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Double charge transfer in low-energy $H^+ + H^-$ collisions

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The cross section for double charge transfer between H^+ and H^- at low collision energies ($E \leqslant 90$ eV) is calculated using a many-state molecular close-coupling model. The wave function is expanded in a diabatic representation of the seven lowest $^1\Sigma_g^+$ and the six lowest $^1\Sigma_u^+$ states of the hydrogen molecule. The calculated cross section shows clear oscillations as a function of the collision energy, similar to those observed experimentally. However, the magnitude of the calculated cross section is larger than found in experiments. Also, the cross section for double charge transfer in collisions between D^+ and H^- is calculated.

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The $H^+ + H^-$ system is the simplest cation-anion system in which electron transfer takes place. In particular, only two protons and two electrons are involved, and only one bound state of the negative ion exists. The reactants are thus well defined and they are also relatively easy to prepare in the laboratory. Electron transfer processes involving H^+ and H^- therefore constitute an important family of prototype reactions for use in experimental as well as theoretical studies.

In an earlier report [1] we presented results on the mutual neutralization (MN) reaction $H^+ + H^- \rightarrow H(1) + H(n)$, where n is the principal quantum number of the hydrogen atom.

In the present study we focus on the related two-electron transfer reaction,

$$H_a^+ + H_b^- \rightarrow H_a^- + H_b^+. \qquad (1)$$

It is assumed that this double-charge-transfer (DCT) process can be distinguished from the direct elastic scattering (DES) process, in which none of the electrons are transferred.

In the late 1970s merged- and crossed-beam experiments on the DCT process (1) were carried out by Brouillard *et al.* [2] and Peart and Forrest [3], respectively. The measured cross sections span the energy range 30 eV $< E_{\text{c.m.}} <$ 570 eV and show oscillatory behaviors. More recently Bräuning *et al.* [4] have investigated this reaction in the center-of-mass energy range 0.5 to 12 keV using crossed beams. Their results confirm the oscillations as a function of energy in the cross section.

O'Malley [5] was the first to point out that symmetric DCT is mathematically identical to one-electron transfer. By using a simple effective model based on the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ diabatic states with ionic character, he was able to predict and estimate the frequency of oscillations in the DCT probability. Also, in analogy with the one-electron case, these oscillations are explained as the interference of gerade and ungerade molecular states. Early semiclassical calculations based on molecular states of H_2 have been performed by Brouillard *et al.* [2]. In that study the interactions between the ion-pair and the $n = 2$ Rydberg states of H_2 were taken into account using the Landau-Zener model. At small and large internuclear distances the dynamics was assumed to proceed diabatically on the ion-pair state. Semiclassical calculations have also been carried out at higher collision energies, ranging from 150 eV up to several kilo–electron volts [6,7]. All of these cross sections show oscillatory patterns but their magnitudes are larger than those observed experimentally. The most recent calculation [4] was based on the two-state approach of Hodgkinson and Briggs [8]. Here, only the diabatic gerade and ungerade ion-pair states were considered. The results show oscillations in the cross section provided that a relative shift in the potentials of O'Malley [5] is introduced. All previous theoretical studies have considered the DCT reaction (1) at rather high collision energies. In the low-energy range, the nuclear dynamics has to be described quantum mechanically. Furthermore, at low relative velocities the dynamics is less diabatic and it is crucial to incorporate the nonadiabatic couplings between the excited states of H_2.

In this paper we present a fully quantum mechanical coupled-channel study of the DCT process that includes the seven lowest $^1\Sigma_g^+$ and the six lowest $^1\Sigma_u^+$ states of H_2. These states correspond to the asymptotic limits $H^+ + H^-$ and $H(1) + H(n)$, with $n = 1,2,3$. The adiabatic potential energy curves of H_2 have previously been calculated *ab initio* using the full configuration interaction technique with a large Gaussian basis set [1]. As the internuclear distance is decreased from infinity (see Fig. 1 in [1]), the ion-pair configuration ($H^+ + H^-$) passes through a series of avoided crossings with states correlating with the $H(1) + H(n)$ covalent limits. At large internuclear distances the potential energy curves of $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetry are very similar. At small distances ($R < 10a_0$) apparent differences between these curves can be seen. The radial nonadiabatic couplings between the molecular states included in the present study have been calculated [1] using a finite-difference method described in [9].

The dynamical treatment is performed here in a strictly diabatic representation. The radial nonadiabatic couplings are used to determine the orthogonal adiabatic-to-diabatic transformation matrix [1,10]. The boundary condition is chosen in such a way that the adiabatic and diabatic states coincide in the asymptotic region.

