Charge exchange of a molecular ion on a neutral molecule with allowance for vibrational transitions in the collision process

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Charge exchange of molecular ions on molecules is discussed in the framework of the theory of sudden perturbations, which permits one to take into account over a wide range of kinetic energies of the collision and in simple analytical form the influence of the vibrational structure of the colliding particles on the probability of charge exchange. The results of the analytical calculations are compared with numerical calculations for the simplest molecules $H_2^+ + H_2$.

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1. In this work we investigate the charge exchange of a diatomic molecular ion on a neutral molecule with allowance for transitions between vibrational states in the molecular ion $(v_1 \rightarrow v_1')$ and in the molecule $(v \rightarrow v')$ in the charge-exchange process:

$$AB^+(v_1) + CD(v) \rightarrow AB(v') + CD^+(v_1') + \Delta E. \tag{1}$$
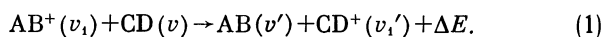
Here

$$\Delta E = I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1 + \omega_2^0 v' + \omega_2^+ v_1',$$

where I_1 and I_2 are the binding energies of the outer electron respectively in the molecules AB and CD which are in their vibrational ground states $(v = v' = 0)$; ω_1^0, ω_1^+ and ω_2^0, ω_2^+ are the vibrational quanta in the molecule and molecular ion respectively before and after charge exchange; v and v' are the vibrational quantum numbers before and after charge exchange. Here and everywhere below we use the atomic system of units: $e = \hbar = m_e = 1$.

The theory of charge exchange of an electron in collision of structureless atomic particles, developed on the basis of the asymptotic method, permits simple analytic expressions to be obtained for the probability of charge exchange of an ion on an atom and permits calculation of the cross section for such processes with an accuracy exceeding the accuracy of present-day experiments. However, generalization of this theory to molecular particles encounters significant difficulties due to the fact that transfer of the electron is accompanied by changes in the vibrational structure of the colliding molecules. Allowance for the motion of the nuclei in the molecular particles complicates the investigation of the charge-exchange process, since reaction (1) becomes substantially single-channel. Numerical integration of the cumbersome system of equations[1-5] which describes the dynamics of the system (1) is rather complicated and laborious[1] even for such a simple system as $H_2^+ + H_2$. In the work of Evseev, Radtsig, and Smirnov[6] an analysis was carried out for the first time, in the framework of the asymptotic theory, of the various mechanisms of transitions between nuclear states of the particles in the charge exchange of a molecular ion on the molecule proper, which permitted establishment of those regions of collision energy E where it is possible to find analytic solutions of the system of equations describing the resonant charge-exchange process. Ivanov and Kozhushner[7] have attempted to take into account the influence of vibrational and rotational degrees of freedom of the nuclei of the molecules on the electronic motion in the process of a sub-barrier transition from one atomic core to the other, by means of the nonstationary asymptotic method.[8] However, the nonadiabatic representation used in the article for the wave function of the molecular system before and after charge exchange is justified only in the far asymptotic region of the electron distribution, which makes practically no contribution to charge exchange.

In the present article we propose a mechanism for the charge-exchange reaction with allowance for the vibrational motion, which permits analytic expressions for the partial probabilities and charge-exchange cross sections to be obtained over a wide range of collision energies as a function of the vibrational states of the molecular particles before and after charge exchange.

2. For simplification of the calculations we shall assume that the trajectories of the centers of gravity of the colliding particles are rectilinear, i.e., $R = (\rho^2 + v^2 t^2)^{1/2}$, where ρ is the impact parameter, v is the relative velocity of the collision, and R and t are respectively the distance between the centers of gravity of the molecular particles and the time of the collision.

