CHARGE EXCHANGE AT VERY LOW COLLISION ENERGIES

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Two of the simplest collision systems one can study are H^+ + H(1s) and H^+ + D(1s). Electron transfer is resonant in the first and nearly resonant in the latter because of the 3.7 meV gap between H(1s) and D(1s). Once the collision velocity becomes small enough quantum effects become more pronounced. However, these very low energies, of a few meV, are inaccessible using standard collision techniques. *We hereby suggest a method in which a dissociating HD^+ molecular ion is the "accelerator" used to measure electron transfer in the H^+ + D(1s) collision system down to a few meV.* When a HD molecule is ionized quickly about 1% of the $HD^+(1s\sigma)$ is in the vibrational continuum. During the dissociation, the electron initially centered on the D core can make a transition to the H core when the $2p\sigma$ and the $1s\sigma$ potential energy curves associated with the two dissociation limits get close to each other. It is important to note that during molecular dissociation the "avoided crossing" is crossed only once in contrast to twice during a full collision.

Slow proton collisions with atomic hydrogen provide the best testing ground for electron transfer studies because of the simplicity of the colliding system. Electron transfer in slow H^+ + H(1s) collisions is a resonant process involving the two lowest electronic states of the transient H_2^+ molecular ion formed during the collision. The transfer between the $1s\sigma$ and $2p\sigma$ states occurs at large internuclear separation where the two states merge together and their coupling is strong. The cross sections for this process were calculated, for example, by Hunter and Kuriyan [1] from 0.1 meV to 10 eV collision energy. Experimental determination of electron transfer cross sections are straight forward at keV energies and higher. However, the task becomes increasingly harder as the collision energy gets smaller. (See review by Gilbody [2]). Using a beam overtaking technique (i.e., neutralizing part of the beam and creating a velocity difference between the neutral and charged beam), Belyaev *et al* [3] managed to measure those cross sections down to about 5 eV. The experimental value is about 40% (2.7σ) above theory as shown in Fig. 1.

One would expect theory to be more precise than experiment for such collision systems and thus associate the difference to systematic experimental uncertainties. We are aware of no other measurements for slower collisions, which leaves the energy range below 1 eV for theorists only. Note that more structure appears as the collision energy is reduced.

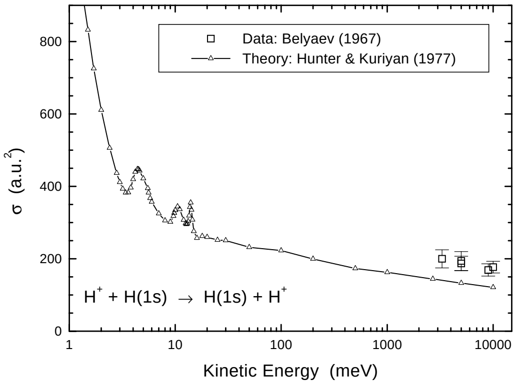

FIGURE 1. Electron transfer cross section in slow H^+ + H(1s) collisions.

The H^+ + D(1s) and D^+ + H(1s) collision systems are similar to the one above in their simplicity. In contrast to the H^+ + H(1s) collision system, however, electron transfer in the heteronuclear systems is only a near resonant process involving the same two lowest electronic states of the transient HD^+ molecular ion formed during the collision. The transfer between the $1s\sigma$ and $2p\sigma$ states occurs near the avoided crossing at around 12 a.u. of internuclear separation. The energy gap of 3.7 meV between the ground $1s\sigma$ state and the first excited $2p\sigma$ molecular state, shown in Fig. 2, is due to the difference in nuclear mass between H and

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D and signals the breakdown of the Born-Oppenheimer approximation.

