2S'+1} e^{-1/\gamma} A(\theta_1) A(\theta_2) R \left(\frac{R}{2}\right)^{2/\gamma-2} e^{-\gamma R}; \quad (6)$$

here  $\theta_1$  ( $\theta_2$ ) is the angle between the axis of the molecule

(molecular ion) and the direction joining the chosen centers of the particles.

5. To find the cross section for the process (1) under discussion, it is necessary to solve the system of equations (3), which with the simplifications made above takes the form

$$i\dot{c}_\alpha^{(1)} = \frac{1}{2} \sum_\beta c_\beta^{(2)} \langle \chi_\alpha^{(1)} | \Delta_{el}(R, \theta_1, \theta_2) | \chi_\beta^{(2)} \rangle \exp\{i(E_\alpha^{(1)} - E_\beta^{(2)})t\},$$

$$i\dot{c}_\beta^{(2)} = \frac{1}{2} \sum_\alpha c_\alpha^{(1)} \langle \chi_\beta^{(2)} | \Delta_{el}(R, \theta_1, \theta_2) | \chi_\alpha^{(1)} \rangle \exp\{-i(E_\alpha^{(1)} - E_\beta^{(2)})t\}, \quad (7)$$

where in writing out the arguments of the exponentials we have taken into account that the modulus of the difference of the matrix elements has the property

$$|\langle \Phi_\alpha^{(1)} | \mathcal{D} | \Phi_\alpha^{(1)} \rangle - \langle \Phi_\beta^{(2)} | \mathcal{D} | \Phi_\beta^{(2)} \rangle| \ll (E_\alpha^{(1)} - E_\beta^{(2)}).$$

To shorten the notation we have introduced the following designations:

$$\Delta_{el}(R, \theta_1, \theta_2) = \Delta_0(R) f(\theta_1, \theta_2), \quad E_\alpha^{(1)} - E_\beta^{(2)} = \omega_{\alpha\beta}.$$

Using the assumption that the translational motion of the molecular particles is not related to their rotational motion, and also the fact that the potential  $\Delta_{el}$  does not depend on the vibrational states of the molecule and the ion, we have

$$\langle \chi_\alpha^{(1)} | \Delta_{el} | \chi_\beta^{(2)} \rangle = \langle j_1, v_1, j_2, v_2 | \Delta_{el} | j_1', v_1', j_2', v_2' \rangle$$

$$= \Delta_0(R) S_{v_1, v_1'} S_{v_2, v_2'} \langle j_1 j_2 | f(\theta_1, \theta_2) | j_1' j_2' \rangle,$$

where  $j$  and  $v$  are the quantum numbers of the rotational and vibrational states of the molecular particles, the subscripts 1 and 2 denote the molecule and the ion, the primes indicate the states of the particles after the transition of the valence electron, and finally  $S_{v_1, v_1'}$  is the overlap integral of the vibrational wave functions of the molecule and the molecular ion. We shall not seek further a solution of the system of equations (7) in the entire region of particle-collision energies  $E$ , but shall present only simple analytic solutions in a series of limiting regions where it is easy to establish from physical considerations the limiting nature of the behavior of the solutions. It turns out in actuality that such "piecewise" solutions can cover the entire region of practical interest of the collision energies of charge-exchanging particles.

We consider first the region of rather fast collisions, where during the characteristic time of interaction of the particles the axis of the molecule cannot rotate appreciably. This corresponds to the condition  $\dot{\theta} \ll v/a$ , where  $\dot{\theta}$  is the angular velocity of the molecule and  $a \sim (R_0/\gamma)^{1/2}$  is the dimension of the region of the electron transition (the charge-exchange cross section is  $\sigma \propto R_0^2$ , and  $\gamma \approx -d \ln \Delta_0 / dR$ ). Since  $\dot{\theta} \sim r_e^{-1} (\epsilon_{r_0}/\mu)^{1/2}$  ( $r_e$  is the distance between the nuclei in the molecule,  $\mu$  is the reduced mass of the molecule, and  $\epsilon_{r_0}$  is the characteristic rotational energy), the inequality given above takes the form