We shall further assume that, as in the case of charge exchange of an electron on atomic particles, the energy of the exchange interaction $\Delta_{el}(R)$ which determines the frequency of the transfer of the electron from the molecule to the molecular ion depends exponentially on the distance R:

$$\Delta_{el}(R) = A \exp(-\gamma R),$$

where $\gamma^2/2$ is the binding energy of the electron in the molecule. In this case charge exchange takes place in a narrow region of variation of the distances between the molecules ΔR near the distance of closest approach between the centers of molecules, which is equal to ρ. In this small region ΔR the dynamics of the motion of the centers of gravity of the molecular particles is described by the equation

$$R \approx \rho + v^2 t^2 / 2\rho. \tag{2}$$

Thus, the motion of a material point without allowances for the forces of interaction between the ion and the molecule is determined only by the centrifugal acceleration v^2/ρ near the turning point. Here the size of the effective region of charge exchange is $\Delta R \sim 1/\gamma$, and the value of the

characteristic time of the collision in charge exchange is determined from Eq. (2) as

$$\Delta t \sim (2\rho/\gamma)^{1/2} v^{-1}. \tag{3}$$

Note that allowance for the forces of interaction or the effect of curvature of the trajectories of the colliding particles on the probability of the process (1) leads to the following equation of motion in a potential $U = \alpha/R^n$ near the turning point R_m:

$$R \approx R_m + \frac{v^2}{2R_m}\left[1 - \frac{U(R_m)}{E}\left(1 - \frac{n}{2}\right)\right] t^2,$$
$$R_m = \rho \left[1 - \frac{U(R_m)}{E}\right]^{-1/2}, \tag{4}$$

where R_m is the distance of closest approach of the centers of gravity of the colliding particles and E is the kinetic energy of the collision.

From comparison of Eqs. (2) and (4) we find that inclusion of the trajectory curvature involves the formal substitution

$$\rho \to R_m = \rho \left(1 - \frac{U}{E}\right)^{-1/2},$$
$$v \to \bar{v} = v \left(1 - \frac{U}{E}\left(1 - \frac{n}{2}\right)\right)^{1/2}. \tag{5}$$

Therefore without loss of generality we can assume[9] for simplification of the calculations that the trajectory of the motion of the colliding particles is rectilinear, and then make the substitution (5) in the final results. This permits the limiting values of the collision kinetic energy at which the quasiclassical impact-parameter method is still applicable to be reduced to energies of the order of tenths of an electron volt.

The upper limit of the collision kinetic energies considered here is determined by the inequality

$$v < v_0 = \sqrt{2I},$$

where v_0 is the velocity of the electron in the molecule and I is the binding energy of this electron. In this case we can assume that the electron velocity in the molecule before and after charge exchange is determined only by its binding energy, and the contribution of the translational motion of the centers of gravity of the molecular particles can be neglected.

3. In the zeroth Born-Oppenheimer approximation we shall represent the wave functions of the system (1) before and after charge exchange in the form of the product of the electronic and nuclear wave functions, and the total Hamiltonian of the system will be written in the form of the sum

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

where $\hat{H}_{\mathrm{el}}$ is the Hamiltonian of the electrons and $\hat{H}_{\mathrm{nuc}}$ is the nuclear Hamiltonian.

The main parameter determining the probability of vibrational excitation of molecules is the Massey parameter:

$$\xi_{\mathrm{vib}} = \omega \Delta t,$$

where ω is the characteristic energy of a transition in the vibrational spectra of the molecular particles and Δt is the characteristic time of charge exchange determined by the expression (3).

We shall consider two limiting cases in which $\xi_{\mathrm{vib}} < 1$ and $\xi_{\mathrm{vib}} > 1$.

If $\xi_{\mathrm{vib}} > 1$, transitions between vibrational states during the time of the collision are adiabatically unlikely and can be neglected. Consequently for a collision velocity

$$v < \omega (2\rho/\gamma)^{1/2}$$

there are no transitions between translational and vibrational motions. However, as the result of jumping of the electron from one center to the other, the Hamiltonian describing the vibrational motion of the nuclei in the molecules changes, and this change occurs with the frequency of the electronic transitions, i.e., suddenly with respect to the nuclear motion.

