Double electron transfer in $H^- + H^+$ collisions

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Abstract. Absolute cross sections for double electron transfer in $H^- + H^+$ collisions have been measured for center-of-mass energies from 0.5 keV to 12 keV. Clear oscillations in the cross section are observed which are in excellent agreement with earlier measurements at lower energies by Brouillard et al. (1979) as well as Peart and Dolder (1979). After an oscillation maximum at 3 keV center-of-mass energy the cross section decreases for increasing energy with no indication of further oscillations.

1. Introduction

Charge-changing collisions between two ions still present serious challenges to theory as well as experiment. This is especially the case, when more than one electron is involved. The electron transfer process is well understood in the simplest single electron ion-ion collision systems like, for example, in the case of $H^+ + He^+$ [1]. 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. One of the simplest collision systems to study double electron transfer is:

$$H^- + H^+_a + H^+_b \rightarrow H^+_a + H^-_b$$

Furthermore, the negative hydrogen ion plays a role in three body Coulombic systems that is comparable to the central place of the neutral hydrogen atom in two-body quantum mechanics. As such, several reaction channels in $H^- + H^+$ collisions like detachment and mutual neutralization have been studied both by experiment [3, 4, 5, 6, 7, 8, 9, 10, 11] and theory [12, 13, 14] (see figure 1). These two channels also dominate the total reaction cross section, whereas the double electron transfer contributes only with about 1%, as shown by the pioneering merged/crossed-beams experiments of Brouillard et al. [10] and Peart and Forrest [11], respectively, at rather low collision energies ($30 \text{ eV} < E_{cm} < 500 \text{ eV}$). The total cross section measured by these two groups indicates an oscillatory behaviour in the energy dependence. However, a convincing interpretation of the cross section could not be established.

Because the stable negative ion state depends strongly on correlation between the two electrons, a precise theoretical treatment of this seemingly simple collision system is rather involved. Early semiclassical calculations were performed by Brouillard et al. [10]. They expanded the collision system in terms of the adiabatic molecular states of $H_2$. While their
Figure 1. Cross sections for associative ionization (Poulaert et al. [15]), mutual neutralization (Szucs et al. [5], Schön et al. [7], Peart et al. [8]), detachment (Peart et al. [4], Melchert et al. [9]), transfer ionization (Schön et al. [6]) and double electron transfer (Brouillard et al. [10], Peart and Forrest [11]).

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 [14] using the semiclassical impact parameter method with rectilinear trajectories 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 cross section as a byproduct. Their cross section also shows some oscillatory structure, not fully inconsistent with the experiments.

2. Experimental setup

The current experiments have been performed using the Giessen ion-ion crossed-beams setup. A detailed description of the setup for collisions between positively charged ions can be found in [16, 1]. For the experiments presented here, only the detectors have been repositioned to take into account the different trajectories of the H\(^+\) and H\(^-\) ions in the outgoing channel. A schematic overview of the interaction region with the charge state analyzers is given in figure 2. 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 for the H\(^-\) ions, the high energy beam line (H\(^+\)) has been tuned to accelerating voltages in the range from 10 kV to 55 kV, thus allowing measurements at different center-of-mass energies between 0.49 keV to 11.88 keV. Both ion beams are charge state selected by two bending magnets and collimated to about 1.5 mm diameter before being crossed at an angle \(\beta = 17.5^\circ\) under UHV conditions with a background pressure around \(7 \times 10^{-11}\) 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 beam line. After the intersection, the reaction products are separated from their parent beams by two electrostatic
Figure 2. Schematic overview of the Giessen ion-ion experiment. EA1-EA6: electrostatic analyzers, F1,F2: Faraday cups, D1: micro channel plates detector, D2: channeltron detector.

Table 1. Typical beam parameters and reaction rates $R$ for a single measurement at the lowest and highest center-of-mass energy $E_{cm}$.

| $E_{cm}$ (keV) | $U_1$ (kV) | $I_1$ (nA) | $U_2$ (kV) | $I_2$ (nA) | Reaction Rate ($s^{-1}$) |
|----------------|-------------|------------|-------------|------------|--------------------------|
| 0.49           | -7.5        | 1.4        | 10          | 125        | 0.014                    |
| 11.88          | -7.5        | 1.8        | 55          | 321        | 0.005                    |