$$E/e_{r_0} \gg R_0/\gamma r_e^2; \quad (8)$$

here  $E \sim \mu v^2$  is the energy of collision of the particles in the  $C$ -system. The system (7) is then written in the following form:<sup>2)</sup>

$$i\dot{c}_{v_1 v_2}^{(1)} = \frac{1}{2} \sum_{v_1' v_2'} S_{v_1 v_1'} S_{v_2 v_2'} \Delta_{el}(R, \theta_1, \theta_2) c_{v_1' v_2'}^{(2)} \exp(i\omega_{v_1} t),$$

$$i\dot{c}_{v_1' v_2'}^{(2)} = \frac{1}{2} \sum_{v_1 v_2} S_{v_1 v_1'} S_{v_2 v_2'} \Delta_{el}(R, \theta_1, \theta_2) c_{v_1 v_2}^{(1)} \exp(-i\omega_{v_1} t),$$

where  $\omega_{v_i}$  is the characteristic difference of energies of vibrational levels of the molecular particles.

Let us consider two opposite limiting cases with respect to vibrational transitions. In the first of these cases, all possible vibrational transitions are allowed and the exponentials in the system (9) can be replaced by unity. This condition is satisfied for a collision velocity

$$v \gg \omega_{v_1} a \sim \omega_{v_1} (R_0/\gamma)^{1/2}. \quad (10)$$

Now introducing new coefficients

$$c_1 = \sum_{v_1 v_2} c_{v_1 v_2}^{(1)}, \quad c_2 = \sum_{v_1' v_2'} c_{v_1' v_2'}^{(2)}$$

and using the sum rules for the overlap integrals

$$\sum_k S_{ki} = \sum_l S_{kl} = 1,$$

we reduce the system (9) to the form

$$i\dot{c}_1 = \frac{1}{2} \Delta_{el}(R, \theta_1, \theta_2) c_2; \quad i\dot{c}_2 = \frac{1}{2} \Delta_{el}(R, \theta_1, \theta_2) c_1.$$

The cross section obtained eventually for resonance charge exchange will correspond to fixed directions of the axes of the molecule and the ion relative to the line joining their centers, and by analogy with the case of charge exchange of atomic particles it is conveniently represented in the form<sup>4</sup>

$$\sigma(\theta_1, \theta_2) = \frac{\pi R_0^2}{2}, \quad \left(\frac{\pi R_0}{2\gamma}\right)^{1/2} \Delta_{el}(R, \theta_1, \theta_2) = 0.28v. \quad (11a)$$

In the case when the reverse inequality with respect to (10) is satisfied, it is necessary to take into account in the system (9) only resonance terms, for which the argument of the exponential vanishes. This corresponds to formation of the ion and molecule in the same vibrational states as before the transition, i.e.,  $v_1' = v_2$  and  $v_2' = v_1$ . The system (9) reduces in this case to two equations, and the charge-exchange cross section turns out to be

$$\sigma(\theta_1, \theta_2) = \frac{\pi R_0^2}{2}, \quad \left(\frac{\pi R_0}{2\gamma}\right)^{1/2} |S_{v_1 v_1'}|^2 \Delta_{el}(R, \theta_1, \theta_2) = 0.28v. \quad (11b)$$

The cross sections for resonance charge exchange given above must be averaged over the angles  $\theta_1$  and  $\theta_2$ . Using the smallness of the parameter of the asymptotic theory  $1/R_0\gamma \ll 1$ , where  $1/\gamma$  is the characteristic dimension of the molecular orbital of the valence electron, the appropriate average can be carried out as follows.

We shall utilize the fact that the strongest dependence of the charge-exchange cross section is produced by a change of the distance between the molecular particles. This occurs as a result of the exponentially rapid dependence on the distance  $R$  of the electron exchange interaction potential:

$$\Delta_{el}(R) \propto \exp(-R/\gamma).$$

We shall convert the dependence  $\Delta_{el}(R, \theta_1, \theta_2)$  to the

form

$$\exp(-R_0/\gamma) f(R_0, \theta_1, \theta_2) = 1,$$

so that the strongest dependence on the distance is contained in the exponential, while  $j(R_0, \theta_1, \theta_2)$  is a slowly varying function. Then we have identically