In this case the wave functions of the vibrational motion of the nuclei in the initial channel of the reaction do not succeed in changing, but we can no longer consider them to be stationary. Therefore in the final channel of the charge exchange (1) in the shaking approximation the wave functions of the vibrational motion must be represented in the form of an expansion

$$\sum_k S_{ik}\chi_k, \quad S_{ik} = \langle \chi_i^* | \chi_k \rangle,$$

where S_{ik} are the overlap integrals between the vibrational wave functions of the nuclei in the initial and final channels. Thus, the wave function which describes the state of the system of colliding particles as a function of time before and after charge exchange should have the form

$$\Psi(t) = c_1(t)\chi_1^0(v)\chi_1^+(v_1)\varphi_1$$
$$\times \exp\{-i(I_1 - \omega_1^0 v - \omega_2^+ v_1)t\} + c_2(t)\varphi_2 \exp(-iI_2 t)$$
$$\times \sum_{v_1'} S_{vv_1}^{(1)}\chi_2^+(v_1')\exp(i\omega_1^+ v_1' t)$$
$$\times \sum_{v'} S_{v_1 v'}\chi_2^0(v')\exp(i\omega_2^0 v' t). \tag{6}$$

Here $\chi_1^0(v)$, $\chi_2^0(v')$ and $\chi_1^+(v_1)$, $\chi_2^+(v_1')$ are the vibrational wave functions of the neutral molecules and molecular ions, φ_1 and φ_2 are the wave functions of the electron centered respectively either in the molecule CD or in the molecule AB, and $c_1(t)$ and $c_2(t)$ are the probability amplitudes for transition of the electron from one molecule to the other in the collision process.

Substituting the expansion (6) into the nonstationary Schrödinger equation

$$i\partial \Psi/\partial t = \hat{\mathcal{H}} \Psi$$

and neglecting[1] terms of order $\langle \varphi_1 | \varphi_2 \rangle$, we obtain a system of equations for c_1 and c_2:

$$i\dot{c}_1 = c_2 e^{-i\varkappa t} \frac{\Delta}{2} \sum_{v_1'} |S_{vv_1}^{(1)}|^2 \exp(-i\omega_2^+ v_1' t) \sum_{v'} |S_{v_1 v'}^{(2)}|^2$$
$$\times \exp(-i\omega_2^0 v' t), \tag{7}$$

$$i\dot{c}_2 = c_1 e^{i\varkappa t} \frac{\Delta}{2} \exp\{i(\omega_2^+ v_1' + \omega_2^0 v')t\},$$

where $\varkappa = I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1$ and $\Delta/2 = \langle \varphi_1 | \hat{H}_{\mathrm{el}} | \varphi_2 \rangle$ is the energy of the exchange interaction.

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If the condition $\xi_{vib} > 1$ is satisfied, then the exponential terms in the system of equations (7), which are under the summation sign, cannot be neglected. In this case the main contribution to the solution of the system of (7) is from its "resonance" terms, for which the following equality is satisfied:

$$I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1 + \omega_2^+ v_1' + \omega_2^0 v' = 0.$$

Leaving in the system of equations (7) only these terms, we obtain

$$i\dot{c}_1 = {}^1\!/_2 c_2 |S_{vv_1'}^{(1)}|^2 |S_{v_1 v'}^{(2)}|^2 \Delta_{el}(R, \theta_1, \theta_2),$$
$$i\dot{c}_2 = {}^1\!/_2 c_1 \Delta_{el}(R, \theta_1, \theta_2).$$

From the expansion (6) it is evident that the probability of charge exchange is

$$W(v \to v', v_1 \to v_1') = |S_{vv_1'}^{(1)}|^2 |S_{v_1 v'}^{(2)}|^2 |c_2(t \to \infty)|^2. \tag{8}$$

It is easy to show that the expression (8) can be reduced to the form

$$W(v \to v', v_1 \to v_1') = |\tilde{c}_2(t \to \infty)|^2,$$

where $\tilde{c}_2$ is determined from the system of equations

$$i\dot{\tilde{c}}_1 = S_{vv_1'}^{(1)} S_{v_1 v'}^{(2)} \frac{\Delta}{2} \tilde{c}_2, \quad \tilde{c}_1(t \to -\infty) = 1,$$
$$i\dot{\tilde{c}}_2 = S_{vv_1'}^{(1)} S_{v_1 v'}^{(2)} \frac{\Delta}{2} \tilde{c}_1, \quad \tilde{c}_2(t \to -\infty) = 0. \tag{8a}$$

Thus, in the case in which transitions between vibrational states are adiabatically unlikely, i.e., when $\xi_{vib} > 1$, the equations (8a) which describe the reaction (1) are identical to the equations for c_1 and c_2 in the case of resonant charge exchange of molecular particles, which was considered in Ref. 6.

