Double-Electron Transfer in $H^- + H^+$ Collisions

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Absolute cross sections for double-electron transfer in $H^- + H^+$ collisions have been measured for center-of-mass energies from 0.5 to 12 keV. Clear oscillations in the cross section are observed shedding new light on earlier measurements. Calculations based on a diabatic approach are shown to reproduce this behavior, but require a larger diabatic ion-pair splitting than previously assumed.

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Elementary atomic rearrangement processes, such as electron transfer, still present serious challenges to theory as well as experiment. While the simplest collision system with only a single-electron involved, e.g., $H^+ + H$ or $H^+ + He^+$ [1], is well understood, our understanding is much reduced as soon as a second electron is involved such as in $He^+ + He^+$ collisions [1,2], even if the second electron does not actively participate in the transfer process. Precious little is known, however, when two electrons initially bound to one collision partner are transferred in a single collision. The fundamental collision system to study double-electron transfer is

$$H_a^- + H_b^+ \rightarrow H_a^+ + H_b^-$$

the subject of our current investigation. Pioneering merged or crossed-beam experiments by Brouillard *et al.* [3] and Peart and Forrest [4], respectively, at rather low collision energies ($30\ \mathrm{eV} < E_{\mathrm{cm}} < 500\ \mathrm{eV}$) provided total cross sections, which indicated an oscillatory behavior of the total cross section with the collision energy, however without convincing interpretation of the measurement.

One electron charge exchange occurs in $H^+ + H$ collisions at low energy and this simplest of all three-body Coulomb systems is the paradigm for formation of an entangled collision system. The cross section shows oscillations as a function of velocity simply because the lowest σ_g and σ_u states interfere coherently. The simplest analogous four-body collision system, $H^+ + H^-$, is exceedingly more complicated since (a) the outer electron is only bound if the inner electron is in its ground state, so that if both electrons transfer they must remain highly correlated during the collision, (b) at molecular distances the ion-pair interaction branches into a multitude of adiabatic states of H_2, including bound, dissociative and autoionizing configurations. It comes as no surprise that the two-electron transfer constitutes merely a small fraction ($\approx 1\%$) of the total reaction cross section, the latter being dominated by detachment [5] and mutual neutralization [6]. Because of the coupling of an enormous number of levels one would expect structureless cross sections as a function of velocity. What is remarkable however, is that the two-electron transfer cross section exhibits clear, regular oscillations indicating the interference of only two dominant channels. Early semiclassical calculations based on adiabatic molecular states of H_2 were performed by Brouillard *et al.* [3]. While their calculations show oscillatory behavior, they overestimate the absolute cross section by an order of magnitude at low energies. Later calculations were done by Shingal and Bransden [7] using the semiclassical impact parameter method and a two-center expansion of traveling atomic orbitals with a 23-state basis on each heavy particle. These calculations focused on the mutual neutralization channel and yielded the double-electron transfer as a byproduct. Their cross section also shows some oscillatory structure, not inconsistent with the experiments.

We have experimentally investigated this reaction in the center-of-mass energy range from 0.5 to 12 keV. The clear oscillations observed in the measured absolute total charge-transfer cross section not only shed new light on the existing early data, but also allow insight into the double-electron transfer mechanism in this simplest symmetric two-electron ion-ion collision system, where the two electrons bound in the rather brittle H^- ion are stabilized only due to electron correlations. Three factors appear particularly noteworthy with regard to the experimental results: (a) the absolute magnitude of experimental cross sections obtained in three different experiments agree, (b) the phase of oscillations agree, and (c) the present data indicate that following a last oscillation maximum at about 3 keV, the two-electron transfer cross section tends to zero at increasing collision energy.

