Investigation of charge transfer in low energy $D_2^+ + H$ collisions using merged beams

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Abstract. $(H_2-H)^+$ is the most fundamental ion-molecule two-electron system. This temporary complex which is formed during charge transfer collisions of $H_2^+ + H$ proceeds through dynamically coupled electronic, vibrational, and rotational degrees of freedom. Using the upgraded ion-atom merged-beams apparatus at Oak Ridge National Laboratory, absolute direct charge transfer cross sections for $D_2^+ + H$ are measured from keV/u collision energies where the collision is considered “ro-vibrationally frozen” to meV/u energies where collision times are long enough to sample vibrational and rotational modes. The measurements presented here are the first to benchmark high energy theory and vibrationally specific adiabatic theory.

1. Introduction

Besides its fundamental aspect and its rich collision dynamics, the charge transfer (CT) process $H_2^+ + H \rightarrow (H-H) + H^+$ is a very important reaction in astrophysics because of its contribution to $H_2$ formation in the early universe [1-5]. Understanding of this simpler system is important for more complex systems which exist in, e.g., biophysics where radical attacks on biomolecules such as DNA potentially involve CT at very low energy [6-8]. Knowledge of CT for $H_2^+$ on H is also necessary for modeling of such plasmas as found in the cold divertor plasma regions of a fusion tokamak or in interstellar clouds where the main constituents are H, H⁻, and H-molecules.

CT for this fundamental system follows three main paths, direct CT (i), CT with nuclear substitution (ii), and CT with dissociation (iii) according to the following:

\[
\begin{align*}
H_2^+ + H_a & \rightarrow H_2 + H_a^+ \quad \text{(i)} \\
(H_0-H_2^\ast)^+ + H & \rightarrow (H-H_2) + H_0^+ \quad \text{(ii)} \\
H_2^+ + H_a & \rightarrow H + H + H_a^+ \quad \text{(iii)}
\end{align*}
\]

Previously McGrath [9] performed experimental studies for collisions of $(H_2^+ + H)$ at high energy along with the identification of possible processes: dissociative and non-dissociative capture and target and projectile ionization. These measurements which were performed between 10 keV/u and 50 keV/u show that toward lower energies CT increasingly dominates over the ionization processes to the point that at 10 keV/u the measured CT cross sections were nearly a factor of ten greater than the measured ionization cross sections. McGrath’s measured CT cross sections are significantly below Errea’s calculations [10] at these high collision energies where ro-vibrational modes can be considered “frozen”. Surprisingly for $H_2^+ + H$ no other CT measurements have been performed at these or lower
collision energies. There is also limited theory at low energies, fully quantal state to state calculations of Krstic [11] are confined to energies 0.2 eV/u to 10 eV/u while state to state semi-classical calculations [11] are confined to energies 20 eV/u to 10 eV/u. Also, both experimental and theoretical investigations on isotopic systems for the reactions denoted by reaction numbers (i-iii) above are completely missing and no calculations or cross section measurements extend to energies where rotational states are not “frozen”.

The direct CT cross sections for D$_2^+$ + H are measured using the upgraded ion-atom merged-beams apparatus at Oak Ridge National Laboratory (ORNL) from keV/u collision energies where the collision is considered “ro-vibrationally frozen” to meV/u energies where collision times are long enough to sample vibrational and rotational modes for initial and final vibrational and rotational states. Preliminary results are reported in this paper within its three sections. The next section presents the Experimental Technique. Results and Discussion, and Summary and Future are found in the third and fourth sections.

2. Experimental technique
Low energy charge transfer is performed at the Multicharged Ion Research Facility (MIRF) at Oak Ridge National Laboratory (ORNL) using the ion-atom merged-beams apparatus which has previously been described in detail [12]. The apparatus, shown schematically in figure 1, has recently been upgraded [13] to accept beams from a CEA/Grenoble all-permanent magnet ECR ion source mounted on a 20-250 kV High Voltage (HV) platform. The higher velocity beams allow access to low energy