In the case in which $\xi_{vib} \ll 1$, transitions between vibrational states as the result of the motion of the colliding particles are not unlikely. Here one can assume that transitions between vibrational states occur suddenly, so that the expansion (6) is justified and reaction (1) is described by the system of equations (7). However, in the case in which $\xi_{vib} \ll 1$ the oscillating factors can be taken outside the summation sign in (7) and, taking into account that

$$\sum_{v'} |S_{vv'}|^2 = 1, \tag{1}$$

we can transform the system of equations (7) to the form

$$i\dot{c}_1 = {}^1\!/_2 c_2 \Delta_{el}(R, \theta_1, \theta_2) e^{-i\varkappa_0 t}, \quad c_1(t \to -\infty) = 1,$$
$$i\dot{c}_2 = {}^1\!/_2 c_1 \Delta_{el}(R, \theta_1, \theta_2) e^{i\varkappa_0 t}, \quad c_2(t \to -\infty) = 0, \tag{9}$$

where

$$\varkappa_0 = I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1 + \omega_2^+ v_1' + \omega_2^0 v'.$$

Here the probability of charge exchange is determined by the formula

$$W(v \to v', v_1 \to v_1') = |S_{vv'}^{(1)}|^2 |S_{v_1 v_1'}^{(2)}|^2 |c_2(t \to \infty)|^2, \tag{9a}$$

where c_2 is the solution of the system of equations (9).

We shall find the solution of the system (9) by the method developed in Ref. 10. For $\gamma\rho \gg 1$ we obtain

$$|c_2(v \to v', v_1 \to v_1')|^2$$
$$= \exp\left[-\frac{\varkappa_0^2 \rho}{\gamma v(1 + \varkappa_0^2/\gamma^2 v^2)^{1/4}} \right] \sin^2 \Phi_0 \left(1 + \frac{\varkappa_0^2}{\gamma^2 v^2} \right)^{-1} \tag{10}$$

$$\times \Phi_0 = B(\theta_1, \theta_2)\, [N_1 N_2 (2S_1 + 1)(2S_2 + 1)]^{1/2} \begin{pmatrix} S_1 & 1/2 & S_1 \\ S_2 & J & S_2 \end{pmatrix}$$

$$\times e^{-1/\gamma} \frac{1}{v} \left(\frac{\pi}{2\gamma} \right)^{1/2} \rho^{\beta + 0.5} \exp\left[-\gamma\rho \left(1 + \frac{\varkappa_0^2}{2\gamma^2 v^2} \right) \right.$$

$$\left. \times \left(1 + \frac{\varkappa_0^2}{\gamma^2 v^2} \right)^{-1/2} \right] \left(1 + \frac{\varkappa_0^2}{\gamma^2 v^2} \right)^{-1/4},$$

where

$$\varkappa_0 = I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1 + \omega_2^+ v_1' + \omega_2^0 v', \quad \beta = 2/\gamma - 1,$$

ρ is the impact parameter, N_1 and N_2 are the numbers of electrons in the outer shells of the molecules CD and AB, $\theta_1(\theta_2)$ is the angle between the axis of the molecule (molecular ion) and the direction joining the selected centers of the particles, and $B(\theta_1, \theta_2)$ is coefficient taking into account the angular distribution of the valence electron relative to the axis of the molecule.