Analyzer pairs (EA4,EA5). In the high energy beam line only the ions which have gained two electrons hit a micro channel plates (MCP) detector (D1). In the low energy beam line only those ions which have lost both electrons are detected with a channeltron detector (D2). 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 absolute cross section is then given by [17]

$$
\sigma = \frac{R \, v_1 v_2 \sin \beta \, q_1 q_2 \, F}{\epsilon_1 \epsilon_2 \, v_{rel} \, I_1 I_2}
$$

(1)

where $R$ is the reaction rate, $\epsilon_{1,2}$ are the detector efficiencies, $v_{1,2}$ the ion velocities, $v_{rel}$ the relative velocity and $q_{1,2}$ the ion charges. The form factor $F$ describes the vertical overlap of the two ion beams and is measured directly at the well defined interaction region by scanning the vertical beam profiles with a horizontal slit of 0.16 mm width. The reaction rate is obtained using the time coincidence technique [17], which measures the time difference between the detection of the respective product ions. All events originating from a single collision will have the same time difference, which shows as a definite peak in the time spectrum (see figure 3). All detected ions coming from unrelated collisions have a random time difference resulting in the flat background of the time spectrum. This technique thus gives a clear signature of the double electron transfer process and discriminates against a 10$^3$ to 10$^4$ higher background rate. The currents $I_{1,2}$ of the primary ion beams are measured with Faraday cups. Table 1 lists the typical beam parameters and reaction rates for a single measurement at the lowest and highest center-of-mass energy. The measurement time was typically in the order of 7 hours. In the energy regime below 1 keV, where
Figure 3. Time spectrum for the coincident detection of the H$^-$ and H$^+$ product ions in the respective detectors. The peak comes from the double electron transfer process.

A minimum in the cross section is observed, two or more measurements have been performed for a given energy to improve the statistical error. All such single measurements agree within their respective error bars demonstrating the reproducibility of the ion optics and beam overlap.

The detector efficiencies $\epsilon_{1,2}$ can be measured directly by comparing the count rate for the attenuated direct beam with the beam current (typically below 1 pA) measured in the Faraday cups. 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. Their error yields the main contribution of the 15% systematic error for our measurements.

3. Results and Discussion

Figure 4 shows our data together with the earlier measurements of Brouillard et al. [10] and Peart and Forrest [11] as a function of the collision velocity. As a whole, the experimental data clearly proves the oscillatory structure of the total cross section. Three factors appear particularly noteworthy with regard to the experimental results: a) the absolute magnitude of the measured 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. Furthermore, the experimental data show the increasing width of the oscillation period with increasing collision velocity.

We also present in figure 4 the semiclassical calculations by Brouillard et al. [10] using a simple Landau-Zener approach in direct comparison with the full experimental data. In their calculations the electronic wavefunction was expanded in terms of the adiabatic molecular states of H$_2$ and the system was assumed to advance diabatically at internuclear distances smaller than 11 au. Only radial coupling was taken into account. The results overestimate the experimental cross section by a factor of 10 and show a wrong phase of the oscillations (solid line in figure 4). However, the phase is very sensitive to the level splitting between the $^1\Sigma_u$ and $^1\Sigma_g$ states.
Figure 4. Total cross sections for the reaction $H^- + H^+_a \rightarrow H^+ + H^-_b$ (open triangles: Brouillard et al. [10], open diamonds: Peart and Forrest [11], closed squares: present data). The error bars represent the statistical error only for the three experimental data sets. Also included are the predictions by Shingal and Bransden [14] (dotted line) and by Brouillard et al. [10] (solid line and dashed line resulting from a lowered $^1\Sigma_u$ state).

Brouillard et al. could show that when the upper $^1\Sigma_u$ state (refer to figure 4 in [10]) is lowered by a small amount of 0.25 eV the oscillation reverses and gives a better agreement with the experimental data (dashed line in figure 4).

Coupled-channel calculations have been reported by Shingal and Bransden [14] using a 23-state basis on each heavy projectile. These calculations are also shown in figure 4. While the calculated cross section is of the correct order of magnitude no detailed agreement is obtained. However, their calculations focused on the neutralization channel where a good agreement was obtained. Thus basis states for which two electrons are centered on each heavy particle, except for the $H^-$ ground state, were not considered although they are evidently necessary for accurate calculation of double electron transfer.

The experimental data now present a unified picture of the double electron transfer in $H^- + H^+$ collisions. This cannot be said in the case of theory. It clearly shows that our understanding of such an elementary two-electron process is still lacking.

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