$$R_0(\theta_1, \theta_2) = R_0(\bar{\theta}_1, \bar{\theta}_2) + \frac{1}{\gamma} \ln \frac{f(R_0, \theta_1, \theta_2)}{f(R_0, \bar{\theta}_1, \bar{\theta}_2)},$$

and since  $R_0\gamma \gg 1$ , we have

$$\sigma(\theta_1, \theta_2) = \frac{\pi R_0^2(\theta_1, \theta_2)}{2} \approx \frac{\pi R_0^2(\bar{\theta}_1, \bar{\theta}_2)}{2} + \frac{\pi R_0}{\gamma} \ln \frac{f(R_0, \theta_1, \theta_2)}{f(R_0, \bar{\theta}_1, \bar{\theta}_2)}.$$

We shall choose the characteristic values of the angles  $\bar{\theta}_1, \bar{\theta}_2$  in such a way that the following integrals vanish:

$$\begin{aligned} \int_{-1}^1 \sigma(\theta_1, \theta_2) \frac{d \cos \theta_1}{2} \frac{d \cos \theta_2}{2} &\approx \frac{\pi R_0^2(\bar{\theta}_1, \bar{\theta}_2)}{2} \\ + \frac{\pi R_0}{4\gamma} \int_{-1}^1 \ln \frac{f(R_0, \theta_1, \theta_2)}{f(R_0, \bar{\theta}_1, \bar{\theta}_2)} d \cos \theta_1 d \cos \theta_2 &= \frac{\pi R_0^2(\bar{\theta}_1, \bar{\theta}_2)}{2}. \end{aligned}$$

As can be seen, the angles  $\bar{\theta}_1$  and  $\bar{\theta}_2$  which determine the resonance charge exchange cross section are found from the equation

$$\int_{-1}^1 \ln |f(R_0, \theta_1, \theta_2)| d \cos \theta_1 d \cos \theta_2 = 4 \ln |f(R_0, \bar{\theta}_1, \bar{\theta}_2)|.$$

The resonance charge exchange cross section calculated in this way for  $\bar{\theta}_1$  and  $\bar{\theta}_2$  automatically coincides with the cross section averaged over angle with accuracy to the first two terms of the expansion of the desired quantity in the small parameter of the asymptotic theory  $1/R_0\gamma \ll 1$ . We note also that the limiting case (8) selected above corresponded to highly different energies of the translational and rotational motion of the molecular particles.

6. Let us turn now to the nature of the distribution of the molecular particles over the rotational levels. We shall show that the criterion (8) corresponds to appearance of nonadiabatic transitions between rotational states. We shall assume that the rotational angular momenta of the molecule and the ion are rather large ( $j \gg 1$ ) and the selection rules for the transitions have the form  $\Delta j \sim 1$ . This is valid for a smooth dependence of the function  $f(\theta_1, \theta_2)$  in the formula for  $\Delta_{el}(R, \theta_1, \theta_2)$  and occurs in a real situation. The change of rotational energy in a transition is  $\Delta \epsilon_{r_0} \sim B j \Delta j \sim B j$ , where  $B$  is the rotational constant of the molecule and  $\Delta j \sim 1$ . Since  $\epsilon_{r_0} \sim B j^2$ , then  $\Delta \epsilon_{r_0} \sim (B \epsilon)^{1/2}$ . Using the Massey criterion for rotational transitions:  $\Delta \epsilon_{r_0} a / v \ll 1$  and substituting in it the expressions for  $\Delta \epsilon_{r_0}$ ,  $\alpha \sim (R_0/\gamma)^{1/2}$ , and  $B \sim 1/\mu r_e^2$ , we obtain eventually the inequality (8).

Thus, when the criterion (8) is satisfied, nonadiabatic transitions are possible to all rotational states of the molecular particles. In addition, the collision time turns out to be so small that in this case interference effects due to the phase shift of the rotational wave functions are unable to develop. This fact has been taken into account in the equations (9) by specifying direction of the axis of the molecule and the ion in the collision process.