4. Thus, we have two limiting cases with respect to the vibrational transitions:

In the first case when $\xi_{vib} > 1$ it is necessary to take into account only resonance terms, for which

$$I_2 - I_1 - \omega_1^0 v - \omega_1^+ v_1 + \omega_2^+ v_1' + \omega_2^0 v' = 0. \tag{11}$$

This corresponds to formation of the ion and molecule only in those vibrational states v_1' and v' which are detrmined from Eq. (11). Here the system of equations (7) reduces to the two equations (8a) which correspond to resonant charge exchange, and the cross section for charge exchange turns out to be[6]

$$\sigma = {}^1\!/_2 \pi R_0^2(\theta_1, \theta_2),$$
$$\left(\frac{\pi R_0}{2\gamma} \right)^{1/2} S_{vv_1'}^{(1)} S_{v_1 v'}^{(2)} \Delta_{el}(R_0, \theta_1, \theta_2) = 0.28v. \tag{12}$$

In the second case, in which $\xi_{vib} < 1$, the cross section is determined by Eqs. (9a) and (10) and by the integral

$$\sigma = 2\pi \int W(\rho) \rho \, d\rho. \tag{13}$$

Substituting the expressions (9a) and (10) into (13), we obtain

$$\sigma(v \to v', v_1 \to v_1') = |S_{vv'}^{(1)}|^2 |S_{v_1 v_1'}^{(2)}|^2 \frac{\pi}{\gamma^2 \mu^4}$$

$$\times \left\{ 1 - \exp\left[-\frac{\gamma\rho_0 \mu^2}{(1+\mu^2)^{1/2}} \right] \left[1 + \frac{\gamma\mu^2 \rho_0}{(1+\mu^2)^{1/2}} \right] \right\}, \tag{14}$$

$$\Phi_0(\rho_0) = 0.28v,$$

where $\mu = \varkappa_0(v, v', v_1, v_1')/\gamma v$ and Φ_0 is the phase which is determined by Eq. (10).

Let us analyze the analytic expressions (12) and (14) obtained for the cross section for charge exchange (1) with participation of molecular particles.

In the region of the collision energy E where the following inequality is satisfied:

$$\varepsilon_{rot} \rho_0 / \gamma r_e^2 < E < \mu\omega^2 \rho_0 / \gamma,$$

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Eq. (12) for the charge-exchange cross section coincides with the cross section obtained in this energy region in Ref. 6. Here r_e is the distance between the nuclei in the molecule and ε_{rot} is the characteristic rotational energy. In this case the distribution in the final vibrational states v' and v_1' is determined by Eq. (11).

In the energy region

$$\omega^2 \rho_0/\gamma < E < 10^4 \text{ eV}$$

the expression for the partial cross sections (14) gives a more complicated distribution in the final vibrational states v' and v_1', which differs from the cross sections obtained in Ref. 6 in this same region of collision energy. The point is that the expression for the cross sections in Ref. 6 corresponds to the total charge-exchange cross section summed over all possible final vibrational states, which does not provide the possibility of obtaining information on the vibrational spectra of the molecular particles after charge exchange (1). However, the total cross-section values

$$\sigma = \sum_{v',v_1'} \sigma(v', v_1') \qquad (15)$$

obtained from Eq. (14) should coincide with the values obtained in Ref. 6 (see Fig. 1).

Note that Eq. (14) provides the possibiliy of finding the velocities v_{max} at which the partial cross sections for reaction (1) take on the values

$$\sigma_{max} = \frac{\pi}{2} \frac{v_{max}^2}{\varkappa^2} \exp\left[-\frac{\varkappa}{\gamma v_{max}}\right],$$

where

$$v_{max} = \frac{\varkappa(v,v',v_1,v_1')}{\gamma}\left[\ln\left(\frac{D\sqrt{\pi/2}}{0.28\varkappa\gamma^{2/\gamma-1}}\right) + \frac{3}{\gamma} - 2,75\right],$$

$$D = B(\theta_1,\theta_2)e^{-1/\gamma}[N_1N_2(2S_1+1)(2S_2+1)]^{1/2}\begin{pmatrix} s_1 & 1/2 & S_1 \\ s_2 & J & S_2 \end{pmatrix}.$$

