VOLUME 86, NUMBER 21 PHYSICAL REVIEW LETTERS 21 MAY 2001

Charge Transfer and Elastic Scattering in Very Slow $H^+ + D(1s)$ Half Collisions

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(Received 19 January 2001)

Charge transfer and elastic scattering probabilities were measured for half collisions between very slow protons and atomic deuterium. Collision energies down to a few meV, lower by more than an order of magnitude and with better energy resolution than previous measurements, were studied using the dissociation of the HD^+ electronic ground state. The collision energy is determined *a posteriori* from the measured momentum vector of the dissociating charged fragments. The experimental results are in good agreement with our coupled channel calculations.

DOI: 10.1103/PhysRevLett.86.4803 PACS numbers: 34.50.Gb, 82.30.Fi, 98.38.Bn

Resonant charge transfer between a slow proton and a hydrogen atom in its ground electronic state is among the most fundamental of atomic collision processes. The heteronuclear $H^+ + D(1s)$ collision system is electronically similar to the homonuclear system, but charge transfer in this case is only a *near* resonant process, since the difference in nuclear mass removes the nuclear exchange symmetry and creates a small energy gap between the lowest two electronic states of the transient HD^+ molecular ion at large internuclear distances. Because of this "symmetry breaking," calculations for the heteronuclear system are profoundly more challenging than for $H^+ + H(1s)$, requiring that HD^+ calculations go beyond the Born-Oppenheimer approximation [1–8]. Note, however, that the $H^+ + D(1s)$ system has the experimental advantage of easily distinguishable final products. Scattering calculations for this one electron system provide a testing ground for theorists wrestling with different approaches to the long-standing problem of electron translation factors within a molecular orbital framework [1,2,7,8]. Furthermore, $H^+ + D(1s)$ collisions at energies below a few eV are of importance in aeronomy, where these charge transfer reactions regulate the amount of neutral hydrogen escaping from planetary atmospheres [9], and astrophysics, where they play a major role in the formation of some deuterated molecules [10–12]. Understanding the chemical reactions involving deuterium in the interstellar medium is especially relevant to attempts to determine the deuterium to proton ratio and hence the primordial baryon density, a fundamental problem in cosmology [13].

Despite the theoretical and applied interest, there are very few measurements of this process at collision energies below 10 eV [14], the region where the theoretical interest is most acute [2]. Low energy measurements of this type are usually conducted using the merged-beams technique. Newman and co-workers [15], for example, used this method to make measurements with collision energies down to 120^{+48}_{-30} meV. At these energies, however, it is very difficult to control the relative velocity of the neutral and ion beams due to the inherent angular and energy spreads of the beams, and thus the energy resolution of the experiment is not sufficient to provide a stringent test of theory.

In this Letter, we describe a new approach to this experimental problem, which allows the measurement of charge transfer and elastic scattering at collision energies down to the threshold for charge transfer with an energy resolution on the order of 1 meV. Furthermore, it enables direct comparison between theory and the experimental results. In this method the dissociation of the vibrational continuum of the electronic ground state of HD^+ is used to produce a very slow $H^+ + D(1s)$ "half" collision. These continuum vibrational states of $HD^+(1s\sigma)$ are populated via vertical single ionization of the HD molecule by fast ion impact, as illustrated in Fig. 1. The number of these "ground state dissociation" (GSD) events relative to total single ionization and the kinetic energy release distribution (E_k) in this dissociation process can be calculated from the Franck-Condon factors linking the neutral and ionic states [16,17]. Ground state dissociation occurs about 1% of the time relative to the dominant single ionization process [17]. The second part of the GSD process can be thought of as "half" a collision, with $H^+ + D(1s)$ starting from the internuclear separation at the time of the vertical ionization, $R \approx R_0$, and then evolving to $R = \infty$. The probability of the kinetic energy released in the GSD process, $P(E_k)$, is maximum at $E_k = 0$ and falls off approximately exponentially with a width of about 300 meV [16,17]. Therefore, most GSD events result in $H^+ + D(1s)$ half collisions with energies that are prohibitively difficult to measure in merged-beams experiments. Furthermore, these GSD events can be distinguished from other processes, such as ionization-excitation and double-ionization, also occurring in collisions between fast ions and HD molecules since fragments produced in the other processes have much larger kinetic energies [17,18]. For example, ionization into the $2p\sigma$ state will result in a $D^+ + H(1s)$ half collision; however, the D^+ energy will be a few eV thus easily resolved from the GSD fragments. In short, GSD is a very slow dissociation from a well-defined initial state. During this dissociation, charge transfer can occur near $R = 12$ a.u., where the two electronic states are strongly