The coupled Schrödinger equation for nuclear motion is numerically solved using a logarithmic derivative method developed by Johnson [11–13]. By combining the calculated values of the logarithmic derivative with the regular and irregular asymptotic solutions, the scattering matrix can be calculated [1,13]. Scattering matrices were calculated separately

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for the gerade ($S^g_{ij,l}$) and ungerade ($S^u_{ij,l}$) sets of states, where i, j are channel indices and l is the angular momentum quantum number.

The corresponding gerade and ungerade scattering amplitudes describe highly symmetrical processes in which neither excitation nor electronic charge is associated with a particular nucleus "a" or "b". As such, they cannot represent the DCT reaction (1), where the electrons travel with either nucleus a (before reaction) or nucleus b (after reaction). Localization of the electron cloud can be achieved by forming linear combinations of the gerade and ungerade scattering amplitudes [14]. The DCT cross section then becomes

$$\sigma^{\mathrm{DCT}}(E) = \frac{\pi}{4k_1^2}\sum_{l=0}^{\infty}(2l+1)\left|S^g_{11,l} - S^u_{11,l}\right|^2, \qquad (2)$$

while the DES cross section can be written as

$$\sigma^{\mathrm{DES}}(E) = \frac{\pi}{4k_1^2}\sum_{l=0}^{\infty}(2l+1)\left|S^g_{11,l} + S^u_{11,l} - 2\right|^2. \qquad (3)$$

Here the ion-pair channel is associated with the "11" element in the scattering matrix ($i = j = 1$). The coupled equations were integrated out to $50a_0$. Enough partial waves have to be included to numerically converge the computed cross sections. Here we have used a convergence criterion similar to that described in [1]. To reach convergence, several hundreds of partial waves at 1 meV and more than 3500 partial waves at 90 eV collision energies had to be included.

In the present study we consider DCT within both the H_2 and the HD systems. In H_2 the nuclei are identical and the electronic wave functions are either symmetric (gerade) or antisymmetric (ungerade) under inversion through the center of mass of the nuclei (CMN). Although the HD system possess no inversion symmetry with respect to the CMN, such a symmetry does exist with respect to the geometrical center of the nuclei (GCN). If the GCN is taken as the origin of the electronic coordinates, the electronic structure calculations for H_2 and HD become completely equivalent and the potentials and nonadiabatic couplings need to be calculated only once. The drawback of this approach is that extra terms discussed, for example, in [14] will appear in the Schrödinger equation. In the present work these terms are neglected and the same form of the Hamiltonian is used for both H_2 and HD.

In Fig. 1(a) the calculated cross sections for DCT between H^+ and H^- as well as between D^+ and H^- (or H^+ and D^-) are shown as a function of the collision energy. The DCT cross sections have a very smooth $1/E$ dependence at low energies ($E < 1$ eV), in accordance with the Wigner threshold law for collisions between two oppositely charged particles [15]. Starting from 1 eV, oscillatory structures in the cross sections can be observed. The overall behavior of the cross sections for the two isotopologues is the same. Moreover, at very low collision energies ($E < 0.9$ eV), the two curves are on top of each other. At higher collision energies a shift in the oscillatory behavior can be observed. This shift can be explained as a result of the different reduced masses of the two colliding systems. In the inset in Fig. 1(a), the two DCT cross sections are shown as a function of the relative velocity. The same phase of the oscillatory structures can then be observed.