5. The expression for the energy of the exchange interaction of the molecular ion and the molecule, Δ, which enters into the system of equations (7), in the framework of the asymptotic theory where $\sqrt{2I}R \gg 1$, was obained in Ref. 11. If the electron binding energies I_1 and I_2 in the molecules CD and AB do not differ too greatly, then he asymptotic method can be used also to find the energy of the exchange interaction of the various molecular particles considered in our work. In the region of electron coordinate which makes the main contribution to the exchange interaction potential Δ and which is located far from the ionic core the wave function of the valence electron can be written in the form

$$\varphi(r,\theta) = A(\theta) r^{1/\tau-1} e^{-\gamma r}, \qquad (16)$$

where r is the distance from the chosen center of the molecular particle, θ is the angle between the radius vector of the electron and the axis of the molecule, and $\gamma = (\gamma_1 + \gamma_2)/2$; here $\gamma_1 = \sqrt{2}I_1$, $\gamma_2 = \sqrt{2}I_2$, where I_1 and I_2 are the binding energies of the electron in the molecules CD and AB.

Representing the wave function of the valence electron in the form (16), i.e., as a one-center function with a separated angular dependence, we can reduce the problem of determining the energy of the exchange interaction of electrons in the system (7) to the atomic case. The specific properties of the charge-exchange of molecular particles appears here in the angular dependence of the electron wave function (16). Since in the asymptotic theory of charge exchange the potential of the exchange interaction is determined by the overlap of the electron wave functions (16) in the coordinate region far from both molecular cores, where the magnitude of the asymptotic coefficient $A(\theta)$ can be considered constant, the desired quantity $\Delta(R)$ will be given, by analogy with the case of transition of an electron from an atom to an atomic ion, by

$$\Delta(R) = Re^{-1/\tau}\varphi_1(R/2)\varphi_2(-R/2),$$

where R is the distance between the centers of the molecular particles undergoing charge exchange and $\varphi_{1,2}(\pm R/2)$ are the values of the wave function (16) of the electron in the corresponding molecule at the center of the interval R. Using the rules of addition of the spin angular momenta of the molecule S and of the molecular ion s into the total spin of the system (1)J, we eventually obtain an expression for the energy of the exchange interaction in the system (1) under discussion as follows[11]:

$$\Delta(R,\theta) = B(\theta_1,\theta_2)[N_1N_2(2S_1+1)(2S_2+1)]^{1/2}$$

$$\times \begin{pmatrix} s_1 & 1/2 & S_1 \\ s_2 & J & S_2 \end{pmatrix} e^{-1/\tau}R^{2/\gamma-1}e^{-\gamma R}.$$
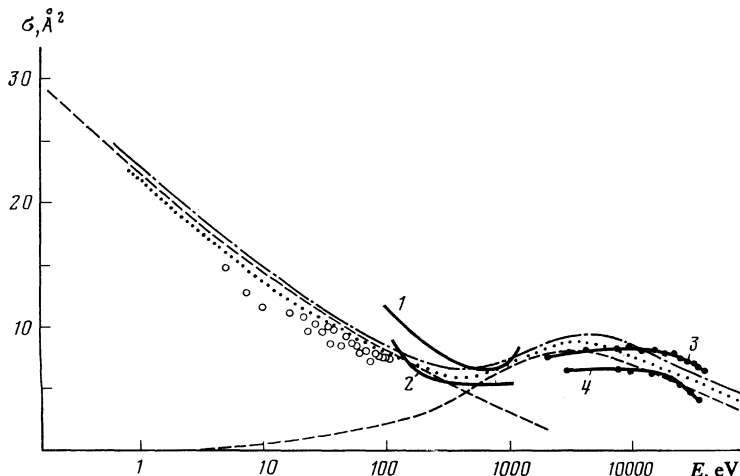

FIG. 1. Charge exchange $H_2^+ + H_2$: the dashed curves are from the present work, the dot-dash curves are from Ref. 17, the dotted curve is from Ref. 1, curve 1 is from Ref. 20, curve 2 is from Ref. 21, curve 3 is from Ref. 18, curve 4 is from Ref. 19, and the open circles are from Ref. 22.
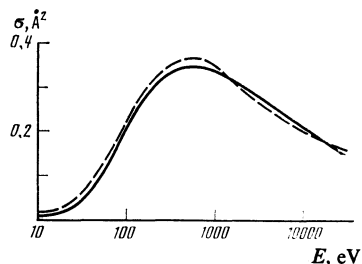
FIG. 2. Partial cross sections for the reaction $H_2^+ + H_2$ with $v_1 = v = 0$, $v' = 0$, and $v_1' = 1$: the dashed curve is from Ref. 1, and the solid curve is from the present work.