Let us consider next the nature of rotational transitions when the inequality (8) and the condition for which the reverse inequality with respect to (10) exists are satisfied. For this purpose we shall analyze the system (7). Under the conditions mentioned, exchange of vibrational states occurs, and all remaining vibrational transitions can be discarded. Using the representation of the function  $\Delta_{\alpha}(R, \theta_1, \theta_2)$ , we obtain from Eq. (7)

$$i\dot{c}_{j_1 j_2}^{(1)} = \frac{1}{2} |S_{\alpha, \alpha}|^2 \Delta_{\alpha}(R) \sum_{j_1' j_2'} \langle j_1 j_2 | f | j_1' j_2' \rangle c_{j_1' j_2'}^{(2)},$$

$$i\dot{c}_{j_1' j_2'}^{(2)} = \frac{1}{2} |S_{\alpha, \alpha}|^2 \Delta_{\alpha}(R) \sum_{j_1 j_2} \langle j_1' j_2' | f | j_1 j_2 \rangle c_{j_1 j_2}^{(1)}$$

here we have omitted the indices of the vibrational states in the probability amplitudes.

We specify the following initial conditions:

$$c_{j_1 j_2}^{(1)}(t=-\infty) = a_{j_1 j_2}, \quad c_{j_1' j_2'}^{(2)}(t=-\infty) = 0.$$

We shall assume that before the collision, rotational states with different  $j$  values are populated. Since in view of the selection rules we have  $\Delta j \sim 1$ , the distribution of particles in rotational states does not change greatly in the collision process. Making the substitution  $c_{j_1 j_2}^{(1,2)} = a_{j_1 j_2} c_{1,2}$ , we can therefore assume that the distribution function over the rotational states  $a_{j_1 j_2}$  does not depend on the time, and the quantities  $c_{1,2}$  do not depend on the rotational states of the molecule and ion. Taking into account this and the normalization rule  $\sum_{j_1 j_2} |a_{j_1 j_2}|^2 = 1$ , we transform the system of equations written out above to the form

$$i\dot{c}_1 = \frac{1}{2} \Delta c_2, \quad i\dot{c}_2 = \frac{1}{2} \Delta c_1, \quad (12)$$

$$\Delta = |S_{\alpha, \alpha}|^2 \Delta_{\alpha}(R) \sum_{j_1 j_2} a_{j_1 j_2} \langle j_1 j_2 | f | j_1' j_2' \rangle a_{j_1' j_2'}.$$

If we choose as initial rotational states of the molecule and ion  $a_{j_1 j_2} \langle j_1 j_2 |$  states corresponding to a definite direction of the axes of the molecule and ion, the solution of the system (12) will lead us to Eq. (11b) for the resonance charge exchange cross section. The procedure of averaging over the initial rotational distribution of the ion and molecule corresponds to averaging over the directions of the axes of the molecule and ion in Eq. (11b) and leads to the resonance charge exchange cross section  $\bar{\sigma}(\bar{v}, \bar{\theta}_1, \bar{\theta}_2)$  given by us previously. When the condition (10) is satisfied it is necessary to average the dependence of the charge-exchange cross section in Eq. (11a) over the angles  $\theta_1$  and  $\theta_2$ .

7. Let us now consider the case in which the reverse inequality to (8) is satisfied, i.e., we have ( $R_0 \gg r_e$  and  $\gamma r_e \sim 1$ )

$$E \ll e_{r_0} R_0 / \gamma r_e^2. \quad (13)$$

Here transitions with change of rotational states of the molecule and ion are adiabatically improbable. Taking this into account in the system (7) and making the same transformations as in obtaining (12), we reduce the system to the following form:

$$i\dot{c}_1 = \frac{1}{2} \bar{\Delta} c_2, \quad i\dot{c}_2 = \frac{1}{2} \bar{\Delta} c_1, \quad (14)$$

$$\bar{\Delta} = |S_{\alpha, \alpha}|^2 \Delta_{\alpha}(R) \sum_{j_1 j_2} |a_{j_1 j_2}|^2 \langle j_1 j_2 | f | j_1 j_2 \rangle.$$