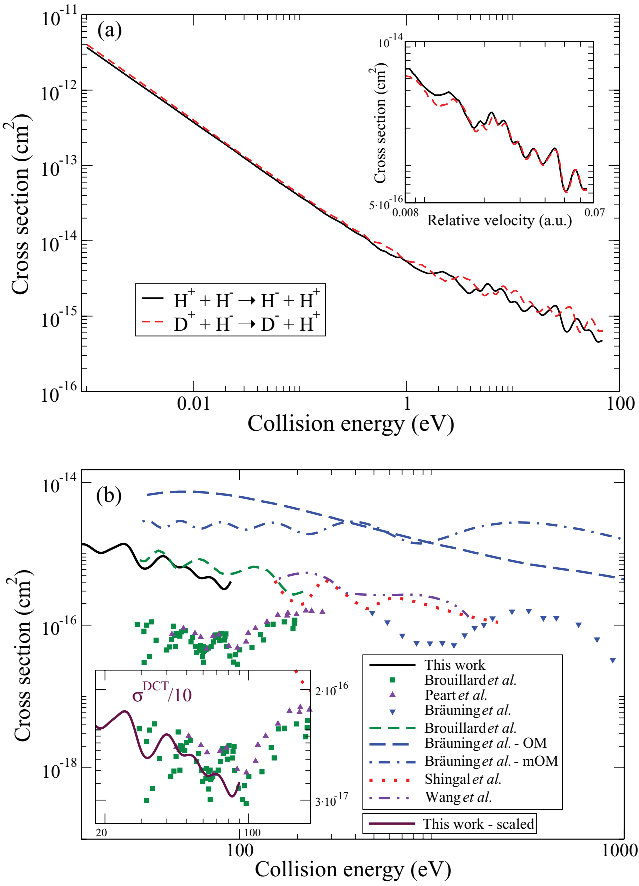

FIG. 1. (Color online) (a) Calculated cross sections for double charge transfer (DCT) in collisions between H^+ and H^- as well as between D^+ and H^- (or H^+ and D^-) are shown as a function of the collision energy. (b) The computed DCT cross section for $H^+ + H^-$ is compared with the measurements made by Brouillard *et al.* [2], Peart and Forrest [3], and Bräuning *et al.* [4]. Comparison is also made with the calculations carried out by Brouillard *et al.* [2], Bräuning *et al.* [4], Shingal and Bransden [6], and Wang *et al.* [7]. The collision energy ranges from 15 eV to 10 keV. In the inset our cross section is scaled ($\sigma^{\mathrm{DCT}}/10$) and compared with the measured cross sections.

In Fig. 1(b) our calculated DCT cross section for $H^+ + H^-$ is compared with other available experimental [2–4] as well as theoretical [2,4,6,7] results. The measured cross sections agree with each other in both magnitude and overall shape. In particular, as shown in the inset in Fig. 1(b), the measured cross sections show similar oscillations above 1 eV. All calculated cross sections are larger in magnitude compared to measured ones, especially at low energies. The present DCT cross section has a shape and magnitude similar to those of the cross section obtained in the semiclassical calculation by Brouillard *et al.* [2]. However, our cross section is an order of magnitude lower than the one calculated by Bräuning *et al.* [4] using the adiabatic states introduced by O'Malley [5] [OM in Fig. 1(b)] and about five times lower than the cross section obtained using shifted potential energy curves and a modified energy difference function [mOM in Fig. 1(b)] [4]. The calculations by Shingal and Bransden [6] and Wang *et al.* [7] based on the semiclassical impact parameter method were performed at higher collision energies ($E > 100$ eV).

In the inset in Fig. 1(b), our calculated cross section is scaled ($\sigma^{\mathrm{DCT}}/10$) to compare the oscillations with the measured structures. Similarities in the oscillatory patterns can be observed. These structures indicate interference effects arising from the dynamics taking place on the manifold of states included in the present study. Technically, the oscillations appear since the cross section of DCT [Eq. (2)] depends on the difference between the S-matrix elements for the gerade and those for the ungerade states. The fact that at low collision energies, all calculated cross sections are substantially larger than the measured ones may indicate that there is a loss mechanism not included in the present study or in the other theoretical models.

There is a general view that in collisions between H^+ and H^- the cross section for DCT constitutes only a small fraction of the total-reaction cross section [4,16,17]. Here we wish to compare the cross sections for different processes competing with DCT. As already discussed, both the DES and the DCT processes yield H^+ and H^- as outgoing fragments, but only the latter of these reactions involves electron transfer. Experimentally the two processes can be distinguished using, for example, a crossed-beam setup at higher energies or by letting one of the ions be deuterated. Also mentioned previously is the MN process in which one of the electrons is transferred and neutral fragments $[\mathrm{H}(1) + \mathrm{H}(n)]$ are formed. At zero collision energy all channels with $n \leqslant 4$ are open, although only those with $n = 2$ and 3 are expected to give any significant contributions to the MN cross section [18–20]. Another possible reaction is associative ionization, where autoionization of the H_2 system forms H_2^+ and a free electron. At zero collision energy, the vibrational levels $v \leqslant 9$ of H_2^+ are energetically open [21]. To describe this reaction, interactions between the neutral states and the ionization continuum have to be included. In the present model these interactions are not incorporated.

In Fig. 2, the calculated cross section for DCT is compared with the cross sections for DES and MN ($n = 1,2,3$), obtained using the same theoretical model. Also shown in the figure is the cross section for associative ionization obtained by Urbain *et al.* [22] using multichannel quantum defect theory. As shown in Fig. 2, the cross section for DES is the dominant one. It is almost 2 orders of magnitude larger than for all other open channels. The cross section for MN is dominated by the formation of $\mathrm{H}(1) + \mathrm{H}(3)$. At low collision energies this cross section is several orders of magnitude larger than for $n = 2$. The formation of products in the $n = 1$ state is insignificant at all energies.

A quantitative comparison shows that our calculated DCT cross section constitutes 30% of the total MN cross section at collision energies ranging from milli–electron volts to several electron volts, and only at higher collision energies does this fraction become a few percent. The cross section for associative ionization is about 2 orders of magnitude smaller than that for DCT. Thus, our model predicts a cross section for DCT that is larger than the expected 1%–2% [4,16,17] of the total-reaction cross section at low energies.