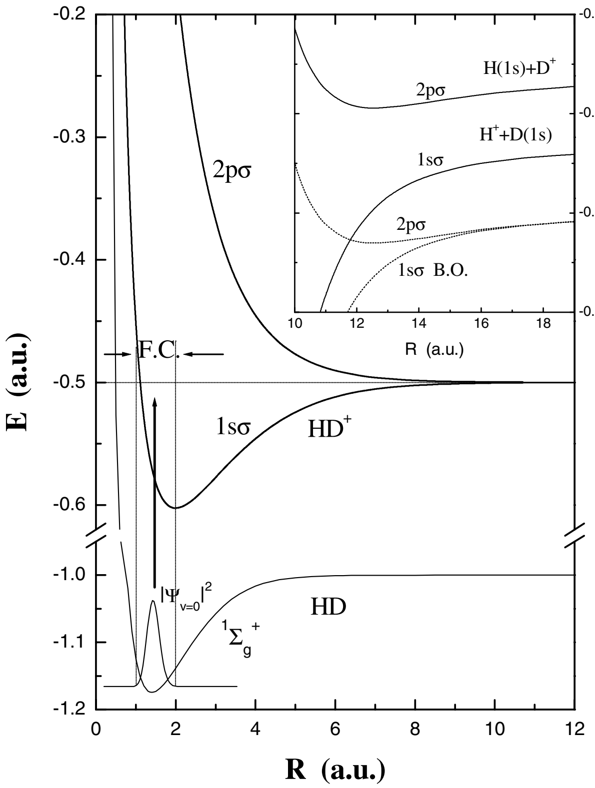

FIG. 1. A schematic view of the GSD process. Sudden ionization of the HD molecule results in vertical transitions to the HD^+ electronic ground state. If the populated $1s\sigma$ vibrational state is in the continuum, a dissociation results. Charge transfer can then occur during the dissociation near the coupling region around $R = 12$ a.u. (shown in the inset). The potential energy curves of HD are taken from Ref. [3] and from Ref. [4] for HD^+. The inset shows the shift in the $1s\sigma$ and $2p\sigma$ curves from those calculated using the Born-Oppenheimer approximation. The energy difference between the $1s\sigma$ and $2p\sigma$ states at the separated atom limit is 3.7 meV.

coupled, resulting in the detection of a slow D^+ fragment. In contrast, if no transfer occurs, a slow H^+ fragment will be detected. Experimentally, the challenge is to measure the energy E_k released in the GSD process for each event and thereby determine the collision energy provided by the natural particle accelerator.