![Figure 1. Schematic of the current ORNL ion-atom merged-beams apparatus. The merge-path (32.5 cm) begins at the exit of the electrostatic spherical deflectors and ends in an Einzel lense (not shown) just before the de-merge magnet.](image)

collisions with a variety of molecular ions on H from keV/u to meV/u. In this technique, intense relatively fast (keV) ion and atomic beams are merged producing center-of-mass collision energies from meV/u to keV/u. Although the ECR source produces the D$_2^+$ molecular ions by high-energy electron impact in diffuse plasma, there is no direct coupling between the power injected into the source and the internal energies of the ions themselves. With no dipole and with the short flight time
to the merge section, the molecular ions are expected to remain in their initial vibrational state distribution, which is most likely determined by Frank-Condon transitions [14,15,16] between ground state $D_2$ and $D_2^+$. The neutral ground state hydrogen beam is obtained by photodetachment of an H$^-$ beam as it crosses the optical cavity of a 1.06 µm cw Nd:YAG laser where kilowatts of continuous power circulate. The H$^-$ is extracted from a duoplasmatron ion source. The ion and neutral beams interact along a field free region, after which H$^+$ product ions are magnetically separated from the primary beams. The neutral beam is monitored by measuring secondary electron emission from a stainless steel plate, and the intensity of the ion beam is measured by a Faraday cup. The product signal H$^+$ ions are detected with a channel electron multiplier operated in pulse counting mode. At these energies it is expected [9] that the beam-beam signal H$^+$ ions are formed by CT and not by ionization. The beam-beam signal rate (Hz) is extracted from (kHz) background with a two-beam modulation technique. The technique has been highly successful in providing benchmark charge transfer total cross sections for a variety of multiply charged atomic ions in collisions with H and D. The charge transfer measurements presented here are the first with molecular ions.

The independently absolute charge transfer cross section is determined at each center-of-mass energy from directly measurable parameters. The center-of-mass collision energy is calculated from the primary beam velocities which are determined by the accelerating voltages and include estimated plasma potential shifts of the two sources (see, e.g., Ref [12]). Below 1 eV/u, the small (non-zero) angle between the merged beams and the angular spread of the interacting beams must be measured. It is the merge angle and angular spread of the beams which effectively determine the lowest collision energy obtainable and energy uncertainty in the meV/u collision energy range.

### Table 1

At low (high) energy the collision times are long (short) enough compared to the characteristic vibrational time of 50 a.u. and to the characteristic rotational time of 3000 a.u. (rotational excitation < 0.01eV and first vibrational excitation energy ~ 0.5 eV).

| Collision energy | 0.01 eV/u | 1 eV/u | 100 eV/u | 10,000 eV/u |
|------------------|-----------|--------|----------|-------------|
| Collision time   | 1000 a.u. | 100 a.u. | 10 a.u. | 1 a.u.      |

At intermediate and lower energies, structures in the cross section as a function of energy are present both in the vibrationally resolved semi-classical calculations at intermediate energy (20 eV/u – 200 eV/u) and the quantal calculations at lower energy (0.2 eV/u – 10 eV/u) [Krstić 2002] summed over all final vibrational states because CT proceeds through dynamically coupled electronic, vibrational and rotational degrees of freedom. Figure 3 shows the predicted structure for initial $v = 0,1,2,3$ vibrational states summed over all final states. Convoluted by a Franck-Condon distribution (see table 2), the calculations are compared to the present measurements (see figure 2) and are seen to be larger, almost a factor of four at intermediate energy. The predicted structure at intermediate energies is not seen in the measurements. This discrepancy may be expected due to the classical approach (straight-line approximation) of the projectile motion coupled with a quantum approach for
Figure 2. Present merged-beam measurements of CT for \( \text{D}_2^+ + \text{H} \) are compared to previous experiment [9] and theory [10,11] for \( \text{H}_2^+ + \text{H} \). The vibrational specific cross section calculations of Krstic [11] are weighted by an expected Franck-Condon distribution of vibrational states produced in the ion source.