The current experiments have been performed using the Giessen ion-ion crossed-beams setup which has been described in full detail previously [1,8]. Only the detectors

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have been repositioned to take into account the different trajectories of the H^+ and H^- ion in the outgoing channel. A schematic overview is given in Fig. 1. The ion beams are produced by two identical 10 GHz all-permanent magnet electron cyclotron resonance (ECR) ion sources. While the low energy beam line utilizes a constant accelerating voltage of -7.5 kV, the high energy beam line has been tuned to accelerating voltages in the range from 10 to 55 kV, thus allowing measurements at different center-of-mass energies between 0.49 to 11.88 keV. Both ion beams are charge state selected and collimated to about 1.5 mm diameter before being crossed at an angle $\beta = 17.5°$ under UHV conditions with a background pressure around 7×10^{-11} mbar. This results in a well-defined interaction region and allows the precise determination of the beam overlap. Electrostatic sector analyzers (EA1-EA3) directly in front of the interaction region clean the beams from any ions, which have undergone charge exchange in the beamline. After the intersection, the reaction products are separated from their parent beams by two electrostatic analyzer pairs (EA4,EA5) and detected with a channeltron detector (D2, low energy beam line) and a micro channel plates (MCP) detector (D1, high energy beam line), respectively. In addition, the product ions in the low energy beam line are deflected out of the scattering plane by a hemispherical deflector to further reduce the background. The coincident detection of an ion having lost two electrons and an ion having gained two electrons gives a clear signature of the double-electron transfer process. In addition to the UHV conditions and the thin targets, which the crossed ion beams constitute, this eliminates all processes involving uncorrelated interactions with the residual gas and discriminates against a 10^3 to 10^4 higher background rate. A possible loss of signal due to electron detachment after a double-electron transfer has occurred is estimated to be below 3×10^{-8} and thus negligible. Typical reaction rates were 0.014 s^{-1} at 0.49 keV center-of-mass energy and 0.005 s^{-1} at 11.88 keV. This resulted in measurement times between 7 and 20 h per data point.

The detector efficiencies yield the main contribution to the 15% systematic error for our measurements. They have been previously measured for a wide range of single and multiply-charged light and heavy ions. All these measurements yielded consistent efficiencies of 60% for the MCP detector and 89% for the channeltron detector.

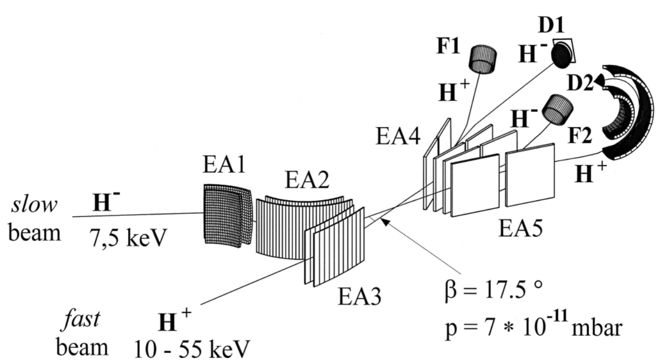

FIG. 1. Schematic overview of the Giessen ion-ion experiment. EA1-EA5: electrostatic analyzers, F1, F2: Faraday cups, D1: microchannel plates , D2: channeltron detector.

Figure 2 shows our data together with the earlier measurements of Brouillard *et al.* [3] and Peart and Forrest [4] as a function of the collision velocity. As a whole the experimental data clearly prove the oscillatory structure of the total cross section. They also show the increasing width of the oscillation period with increasing collision velocity. The cross section appears to drop to zero at collision velocities beyond 1 a.u.

O'Malley [9] was the first to point out that symmetric double charge exchange is mathematically identical to the single-electron transfer process. He explored the diabatic states which could be used to describe elastic collisions to the extent that curve crossings can be neglected. He finds two groups of diabatic state pairs for molecular hydrogen, each with the notation $^1\Sigma_{g,u}$, one with ionic and singly excited character, the other with covalent and doubly excited character. His result for the ionic pair splitting $\Delta E(R) = E_g(R) - E_u(R)$ (where R is the internuclear separation and $E_{g,u}(R)$ are the diabatic potential energy curves) is shown in Fig. 3.