Cold target recoil ion momentum spectroscopy (COLTRIMS) [19,20] is ideally suited for imaging the momentum of these low energy molecular fragments. Our apparatus, shown in Fig. 2 and described in more detail in Refs. [17,18,21], utilizes many COLTRIMS principles. A cold, localized HD target is provided by a precooled effusive jet. The HD molecules in this jet are vertically ionized by fast ions from a high energy accelerator. The ion beam, typically consisting of 4 MeV protons, is bunched to less than 1 ns width. The recoil ions are extracted by the electric fields of the spectrometer and accelerated toward a two-dimensional position sensitive detector with a position resolution of 0.18 mm. A timing signal is taken from the back microchannel plate and the time-of-flight of the recoil ion is measured relative to a signal synchronized with the beam bunch. The time resolution is approximately 1 ns, and is dominated by the width of the beam bunch. The spectrometer includes a weak electrostatic lens which focuses the recoil ions in order to compensate for the finite size of the gas target. The detector position and spectrometer voltages are chosen to achieve the best focusing in all three spatial dimensions [17,18,21]. From the detected time-of-flight and position information, the three-dimensional velocity vector relative to the center of mass of the dissociating HD^+ molecular ion is determined for each recoil ion. Since the time-of-flight is proportional to $\sqrt{m/q}$, the recoil ions are identified, and the yield of each species as a function of E_k is determined.

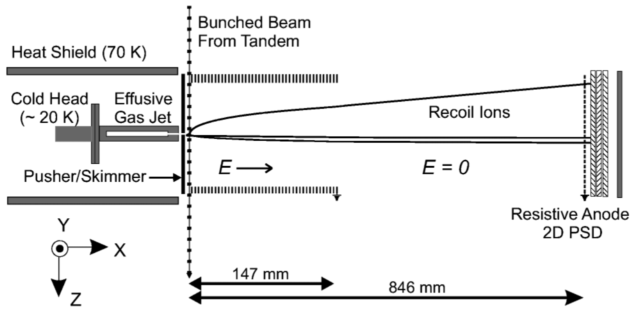

FIG. 2. Conceptual figure of the cylindrical COLTRIMS-style apparatus used in these experiments. A more detailed description of the apparatus is found in Refs. [17,21].

If $\mathrm{H}^+(E_k)$ and $\mathrm{D}^+(E_k)$ are the measured yields of the GSD events, the probability for charge transfer is defined as

$$P_t(E_k) = \frac{D^+(E_k)}{H^+(E_k) + D^+(E_k)} = \frac{\sigma_t}{\sigma_e + \sigma_t}, \quad (1)$$

where σ_e and σ_t are the theoretically computed values for $\mathrm{H}^+(E_k)$ and $\mathrm{D}^+(E_k)$ production, respectively [17]. While $P_t(E_k)$ is typically expressed in terms of the S-matrix element, Eq. (1) has the advantage of allowing a direct comparison between experiment and theory. Similarly, the probability for elastic scattering is

$$P_e(E_k) = \frac{H^+(E_k)}{H^+(E_k) + D^+(E_k)} = \frac{\sigma_e}{\sigma_e + \sigma_t}. \quad (2)$$

Finally, the ratio of the bound-free transitions to total single ionization, calculated from the Franck-Condon factors, can be expressed as

$$P(E_k) = \frac{H^+(E_k) + D^+(E_k)}{\sigma^+}, \quad (3)$$

where σ^+ is the single ionization cross section.

The experimental energy resolution is influenced by two kinds of effects. First, there are factors related to the measurement itself, such as the timing and position resolution of our detection system. These factors scale as $\delta E_k = \alpha\sqrt{E_k}$ where α depends on the extraction field

[21]. By reducing the extraction field, the value of α is reduced, and therefore our apparatus achieves maximum resolution for the lowest energy fragments. Second, there are factors that influence the center-of-mass motion of the transient HD^+ molecular ion, including the thermal motion of the target and the recoil of the target from the ionized electron. The first is reduced by precooling the HD gas to about 15 K, as determined by fitting a Maxwell-Boltzmann curve to the measured energy distribution of the HD^+ molecular ions. The recoil of the HD^+ from the ionized electron is presently neglected, leading to an average uncertainty of about 0.5 meV [22].