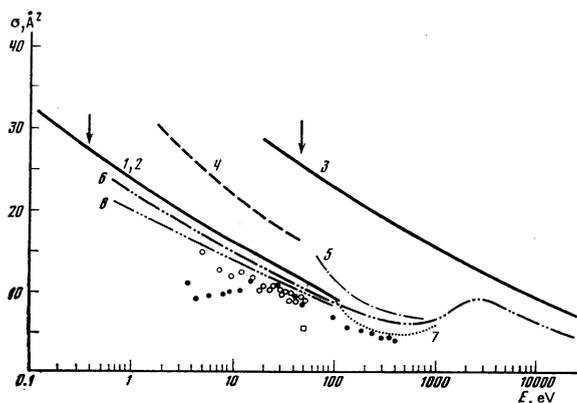


FIG. 2. Cross sections for resonance charge exchange of a molecular ion  $H_2^+$  on a molecule  $H_2$ . The solid curves are according to the asymptotic theory: 1—Eq. (11a), 2—Eq. (11b), 3—Eq. (11c). The experimental curves are as follows: 4—Ref. 6, 5—Ref. 7, 6—Ref. 1, 7—Ref. 8, 8—Ref. 9; the experimental points are as follows:  $\circ$ —Ref. 10,  $\bullet$ —Ref. 11,  $\square$ —Ref. 12. The arrows indicate the limiting energy values corresponding to satisfaction of the equalities (8)—the left arrow—and (10)—the right arrow.

It can be seen that the function  $f(\theta_1, \theta_2)$  averaged over the initial rotational states of the molecule and molecular ion enters into the expression for the exchange interaction potential  $\bar{\Delta}$ . However, the value of this function is practically independent of the initial state. Designating this averaged value by  $\bar{f}$ , we obtain for the resonance charge exchange cross section

$$\sigma = \frac{\pi R_0^2}{2}, \quad \left( \frac{\pi R_0}{2\gamma} \right)^{1/2} |S_{\alpha, \alpha}|^2 \Delta_{\alpha}(R_0) \bar{f}(\theta_1, \theta_2) = 0.28 v. \quad (11c)$$

Representation of the charge exchange cross section in the form (11c), in view of the condition (13), has no obvious physical meaning: During the collision the molecule and ion are penetrated many times and the electron transition corresponds to an exchange interaction potential averaged over the rotational states of the molecular particles.

We can present also a somewhat different criterion

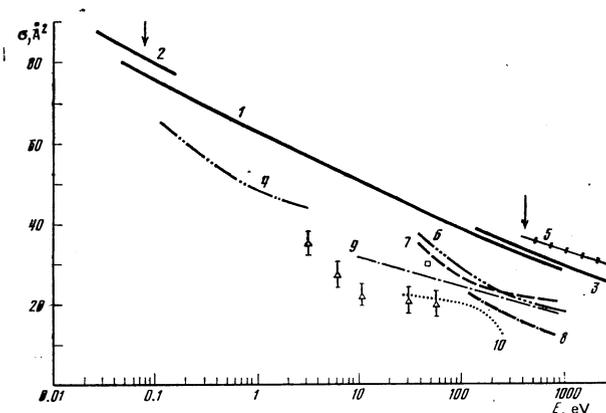


FIG. 3. Cross sections for resonance charge exchange of a molecular ion  $N_2^+$  on a molecule  $N_2$ . The theoretical curves are as follows: 1—Eq. (11a), 2—Eq. (11b), 3—Eq. (11c). The experimental curves are as follows: 4—Ref. 13, 5—Ref. 14, 6—Ref. 15, 7—Ref. 16, 8—Ref. 17, 9—Ref. 18, 10—Ref. 19; the experimental points are as follows:  $\square$ —Ref. 7,  $\triangle$ —Ref. 6. The arrows are the same as in Fig. 2.