If electrons in σ or π states take part in charge exchange, then[11]

$$B_\sigma = A_1(\theta_1) A_2(\theta_2),$$

$$B_\pi = 3A_1(\theta_1) A_2(\theta_2) \left(1 - \frac{\delta_{M0}}{2}\right) \cos \vartheta \frac{(1-|m|)!}{(1+|m|)!(2\gamma)^{|m|}},$$

where $A_i(\theta_i)$ is the asymptotic coefficient of the wave function (16), m and M are respectively the projections of the orbital angular momentum of the valence electron undergoing the transition and of the orbital angular momentum of the molecule on the axis joint the nuclei, and ϑ is the angle between the axes of the molecules.

A detailed analysis of the role of rotational transitions and inclusion of the angular dependence $\Delta (R, \theta)$ in this case has been made in Ref. 6. However, we shall consider the region of rather fast collisions in which during the characteristic time of interaction of the particles the axis of the molecule does not rotate appreciably, i.e., in which we have the inequality

$$E \gg \varepsilon_{rot} R_0 / \gamma r_e^2,$$

where E is the collision energy of the particles in the center-of-mass system and R_0 is the distance between the centers of mass of the molecular particles at which charge exchange effectively occurs. In this case the main contribution to the charge-exchange cross section is from the angles $\hat{\theta}_1$ and $\hat{\theta}_2$; the procedure for finding these angles is given in detail in Ref. 6.

6. The correctness of our model assumptions, which permit us to obtain analytic expressions for the particle cross
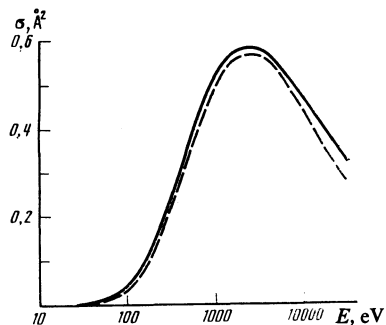

FIG. 3. Partial cross sections for the reaction $H_2^+ + H_2$ with $v_1 = v = 0$, $v' = 1$, and $v_1' = 2$: the dashed curve is from Ref. 1, and the solid curve is from the present work.
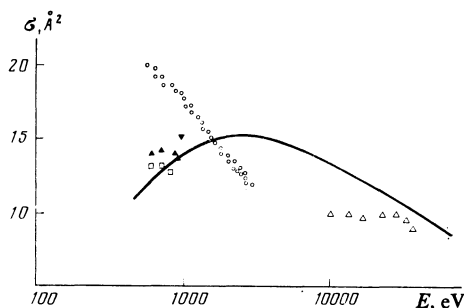

FIG. 4. Charge exchange $Ar^+ + H_2$: the solid curve is from the present work, the circles are from Ref. 12, ▼ are from Ref. 14, the hollow squares are from Ref. 15, ▲ are from Ref. 16, and △ are from Ref. 23.

sections for the charge exchange (1) and to determine the distribution of the final products of the reaction (1) in their vibrational states, is confirmed by comparison of the results (12) and (14) with similar numerical calculations carried out in Ref. 1 for the very simple system

$$H_2^+(v_1) + H_2(v) \rightarrow H_2(v') + H_2^+(v_1'). \tag{17}$$
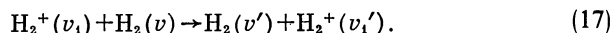
In order to illustrate the possibilities of the analytic calculations which have been presented, we give here a comparison of the numerical calculation of Bates *et al.*[1] with our calculations for two channels of the reaction (17): 1) $v_1 = v = 0$, $v' = 0$, and $v_1' = 1$ (Fig. 2); 2) $v_1 = v = 0$, $v' = 0$, and $v_1' = 2$ (Fig. 3). Exactly the same agreement with the numerical calculations of Ref. 1 occurs for all other channels of the charge-exchange reaction. The results of the theoretical calculations of various authors in comparison with experimental data for the total cross sections for the charge exchange (17) are given in Fig. 1.