When using a HD target, the largest experimental complication arises from the presence of H_2 and D_2 in the target. In our case, nondissociative single ionization of the H_2 contamination results in H_2^+ molecular ions with the same m/q as the D^+ GSD fragments. We have developed two methods for determining the amount of H_2 contamination in our target [17,18]. To measure the relative yield of H^+ and D^+ as a function of E_k, however, we must also determine the H_2 contamination as a function of E_k in order to subtract it properly. In other words, it is not enough to know the amount of H_2 in the target, we must also know the energy distribution of the H_2^+ molecular ions. Since the H_2, D_2, and HD molecules in the target come from the same heat reservoir, and therefore should have the same thermal distribution, the abundant HD^+ events collected in our measurement serve as a high precision simulation of the H_2^+ events. In short, we determine the *number* of H_2^+ events using the methods described previously [17,18], and the *shape* of the H_2^+ energy distribution by scaling the HD^+ distribution.

In addition to the H_2 contamination, an accurate determination of the relative yields can be hindered by the following systematic problems: (i) The detection efficiency must be set the same for all recoil ions [17]. (ii) The target must be dilute enough that chemical reactions forming H_2D^+ or HD_2^+ do not occur, since the former ions would affect the determination of the D_2^+ contamination. This is verified by the absence of the $m/q = 5$ peak associated with HD_2^+ formation in the time-of-flight spectrum. (iii) Contributions of H^+ and H_2^+ from residual water vapor in the experiment chamber must be subtracted. This is accomplished by making two measurements, with and without the HD target, under otherwise identical conditions. The background run is then subtracted from the HD run after normalization of the H_2O^+ peaks. H^+ fragments from water are the major source of uncertainty in the evaluation of the yield of H^+ GSD fragments.

We have conducted coupled channel scattering calculations for both the half [17] and full [8] $H^+ + D(1s)$ collision systems using the $1s\sigma$ and $2p\sigma$ adiabatic potentials calculated by Esry and Sadeghpour [4]. The coupled channels part of the calculation is essentially the same for both the half and full collisions and is discussed in detail in Ref. [8]. Briefly, the coupled channels problem was solved using an R-matrix formulation with incoming wave boundary conditions. In the half collision, the Franck-Condon transition from the neutral molecule is taken into account by projecting the ground state of the neutral HD molecule onto the continuum states of HD^+ [17]. The comparison between our measurements and calculations are shown in Figs. 3 and 4. It is important to note that since the target is cooled below 20 K, our calculations include only $J = 0$, since it is essentially the only rotational state initially populated at that temperature. In the elastic channel, our calculations show two $J = 0$ Feshbach resonances located below the threshold for charge transfer. The full collision calculations include much higher values of J and most of the structure seen in those calculations results from shape resonances for $J \geq 10$ [8].

The measured probability for charge transfer, defined in Eq. (1), is shown in Fig. 3. We find good agreement between theory and experiment, except in the region where the systematic error in the subtraction of the H_2^+ contamination affects the charge transfer measurement. This error is most likely related to the momentum transferred to the molecular ion in the ionization process, and will be discussed in detail in a forthcoming publication. The affected region, shown in the inset of Fig. 3, is limited to about 20 meV above the charge transfer threshold. For the elastic channel, it is more convenient for us to compare

$$\sigma_e = P_e(E_k) \times P(E_k) = \frac{H^+(E_k)}{\sigma^+} \tag{4}$$

to theory since Eq. (4) does not contain the D^+ channel and therefore the systematic problems caused by the H_2 contamination are not a concern. The results for the