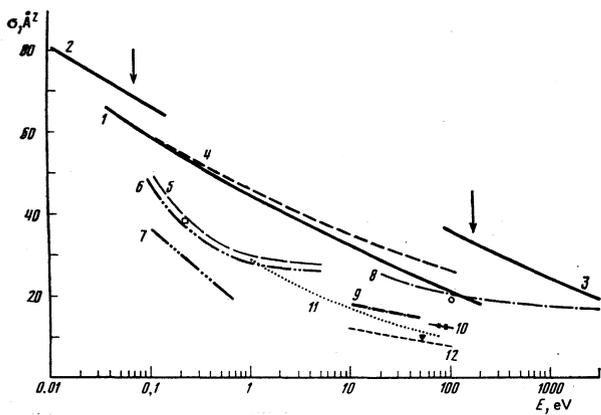


FIG. 4. Cross sections for resonance charge exchange of a molecular ion  $O_2^+$  on a molecule  $O_2$ . The asymptotic theory: curve 1—Eq. (11a), curve 2—Eq. (11b), curve 3—Eq. (11c). Experiment: curve 4—Ref. 3, curve 5—Ref. 13, curve 6—Ref. 20, curve 7—Ref. 21, curve 8—Ref. 18, curve 9—Ref. 22, curve 10—Ref. 23, curve 11—Ref. 13, curve 12—Ref. 19; points:  $\circ$ —Ref. 17,  $\square$ —Ref. 24,  $\blacktriangledown$ —Ref. 12. The arrows are the same as in Fig. 2.

for applicability of the formula for the charge-exchange cross section (11c). Let us take into account the change of rotational energy due to the fact that after charge exchange the angular momentum of the ion is replaced by the angular momentum of the molecule and vice versa. The corresponding change of rotational energy is  $\Delta \epsilon_{ro} \sim j^2 \Delta B \sim \epsilon_{ro} \Delta r_e / r_e$ , where  $\Delta r_e$  is the difference in the equilibrium distances between the nuclei of the molecule and the ion. We consider this transition allowed, so that the Massey parameter for it is small:

$$\frac{\Delta \epsilon_{ro} a}{v} \ll 1, \quad E \gg \epsilon_{ro} \frac{(\mu \Delta r_e^2) R_0}{r_e^2 \gamma} \quad (13a)$$

In certain cases the factor in parentheses will be small, and in this way conditions (13) and (13a) turn out to be satisfied simultaneously. We note also that in addition to the conditions (13) and (13a) it is necessary that the electrostatic interaction of the ion with the molecule not lead to a change of the characteristic conditions of the rotational transitions. Under these con-

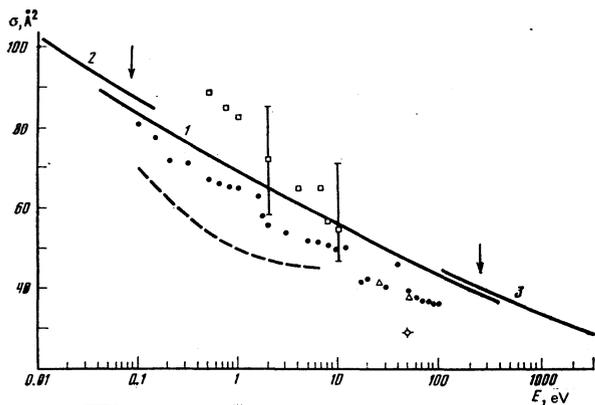


FIG. 5. Cross sections for resonance charge exchange of a molecular ion  $CO^+$  on a molecule  $CO$ . Asymptotic theory: curve 1—Eq. (11a), curve 2—Eq. (11b), curve 3—Eq. (11c). Experiment:  $\square$ —Ref. 25,  $\bullet$ —Ref. 3,  $\circ$ —Ref. 12,  $\triangle$ —Ref. 15, dashed curve—Ref. 13. The arrows are the same as in Fig. 2.

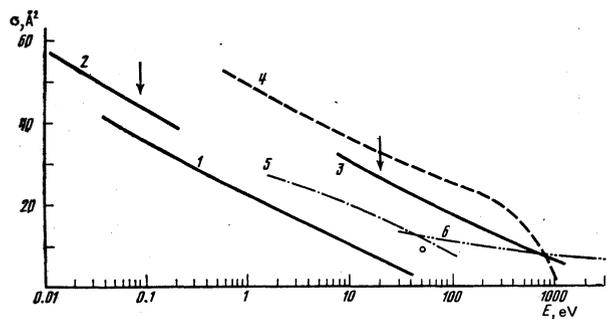


FIG. 6. Cross sections for resonance charge exchange of a molecular ion  $NO^+$  on a molecule  $NO$ . Asymptotic theory: 1—Eq. (11a), 2—Eq. (11b), 3—Eq. (11c). Experiment: 4—Ref. 3, 5—Ref. 26, 6—Ref. 18,  $\circ$ —Ref. 12. The arrows are the same as in Fig. 2.