Figure 3. CT cross sections for \( \text{H}_2^+ \) on \( \text{H} \) specific to the initial vibrational state but summed over the final vibrational states. The calculations, freezing the target rotation, used straight line approximation for 25 – 150 eV/u and IOSA for lower energy [11].
Table 2. H$_2$ (ground state) to H$_2^+$ Franck-Condon distribution and the corresponding distributions for the isotopic systems [14-16]. The fits presented in figure 2 use the distribution for H$_2^+ + H$.

| ν | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
|---|----|----|----|----|----|----|----|----|----|
| H$_2^+$ | 0.119 | 0.190 | 0.188 | 0.152 | 0.125 | 0.075 | 0.052 | 0.037 | 0.024 |
| HD$^+$ | 0.090 | 0.160 | 0.185 | 0.155 | 0.120 | 0.095 | 0.060 | 0.045 | 0.030 |
| D$_2^+$ | 0.045 | 0.104 | 0.141 | 0.148 | 0.134 | 0.111 | 0.085 | 0.063 | 0.042 |

the vibrational and electronic resonant states increasing the calculated cross section especially for high \( ν \). Note the discontinuity in the calculations for the different initial excited vibrational states at 10 eV/u and 25 eV/u.

At low energies (0.2 eV/u - 10 eV/u), the Infinite Order Sudden Approximation (IOSA) calculations [11] are larger than the measurements by a factor of ~1.7. The difference in the structure suggested in our present measurements and the theoretical calculations might be expected as (D$_2^+$, D$_+$) and (H$_2^+$, H$_+$) are dynamically different in their vibrational modes. As direct CT and CT with nuclear substitution are not distinguishable in the calculations, the fact that the theoretical values (with substitution) are nearly a factor of two higher than the measured CT values (without substitution) suggest that substitutional CT could be an important process at these energies. Future measurements on H$_2^+ + H$ compared to the present D$_2^+ + H$ would directly assess this contribution.

Toward lower energy (0.1 eV/u) where even rotational modes cannot be considered frozen anymore, our measurement seems to increase faster than the theoretical predictions. This difference may be an indication that the D$_2^+$ produced by our ECR source are rotationally hot as it was observed for other electron impact ion sources [17]. The sharp increase in the total cross section at the low energies might be understood as due to trajectory effects caused by the ion-induced dipole potential. Trajectory effects [18] are accounted for in the Langevin model [19] and have been observed in CT for several exoergic atomic ion – H collision systems, e.g., Si$^+$ + H [20, 21]. It is important to point out that the measurements below 1 eV/u were performed with a limited signal/noise which precluded extensive diagnostics on the beam-beam signal. Further measurements with better signal/noise are underway.

4. Summary and Future
The absolute cross sections of CT for D$_2^+$ on H, from keV/u collision energies where the collision is considered "ro-vibrationally frozen" to meV/u energies where collision times are long enough to sample vibrational and rotational modes, are measured for the first time. Our measurements of direct and dissociative CT above 400 eV/u benchmark existing theory and are consistent with previous measurements. At intermediate energy, the measurements are expected to disagree with the available theoretical calculations which use the straight line approximation. At low energy, one can see that IOSA calculations summed over all H$_2$ final vibrational states and convoluted by Franck-Condon vibrational distribution reproduce the general structure seen in our measurements but are consistently higher. The differences in the structure may be due to the difference in the dynamics of the two isotopes used in the calculations and measurements. The larger theoretical predictions also suggest that CT with substitution might be a very important process at low energy. Measurements are needed for H$_2^+ + H$ for a more straightforward comparison with theory and, when compared to D$_2^+ + H$, CT with substitution can be inferred. With an improved signal/noise measurements will be extended to collision energies as low as 10 meV (practical low energy limit of the apparatus) to explore structure which may be present due to rotational or vibrational states and to investigate whether the total cross section follows the simple Langevin model. The use of a cold ion source will obviously allow us to investigate the effect of rotational excitations similar to the previous study of dissociative...
recombination of H$_3^+$ in a storage ring [17]. A better understanding of this fundamental CT processes may help in more complicated systems such as low energy radical H attack on DNA. This has been investigated for the dissociative electron attachment inducing DNA double strand break [6]. Our measurements which are the first involving molecular ions in the upgraded merged beams apparatus at ORNL can easily be extended to other molecular ions such as D$_3^+$, HeH$^+$, OH$^+$, and CH$^+$.

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