A cross section evaluated solely on the basis of diabatic states which neglects the dominating open channels of mutual neutralization and detachment will greatly overestimate the magnitude of the charge-transfer cross section. However, since the branching into molecular states of H_2 is such a decisive feature, it can be argued that the fraction of collision events which branch will never return to the ion-pair exit channel when the collision system

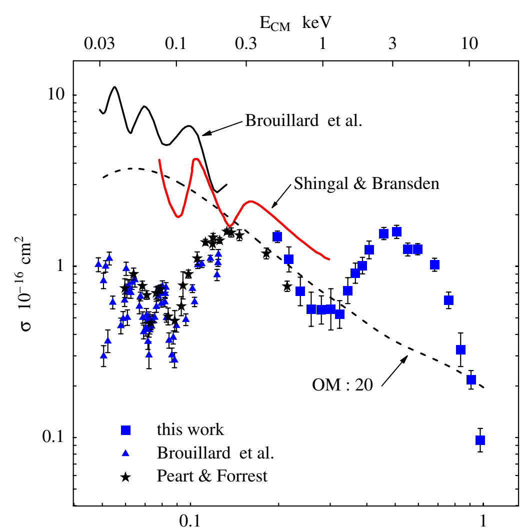

FIG. 2 (color online). Total cross sections for the reaction $H_a^- + H_b^+ \rightarrow H_a^+ + H_b^-$. Error bars represent the statistical error only for the three experimental data sets. Also included are the predictions by Shingal and Bransden [7] and by Brouillard *et al.* [3]. OM is the prediction of Eq. (1), based on the splitting of the ionic diabatic states of O'Malley [9] (stars in Fig. 3).

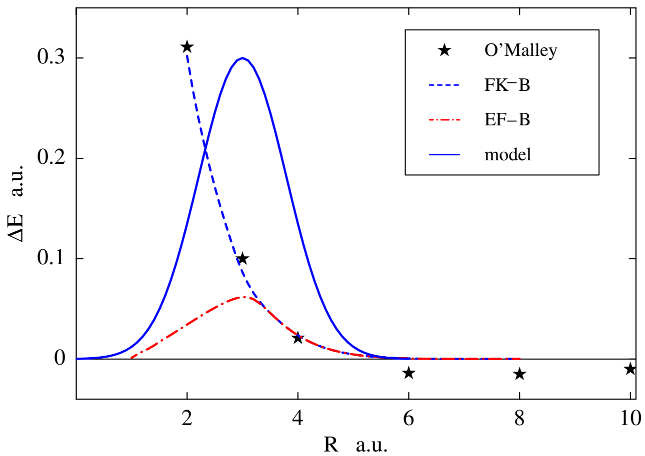

FIG. 3 (color online). Ion-pair splitting discussed in this work.

evolves from molecular distances into separated atoms. Thus the purely diabatic approach may be sufficient for characterizing the oscillatory structure of the two-electron transfer cross section.

The oscillatory nature of the total charge-transfer cross section was considered in the two-state approach by Hodgkinson and Briggs [10]. Assuming straight line trajectories, the total elastic charge exchange cross section is

$$\sigma = 2\pi \int_0^\infty b db \sin^2\Gamma(b). \tag{1}$$

Here b is the impact parameter and $\sin^2\Gamma(b)$ the probability for exchange

$$\Gamma(b) = \frac{1}{v}\int_b^\infty \frac{RdR}{\sqrt{R^2 - b^2}}\Delta E(R), \tag{2}$$

with v being the impact velocity and $\Delta E(R)$ the energy difference between gerade and ungerade states of the pseudomolecule formed.

We have applied this formalism using for ΔE the ion-pair splitting predicted by O'Malley. The resulting cross section (divided by a factor of 20) is included in Fig. 2. It shows a broad maximum near $v = 0.06$, quite inconsistent with the observations. The predicted total cross section is substantially higher than the observations. This disagreement in magnitude is expected, as discussed above; however, the disagreement in the oscillatory structure points to a shortcoming of the physical parameters, as the frequency of oscillations is a measure of the phase difference accumulated during the collision along the g and u paths of the ion-pair configuration.