ditions both the rotational angular momenta of the particles and their projections on a specified direction do not change greatly. However, these parameters determine the interaction of the ion with the quadrupole moment of the molecule. Since the transition of the electron is accompanied by a change of the type of particle, in this case the quadrupole interaction also changes. For validity of the expressions written above it is necessary that the change of the quadrupole interaction not lead to adiabatic forbiddance of the transition.

8. The equations (11) obtained above for the charge-exchange cross sections are valid in the range of particle-collision energies  $E$  satisfying the inequalities (8) and (10), (8) and the inequality inverse to (10), also (13) and (13a). At still lower collision velocities, transitions between rotational states of the particles become adiabatically improbable and the cross section should drop sharply with decrease of  $v$ . However, the polarization capture of the molecule by the ion can have an effect here, since the cross section for this process increases with decrease of the velocity.

It should be noted that the transition from one formula of the cross section to the other actually involves a small change in the value of the charge exchange cross section. For this purpose let us compare the dependence (11a) averaged over the angles  $\theta_1$  and  $\theta_2$  and the expression (11c). For the relative difference of these cross sections we obtain

$$\frac{\Delta \sigma}{\sigma} = \frac{2}{R_0 \gamma} (\overline{\ln f(\theta_1, \theta_2)} - \overline{\ln f(\theta_1, \theta_2)}) = \frac{4}{R_0 \gamma} (\overline{\ln A(\theta)} - \overline{\ln A(\theta)}), \quad (15)$$

where we have used an expression for  $f(\theta_1, \theta_2)$  in terms of the asymptotic coefficients of the electrons  $A(\theta)$ . Since  $R_0 \gamma \gg 1$ , this difference is small. Thus, in the case of resonance charge exchange for a collision energy  $E = 0.1$  eV corresponding to equality of the left and right sides in Eq. (8), we obtain from (15) the following values:  $\sim 0.2\%$  ( $H_2^+ - H_2$ ),  $\sim 5\%$  ( $N_2^+ - N_2$ ),  $\sim 10\%$  ( $O_2^+ - O_2$ ), and  $\sim 4\%$  ( $CO^+ - CO$ ).

Taking into account the fact that the discrepancy between the cross-section values coincides in order of magnitude with the error in the calculations of the cross sections themselves (as the result of the accuracy of the parameters utilized), we can consider as

valid in the transition region of velocities the cross-section formulas from regions of determination lying both below and above the transition value of velocity. The discrepancies which arise can be assigned to inaccuracy of the concepts of the asymptotic theory of resonance charge exchange of molecular ions.

In Figs. 2-6 we have shown the values calculated in this way for the cross section for resonance charge exchange of the ions  $H_2^+$ ,  $N_2^+$ ,  $O_2^+$ ,  $CO^+$ , and  $NO^+$  in the range of collision energy  $0.01-10^3$  eV. The arrows on the curves indicate points which correspond to transition values of the collision energy. The experimental cross-section curves have also been plotted in the figures. At collision energies of the order of thermal, the resonance charge exchange cross section has a maximum and then drops rapidly with decrease of the collision velocity. This drop in the cross section is due to adiabatic forbiddenness of rotational transitions. Since this region of variation of the cross section is determined by the distribution of the molecules and molecular ions over the rotational levels, which can differ substantially, depending on the source of molecular ions used, we shall not discuss this branch of the cross section. The accuracy of the calculated cross sections, which is determined by the error of the molecular parameters used and is related to the assumption regarding the nature of the rotational transitions, is estimated as 10-20% for the pairs of particles considered in the region of low collision energies. We note that the approach discussed can be extended also to the case of nonresonance charge exchange with participation of molecules.

<sup>1</sup>) We use below the system of atomic units:  $\hbar = m = e = 1$ .