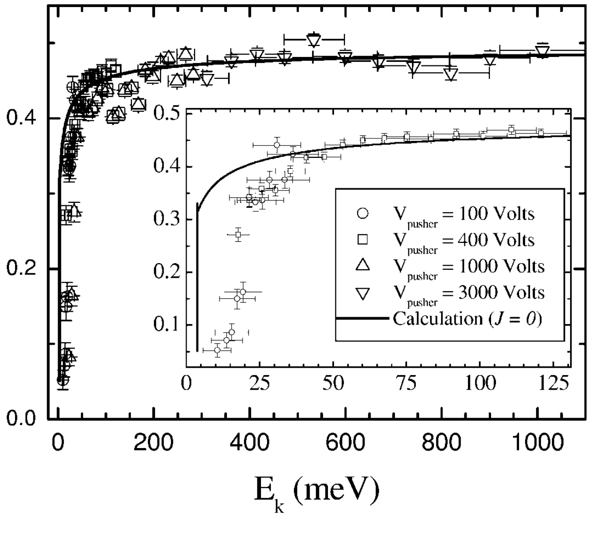

FIG. 3. Calculated and measured values for $P_t(E_k)$ (V_{pusher} determines the extraction field strength, see Fig. 2). The inset shows an expanded view of the region near the threshold for charge transfer. The disagreement between theory and experiment near threshold is due to the difficulties associated with subtracting the H_2^+ contamination (see Ref. [21]).

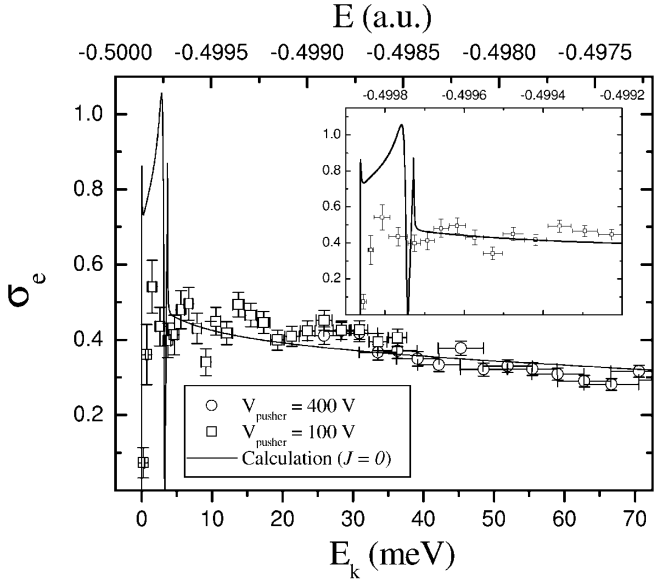

FIG. 4. Measured and calculated values of σ_e [see Eq. (4)] as a function of energy. The bottom axis gives kinetic energy release (E_k) in meV while the top axis gives total energy (E) in atomic units. The inset shows an expanded view around the threshold for charge transfer. Note the two Feshbach resonances at $E = -0.499\,754\,675$ and $E = -0.499\,728\,207$ a.u.

elastic channel are shown in Fig. 4. Again, we find theory and experiment to be in good agreement. We currently lack the resolution, however, to map the structure caused by the Feshbach resonances in the elastic channel. It is important to note that Figs. 3 and 4 represent a direct comparison, described in Eqs. (1) and (4), between theory and experiment, without the need to scale by some arbitrary factor. These results demonstrate the feasibility of using the GSD process to study this basic ion-atom collision at energies much lower, and with better resolution, than presently possible using traditional merged-beams techniques. Modifications to the apparatus are underway in order to improve the energy resolution and reduce the systematic errors in the subtraction of the H_2^+ and water-fragments contaminations.

In summary, we have developed a new method for studying very slow collisions between a proton and a deuterium atom. Ground state dissociation of $HD^+(1s\sigma)$ is used to produce very slow $H^+ + D(1s)$ half collisions. Momentum imaging of the dissociating charged GSD fragments with a COLTRIMS-style apparatus is used to determine the collision energy. We have extended the energy range down by more than 1 order of magnitude and obtain much better energy resolution than is presently possible in merged-beams experiments. These experimental results provide a direct test of half collision scattering calculations. Since our half collision calculations were done using the same techniques as for the full collision problem [8], our results provide an experimental test of the theory for this fundamental, very slow, ion-atom collision system. Forthcoming improvements in the experiment should yield benchmark results that can test theory all the way down to the threshold for charge transfer, as well as measure the structure in the elastic channel caused by the Feshbach resonances below this threshold.

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

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