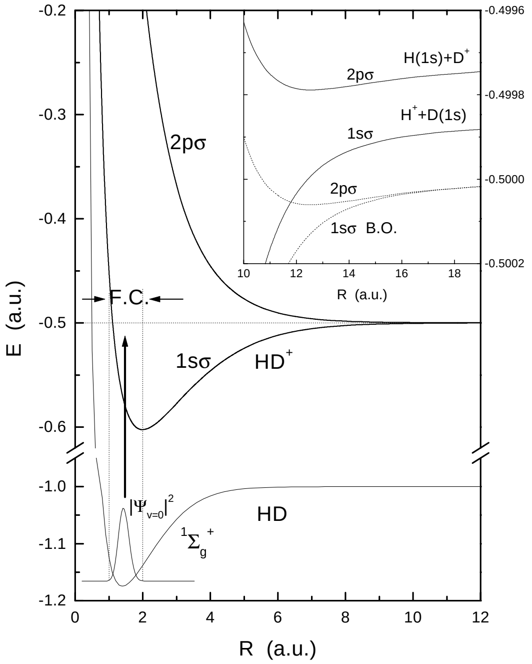

FIGURE 2. Potential energy curves of HD$^+$ (from Chen 1991 [4]) and HD (H_2 from Kołos *et al* [5]). Note that the Born-Oppenheimer approximation is valid near the minimum and the difference between HD and H_2 is in the vibrational part.

The cross sections for electron transfer in these collision systems were calculated by Hunter and Kuriyan [6] and also by Davis and Thorson [7]. The two calculations for H$^+$ + D($1s$) collisions are compared to each other in Fig. 3. Both calculations show more structure at lower energies that both groups attribute mostly to the interference between electron transfer on the way in and out, i.e. the two times the avoided crossing is traversed during the collision. According to Davis and Thorson [7], the finer structure might be due to the finer grid they used in their calculations. Surprisingly, the agreement between the two calculations is not as good as one would expect at the lower energy end. In spite of this disappointing disagreement, we failed to find any recent and more precise calculation. Theory is in good agreement with merged beam measurements of Newman *et al* [8], which extend down to 0.1 eV. However, the experimental precision deteriorates as the collision energy is reduced, both for the cross section measurement and for determining the collision energy. It seems important to extend the experimental work to lower collision energies in order to revive interest in this simple collision system, especially if one could reach collision energies of the order of the energy gap. In contrast to the simplicity of this collision system from the theorist's view point, conducting an experiment with sufficient energy resolution down to a few meV provides the experimentalist with quite a challenge, as can be seen from the data presented. *In this paper we suggest a new approach to bypass these experimental difficulties.*

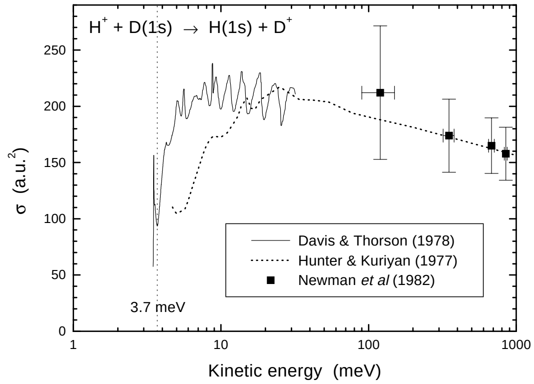

FIGURE 3. Electron transfer cross section in slow H$^+$ + D($1s$) collisions.

We suggest using ground state dissociation of HD$^+$ as a means to measure electron transfer from the $1s\sigma$ to the $2p\sigma$ state at large internuclear separation. Ground state dissociation of HD$^+$ is the process in which first a vertical ionization (fixed internuclear distance, R) of HD populates the vibrational continuum of the HD$^+$ ground state (i.e. the $1s\sigma$ state which is associated with H$^+$+D($1s$) at the separated atom limit). This is then followed by a dissociation into either H$^+$ + D($1s$) if no transition occurs, or H($1s$) + D$^+$ if the electron is transferred to the $2p\sigma$ state. It has been shown that this dissociation channel can be experimentally distinguished from the dissociation of the excited electronic states of HD$^+$ because the fragments have much lower dissociation energies [9,10]. For example, if the $2p\sigma$ state is populated directly by vertical ionization then the fragments have about 15 eV of kinetic energy while those associated with the $1s\sigma$ ground state have energies ranging from zero to less then 0.5 eV, thus enabling the separation of these dissociation channels [9,10].