We consider the origin for this disagreement to be that the gerade ion-pair states calculated by O'Malley do not adequately account for the ion-pair character which is being fed into the electronic ground state, $H_2(1^1\Sigma_g)$. The interaction of ${}^1S_0 H^-(1s\sigma^2)$ with H^+ gives rise to only H_2 singlet states, one with gerade and one with ungerade character according to the molecular state wave functions

$$\Psi^\pm = \frac{1}{\sqrt{2(1 \pm \mathcal{N})}}[\Phi(\mathbf{r}_{1A}, \mathbf{r}_{2A}) \pm \Phi(\mathbf{r}_{1B}, \mathbf{r}_{2B})]. \tag{3}$$

Here r_1 and r_2 denote the coordinates of electron 1 and 2 centered at proton A and B, respectively. $\mathcal{N}$ is the normalization integral

$$\mathcal{N} = \int \Phi^\star(\mathbf{r}_{1A}, \mathbf{r}_{2A})\Phi(\mathbf{r}_{1B}, \mathbf{r}_{2B}) d\mathbf{r}_1 d\mathbf{r}_2. \tag{4}$$

The spatial distribution of the electron density between the two protons in Eq. (3) predicts that two-electron exchange leads to stronger binding in the gerade combination Ψ^+ as opposed to the ungerade combination Ψ^- which should be weaker bound. As a result we expect the gerade ion-pair state to lie energetically *below* the ungerade state. At infinite separation the ion-pair lies 10 meV above the dissociation limit $H(1s) + H(4\ell)$. The attractive ion-pair crosses molecular states formed from $H(1s) + H(4\ell)$ and $H(1s) + H(3\ell)$ at 284 and 36 a.u., respectively, before reaching the energy of $H(1s) + H(2\ell)$ at ≈ 11 a.u. and distributes its character over many ${}^1\Sigma_{g,u}$ states of H_2. Among the most obvious features in this regard are the long-range wells of the $3^1\Sigma_u$ and $4^1\Sigma_g$ states near $R \approx 11$ a.u. (see Fig. 4) and the strong long-range attraction of the $1^1\Sigma_u$ and $2^1\Sigma_g$ states. Triplet states are free from ion-pair character; hence, the differences between the adiabatic ${}^1\Sigma$ and ${}^3\Sigma$ states (see, for example, Fig. 1 of Ref. [11]) also reflect the configuration mixing with the ion-pair state.

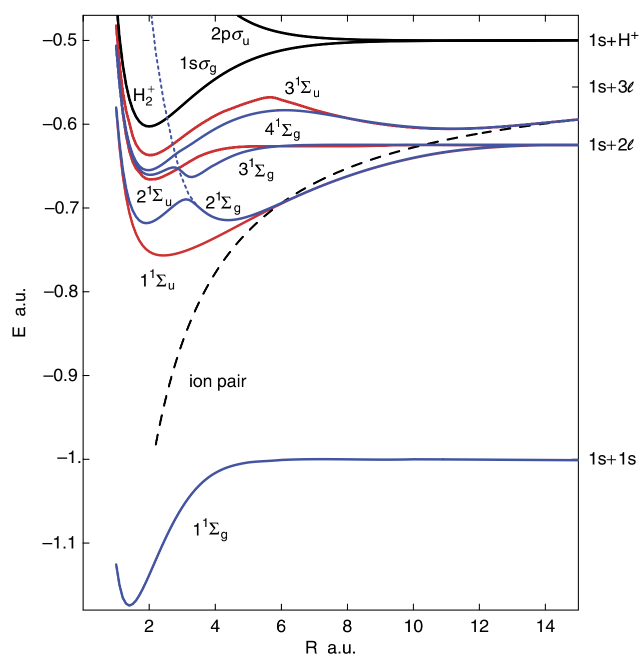

FIG. 4 (color online). Potential energy curves of the lowest states of H_2 and H_2^+, taken from Refs. [13,14]. The curves shown in blue are of ${}^1\Sigma_g$ character, those in red of ${}^1\Sigma_u$ character. State labels for 1, 2, $3^1\Sigma_u$ are B, B', B'' and for 1, 2, 3, $4^1\Sigma_g$ they are X, EF, GK, $H\bar{H}$. The short dashed line gives the diabatic 2, $3^1\Sigma_g$ state. The long dashed line is the attractive Coulomb curve.