In Fig. 4 we give the experimentally measured total cross sections for nonresonant charge exchange[12-16,23]

$$Ar^+ + H_2(v) \rightarrow Ar + H_2^+(v') + \Delta E(v, v').$$
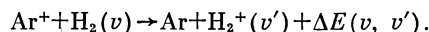
They are compared with the results of our calculations on the basis of Eqs. (12), (14), and (15). Here a greater discrepancy is observed between theory and experiment, which is apparently due to inaccuracy of the experiment since the cross sections measured by different authors in the same region of collision kinetic energy have large discrepancies.

[1] D. R. Bates and R. H. G. Reid, Proc. Roy. Soc. **A310**, 1 (1969).
[2] T. F. Moran, M. R. Flannery, and D. L. Albritton, J. Chem. Phys. **62**, 2689 (1975).
[3] T. F. Moran, M. R. Flannery, and P. C. Cosby, J. Chem. Phys. **61**, 1261 (1974).
[4] T. F. Moran, K. J. McCann, and M. R. Flannery, J. Chem. Phys. **63**, 3857 (1975).
[5] T. F. Moran and J. R. Roberts, J. Chem. Phys. **49**, 3411 (1968).
[6] A. V. Evseev, A. A. Radtsig, and B. M. Smirnov, Zh. Eksp. Teor. Fiz. **77**, 560 (1979) [Sov. Phys. JETP **50**, 283 (1979)].
[7] G. K. Ivanov and M. A. Kozhushner, Dokl. Akad, Nauk SSSR **257**, 1394 (1981) [Doklady Physical Chemistry **256–258**, 342 (1981)]. G. K. Ivanov and M. A. Kozhushner, Zh. Khim. Fiz. 1039 (1982) [sic].
[8] Yu. N. Demkov and V. N. Ostrovskiĭ, Zh. Eksp. Teor. Fiz. **69**, 1582 (1975) [Sov. Phys. JETP **42**, 806 (1975)].
[9] B. M. Smirnov, Dokl. Akad. Nauk SSSR **157**, 325 (1964) [Sov. Phys. Doklady **9**, 570 (1965)].
[10] E. L. Duman, Zh. Eksp. Teor. Fiz. **81**, 139 (1981) [Sov. Phys. JETP **54**,

1112   Sov. Phys. JETP **58** (6), December 1983

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68 (1981)].

[11]B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolkno-veniĭ (Asymptotic Methods in the Theory of Atomic Collisions), Moscow, Atomizdat, 1973.

[12]A. F. Hedrich, T. F. Moran, K. J. McCann, and M. R. Flannery, J. Chem. Phys. **66**, 24 (1977).

[13]E. Gustafsson and E. Lindholm. Ark. Fys. **18**, 219 (1960).

[14]H. B. Gilbody and J. B. Hasted, Proc. Roy. Soc. **A238**, 334 (1956).

[15]S. N. Ghosh and W. F. Sheridan, Ind. J. Phys. **31**, 337 (1957).

[16]R. C. Amme and J. F. McIlwain, J. Chem. Phys. **45**, 1224 (1966).

[17]E. L. Duman, A. V. Yevseyev, A. V. Elezky, A. A. Radzig, and B. M. Smirnov, Preprint IAE-3532/12, Institute of Atomic Energy, 1982.

[18]J. P. Keene, Phil. Mag. **40**, 369 (1949).

[19]J. B. H. Stedeford and J. B. Hasted, Proc. Roy. Soc. **A227**, 446, 476 (1954).

[20]H. C. Hayden and R. C. Amme, Phys. Rev. **172**, 104 (1968).

[21]J. A. Dillon, Jr., W. F. Sheridan, H. D. Edwards, and S. N. Ghosh, J. Chem. Phys. **23**, 776 (1955).

[22]D. W. Vance and T. L. Bailey, J. Chem. Phys. **44**, 486 (1966).

[23]C. J. Latimer, J. Phys. **B10**, 515 (1977).

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