Many different schemes can be used to ionize the HD molecule to the $1s\sigma$ state keeping the internuclear distance fixed. We have chosen to use fast proton impact ionization, which populates the vibrational continuum of the HD$^+$ ground state while producing only a small amount of fast fragments (from the dissociation of excited states of HD$^+$ and its double ionization [10,11]). Fast electron impact or photo-ionization would also be reasonable choices. In Fig. 4 we show the calculated kinetic energy release distribution for ground state dissociation of HD^+ [12]. The calculations are just the Franck-Condon factor between the HD(v=0) wave function and the $HD^+(1s\sigma)$ vibrational continuum wave functions. We have used many discrete vibrational states to represent the continuum as discussed in [10,12,13]. This distribution peaks at zero kinetic energy, i.e. the dissociation threshold, and falls off approximately exponentially with a FWHM of about 250 meV. It amounts to about 1% of the $HD(^1\Sigma^+)$ to $HD^+(1s\sigma)$ transitions.

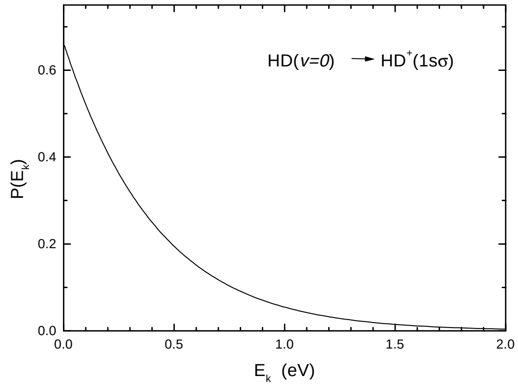

FIGURE 4. Computed kinetic energy release distribution for HD^+ ground state dissociation.

Using a fast proton beam to prepare the HD^+ in the dissociating $1s\sigma$ state of interest, the whole energy range from zero to about 0.5 eV in CM will be measured "simultaneously". Thus, instead of tuning the collision energy prior to the interaction, as done in most collision experiments, we will determine it afterwards by measuring the charged fragment energy. Clearly the energy resolution of such a measurement is the key issue in this method. The fragment ions are extracted toward a micro channel plate detector using a weak electric field, and time-of-flight is used to identify the H^+ and D^+ fragments. The deviation of each ion from the time-of-flight expected if it had no initial velocity toward the detector ($v_x = 0$) is used to determined this component of velocity. The other velocity components, perpendicular to the extraction field, are evaluated using the impact position of each fragment on the detector. A 2D resistive anode decodes this position information with resolution of about 0.15 mm. The main limiting factors in the energy resolution are: (1) thermal motion of the HD target molecules (about 25 meV at room temperature); and (2) extended target length along the beam direction. To reduce these energy-broadening effects an effusive gas HD target jet is used after pre-cooling the HD gas to about 10-30 K in a small cell mounted on a cold head of a cryo-pump . A schematic view of the experimental setup is shown in Fig. 5. This cooling is also expected to reduce the water contaminant in the target, thus improving the quality of the H^+ fragment data (see Ref. [13] for details). To further reduce the energy broadening caused by the target length along the beam direction, space focusing by the extraction field is used as discussed by Mergel *et al* [14]. The fragment energy resolution also depends on the strength of the extraction field, and it can be improved by lowering the field strength. However, while using a weaker extraction field only part of the dissociating vibrational continuum shown in Fig. 4 will be detected simultaneously. The best expected energy resolution is about 2 meV.

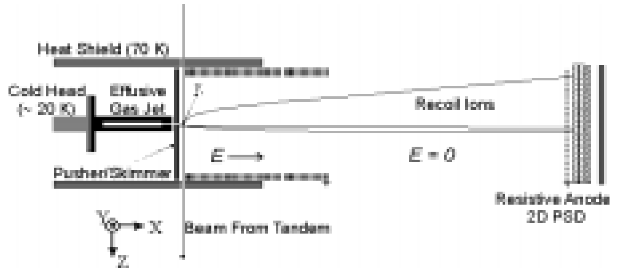

FIGURE 5. Schematic view of experimental set-up. .