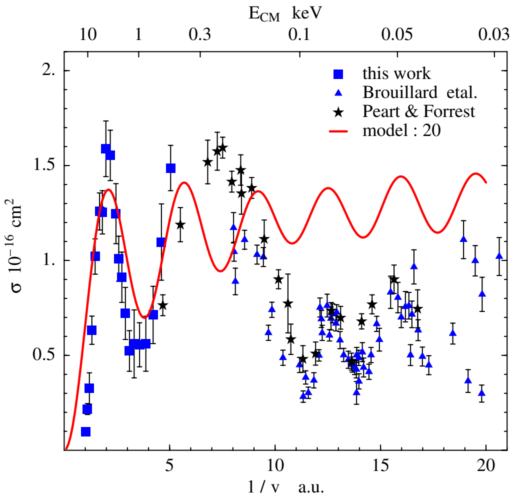

FIG. 5 (color online). Predicted cross section (divided by a factor of 20) based on the ion-pair splitting labeled *model* in Fig. 3.

The above argument suggests that the diabatic splitting to be used in Eq. (2), could be unraveled from the energy separations between the adiabatic $^1\Sigma_{g,u}$ states or else be found from comparing the respective $^1\Sigma$ and $^3\Sigma$ states. To this end we show in Fig. 3 the energy splitting between the adiabatic $2^1\Sigma_g$ and $1^1\Sigma_u$ curves (labeled EF-B) and the separation between the diabatic 2, $3^1\Sigma_g$ state (short dotted line in Fig. 4) and $1^1\Sigma_u$ curve (labeled FK-B). It is quite clear that the ionic diabatic splitting predicted by O'Malley follows quite precisely the opening gap between the adiabatic $2^1\Sigma_g$ and $1^1\Sigma_u$ curves and continues as the gap between the diabatic 2, $3^1\Sigma_g$ state and the $1^1\Sigma_u$ state.

The agreement of O'Malley's *ionic* splitting with the energy separation labeled FK-B suggests that his calculation does not account for the gerade ion-pair character which is being fed into the *lowest* singlet gerade state, the electronic ground state, $1^1\Sigma_g$. The ground state syphons off a substantial fraction of the gerade ion-pair character and this is likely to be the origin for the apparent reverse ordering of the adiabatic g and u states in the $n = 2$ manifold, the $2^1\Sigma_g$ state lying *above* the $1^1\Sigma_u$ state. Gerade ion-pair character embedded in the ground state of H_2 does not contribute to O'Malley's gerade diabate because of the conflicting choice that has to be made when calculating *neutral* states above the ionization limit: the $H_2^+(1s\sigma_g)$ configuration has to be excluded from the basis states in order to avoid autoionization. On the other hand, the presence of the ion-pair character in the electronic ground state of H_2 is well documented from the magnitude of its nonadiabatic corrections at intermediate internuclear distances [12]. We conclude that the diabatic ion-pair splitting at molecular distances should be higher than given by O'Malley and that the energetic order of gerade and ungerade diabates should be inverse to that of Table III in Ref. [9]. On general grounds one expects the diabatic ion-pair splitting to be even larger than the $g - u$ splitting of ground-state H_2^+ which lives off single-electron exchange and which is 0.2 a.u. at $R = 3$ a.u.. We have somewhat arbitrarily increased the magnitude of O'Malley's splitting and truncated it at shorter values of R to account for the loss into the autoionization continuum. This empirical splitting (labeled "model") is shown in Fig. 3 by the full curve. It predicts oscillations which are in agreement with the experimental findings at low and at high energies, as seen in Fig. 5 where the cross section is plotted against $1/v$. In contrast to Fig. 2 the experimental data in this plot show *regular* oscillations which lends strong support to the validity of Eq. (2). The absolute magnitude of the cross section is overestimated as expected from the diabatic approach.

We have measured the $H^- + H^+$ double-electron transfer cross section over a wide range of energy and confirmed pronounced oscillations, which suggests an interpretation in terms of only two dominant channels. A semiempirical model of the two-channel $g - u$ splitting reproduces these oscillations *and* the sharp decrease of the cross section above 3 keV. Because of the delicate role of electron correlations and the enormous number of involved channels, this simplicity is very surprising and poses a great challenge for future elaborate coupled-channels calculations tracking down the transient formation and decay of H_2, the simplest of all molecules, through the single ion-pair channels available.

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