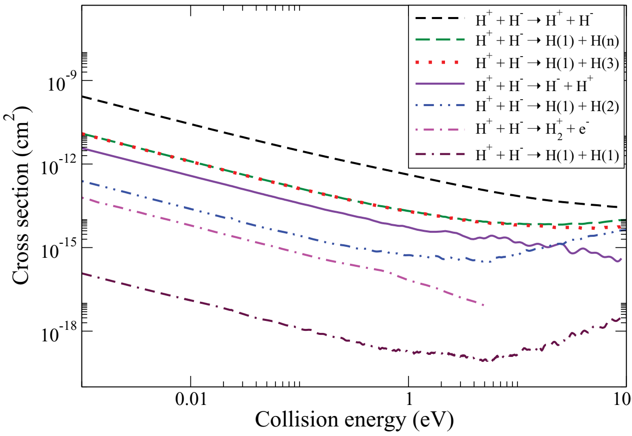

FIG. 2. (Color online) Comparison (from top to bottom) of the double-charge-transfer cross section (solid line) with the cross sections for direct elastic scattering, total and state selective mutual neutralization [1], and associative ionization [22] for low-energy collisions of H^+ and H^-.

The discrepancies found between theory and experiment make it appropriate to point out the limitations of the present model. The number of adiabatic states included in this study is limited by the electronic structure calculations. With the present level of accuracy we are not able to obtain the states associated with the $n \geqslant 4$ limits. The calculations by Wang *et al.* [7] performed at higher collision energies show that inclusion of the $n = 4$ atomic states reduces the DCT cross section by about 5%–10%. To still examine how our DCT cross section depends on the number of adiabatic states included, we have performed a series of calculations where we systematically remove adiabatic states from our model. The conclusion from this study is that the magnitude of the DCT cross section is quite insensitive to the number of states included in the model, especially at the lower energies. Also, the oscillatory structures remain, but with a modified shape. Although this simple test may yield information on the convergence of the DCT cross section with respect to the number of states included in the model, it cannot *a priori* say something about the behavior of this cross section when states beyond $n = 3$ are added. To explicitly examine the role of higher excited states, the Rydberg states of H_2 should be included by combining a description of the system using multichannel quantum defect theory at small distances with *ab initio* computed adiabatic states and nonadiabatic couplings at large distances [22]. This will be addressed in a future study.

In the present study autoionization from the H_2 complex is not included. The inclusion of autoionization would in principle reduce the cross section for DCT. Calculations by Urbain *et al.* [22] show that the cross section for associative ionization is 2 orders of magnitude smaller than the present DCT cross section (see Fig. 2). It is therefore not probable that autoionization alone can explain the discrepancy between the calculated and the measured cross sections for DCT.

Bates and McCarroll [23] pointed out that in the description of atomic collisions the scattering states should incorporate factors representing the translation of the electrons along with the nuclei. In a series of papers Thorson *et al.* [24] showed how the absence of these factors could generate nonvanishing asymptotic couplings, which in turn may affect the scattering cross sections. However, in our previous study on MN [1] we found the cross section to be insensitive to these couplings.

Finally, the rotational part of the Hamiltonian will in general couple the $^1\Sigma$ states to states of $^1\Pi$ symmetry. We have neglected these couplings. It is well known that the rotational couplings play a minor role in the presence of avoided crossings [14]. However, away from such crossings their importance might become comparable to that of the radial couplings. Due to the factor R^{-2} the rotational couplings are enhanced at small internuclear distances and become increasingly important as the collision energy is raised. Theoretical studies of predissociation in H_2 [25,26] have shown that the inclusion of rotational couplings leads to an increase in the dissociation rates. The inclusion of $^1\Pi$ states in our model would lead to an increased neutralization rate and, consequently, a lowering of the DCT cross section. We are not able to estimate the significance of such a lowering.

We have presented a quantum mechanical *ab initio* study of DCT in H^+ and H^- low-energy collisions. We obtain structures in the cross section similar to those observed experimentally. However, the discrepancy between all calculated cross sections, on one hand, and all so far reported measured cross sections, on the other hand, persists and calls for more extensive theoretical as well as experimental studies. Presently a double-electrostatic storage device DESIREE [27] is under construction in Stockholm, Sweden. One of the plans for this instrument is to use it to study low-energy anion-cation collisions. Studies of DCT in a merged-beam setup such as DESIREE require that the nuclei can be differentiated by some means, such as in collisions between D^+ and H^-. Detailed comparisons between theory and experiments can then be performed.

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