<sup>2</sup>) The solution of the system of equations (9) in the case of a  $H_2^+ - H_2$  collision has been analyzed in detail by Bates and Reid.<sup>1</sup> In particular, their work demonstrates the appearance of a relative maximum in the resonance charge exchange cross section in the transition from large to small collision energies.

<sup>1</sup>D. R. Bates and R. H. G. Reid, Proc. Roy. Soc. A310, 1

- (1969).
- <sup>2</sup>E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237 (1957).
- <sup>3</sup>M. R. Flannery, P. C. Cosby, and T. F. Moran, J. Chem. Phys. 59, 5494 (1973). P. C. Cosby, T. F. Moran, and M. R. Flannery, J. Chem. Phys. 61, 1259 (1974). T. F. Moran, M. R. Flannery, and P. C. Cosby, J. Chem. Phys. 61, 1261 (1974). T. F. Moran, K. J. McCann, and M. R. Flannery, J. Chem. Phys. 63, 3857 (1975).
- <sup>4</sup>V. I. Bylkin, L. A. Palkina, and B. M. Smirnov, Zh. Eksp. Teor. Fiz. 59, 992 (1970) [Sov. Phys. JETP 32, 540 (1971)]. B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolknovenii (Asymptotic Methods in Atomic Collision Theory), Atomizdat, 1973.
- <sup>5</sup>P. E. Cade and W. Huo, At. Data Nucl. Data Tables 12, 415 (1973); 13, 339 (1974); P. E. Cade and A. C. Wahl, At. Data Nucl. Data Tables 15, 1 (1975).
- <sup>6</sup>J. J. Leventhal, T. F. Moran, and L. Friedman, J. Chem. Phys. 46, 4666 (1967).
- <sup>7</sup>H. C. Hayden and R. C. Amme, Phys. Rev. 172, 104 (1968).
- <sup>8</sup>D. W. Koopman, Phys. Rev. 154, 79 (1967).
- <sup>9</sup>R. M. Snuggs, D. J. Volz, J. H. Schummers, D. W. Martin, and E. W. McDaniel, Phys. Rev. A3, 477 (1971).
- <sup>10</sup>D. W. Vance and T. L. Bailey, J. Chem. Phys. 44, 486 (1966).
- <sup>11</sup>W. H. Cramer, J. Chem. Phys. 35, 836 (1961).
- <sup>12</sup>D. L. Smith and L. Kevan, J. Am. Chem. Soc. 93, 2113 (1971).
- <sup>13</sup>N. Kobayshi, J. Phys. Soc. Japan 38, 519 (1975).
- <sup>14</sup>H. W. Berry, Phys. Rev. 74, 848 (1948).
- <sup>15</sup>E. Gustafsson and E. Lindholm, Ark. Fysik 18, 219 (1960).
- <sup>16</sup>E. Gustafsson and G. H. Miller, Rev. Sci. Inst. 32, 1101 (1961).
- <sup>17</sup>S. N. Ghosh and W. F. Sheridan, J. Chem. Phys. 27, 1436 (1957).
- <sup>18</sup>R. F. Stebbings, B. R. Turner, and A. C. H. Smith, J. Chem. Phys. 38, 2277 (1963).
- <sup>19</sup>R. F. Potter, J. Chem. Phys. 22, 974 (1954).
- <sup>20</sup>D. Rapp and W. E. Francis, J. Chem. Phys. 37, 2631 (1962).
- <sup>21</sup>D. R. Gray and J. A. Rees, J. Phys. B5, 1048 (1972).
- <sup>22</sup>R. C. Amme and N. G. Utterback, in: Atomic Collision Processes, Amsterdam, 1964, p. 847.
- <sup>23</sup>J. A. Dillon, Jr., W. F. Sheridan, H. D. Edwards, and S. N. Ghosh, J. Chem. Phys. 23, 776 (1955).
- <sup>24</sup>R. N. Varney, Phys. Rev. A2, 370 (1970).
- <sup>25</sup>D. L. Smith and J. H. Futrell, J. Chem. Phys. 59, 463 (1973).
- <sup>26</sup>T. Baer, P. T. Murray, and L. Squires, J. Chem. Phys. 68, 4901 (1978).

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