The measured yields of H^+ and D^+ fragments as a function of the dissociation energy in the CM frame of reference provide a direct measure of the electron transfer cross section because each slow D^+ detected indicates an electron transfer from the initial $1s\sigma$ to the final $2p\sigma$ state. Note that this dissociation process which provides an experimental probe for very slow collisions is not identical to the $H^+ + D(1s)$ collisions calculated by Hunter and Kuriyan [6], and by Davis and Thorson [7]. In molecular dissociation the avoided crossing is encountered only once, and it can be viewed as a "single pass" collision in contrast to the full collision. As a result, the interference between electron transfer on the way in and out is removed, and the calculations discussed above can not be directly compared to the measurement. In "single pass" collisions the transition probability is proportional to the square of the transition amplitude, to which it can be compared directly if available. We have used instead the Meyerhof formula [15] to evaluate the total electron transfer probability and found it to be in agreement with our measurement of the ratio $D^+/[H^++D^+]$ integrated over all dissociation energies [12]. We show in Fig. 6 the predictions of this model calculation for the H^+ and D^+ yields as a function of the dissociation energy, E_k. Note that when E_k is below the energy gap only H^+ is expected. While at high dissociation energies, $E_k \gg E_{gap}$, the yields approach the same value. The prediction of the behavior of these yields just above the energy gap, when electron transfer between the two states starts happening, is in question because this model is not expected to be valid unless $E_k \gg E_{gap}$. New theoretical calculations of the HD^+ ground state dissociation process focusing on the energy region near the gap are under way.

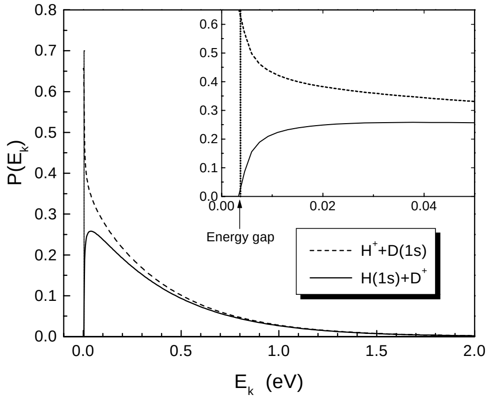

FIGURE 6. The yields of H^+ and D^+ as a function of dissociation energy as predicted by the Meyerhof formula (see text).

If one looks at the magnified view of the potential-energy curves around the energy gap shown in Fig. 7, one can see that the $2p\sigma$ state can sustain some vibrational states (see Carrington *et al* [16]). When the coupling to the $1s\sigma$ vibrational continuum is included, such states might become Feshbach resonances appearing in the $H^+ + D(1s)$ cross section. It is clearly questionable whether one can achieve the needed energy resolution to see these resonances. However, one can hope to use the new theoretical calculations of HD^+ ground state dissociation to estimate what energy resolution is needed before these resonances smear out.

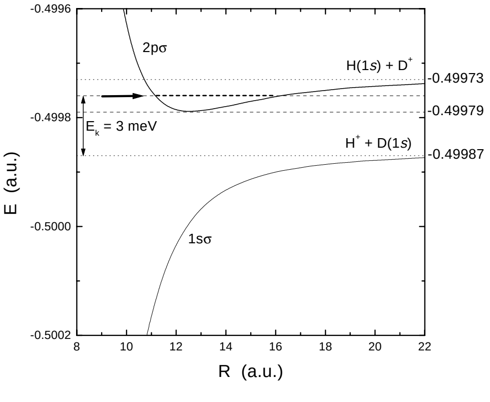

FIGURE 7. Magnified view of the potential energy curves of HD^+ around the energy gap.

In summary, the use of ground state dissociation of HD^+ has been suggested as a method to study $H^+ + D(1s)$ "single pass" collisions down to collision energies of a few meV. As for the energy resolution one can achieve, this is still to be determined.

ACKNOWLEDGMENT

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