

Symmetry Breakdown in Ground State Dissociation of HD^+

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Experimental studies of the dissociation of the electronic ground state of HD^+ following ionization of HD by fast proton impact indicate that the $\text{H}^+ + \text{D}(1s)$ dissociation channel is more likely than the $\text{H}(1s) + \text{D}^+$ dissociation channel by about 7%. This isotopic symmetry breakdown is due to the finite nuclear mass correction to the Born-Oppenheimer approximation which makes the $1s\sigma$ state 3.7 meV lower than the $2p\sigma$ state at the dissociation limit. The measured fractions of the two dissociation channels are in agreement with coupled-channels calculations of $1s\sigma$ to $2p\sigma$ transitions.

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The sudden ionization of a hydrogen molecule preferentially leads to the electronic ground state of the molecular ion. The final vibrational state is determined by the Franck-Condon factor linking the neutral state to the ionic state. This final state may be a bound state of the molecular ion or a continuum state that dissociates into a hydrogen ion and a hydrogen atom. These vertical transitions are shown schematically in Fig. 1. Dissociation of the electronic ground state results in fragments having very low kinetic energy (typically < 1 eV). Excited electronic states can be produced during ionization but the relatively high kinetic energy of the fragments clearly distinguishes these processes from “ground state dissociation” (GSD) (see, for example, Ref. [1]). The question we are concerned with in this Letter is whether or not GSD of HD^+ is symmetric; that is, *is there a measurable difference between the two distinguishable dissociation channels, $\text{H}(1s) + \text{D}^+$ and $\text{H}^+ + \text{D}(1s)$?*

It is well known from structure calculations of HD^+ (see, for example, Refs. [3–5]) that this isotope differs from the homonuclear isotope due to the finite mass of the nucleus, which results in the $\text{D}(1s)$ threshold being 3.7 meV lower than the $\text{H}(1s)$. This isotope effect produces the avoided crossing of the molecular $1s\sigma$ and $2p\sigma$ states [which adiabatically dissociate to $\text{H}^+ + \text{D}(1s)$ and $\text{H}(1s) + \text{D}^+$, respectively] shown in Fig. 1. This breakdown of the Born-Oppenheimer approximation was experimentally studied by Carrington *et al.* [6], who measured the vibration-rotation transitions of the HD^+ near the dissociation limit. These spectroscopic measurements were in good agreement with *ab initio* calculations only if corrections to the Born-Oppenheimer approximation were included. Furthermore, using the measured hyperfine multiplet splitting, they showed that the electron becomes more localized around the deuteron for high vibrational states near the dissociation threshold.

One would expect a similar behavior just above the dissociation threshold. Explicitly, within the energy gap, only dissociation into $\text{H}^+ + \text{D}(1s)$ should occur because the upper dissociation limit is energetically forbidden. The

two states start mixing above the $\text{H}(1s)$ threshold and approach equal probabilities as the energy above threshold increases. This mixing between the adiabatic $1s\sigma$ and $2p\sigma$ states can be described using a scattering approach. Within this description, a vertical transition into the vibrational continuum of the $\text{HD}^+(1s\sigma)$ occurs, followed by a possible transition to the first excited $2p\sigma$ state during dissociation, resulting in D^+ fragments. The $1s\sigma$ to $2p\sigma$ transition probability increases from zero at the $\text{H}(1s)$ threshold and approaches 0.5 just below the $n = 2$ manifold, so that the two dissociation channels are equally likely. Thus, qualitatively, the lower dissociation channel, $\text{H}^+ + \text{D}(1s)$, should be more likely because below the $\text{H}(1s)$ threshold it is the only allowed channel. But

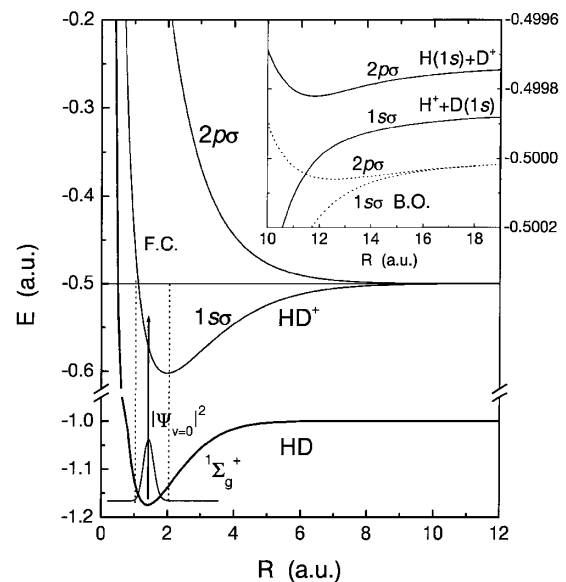


FIG. 1. Schematic view of the vertical transitions between the ground states of HD and HD^+ . The potential energy curve of the hydrogen molecule was taken from Ref. [2] and from Ref. [3] for the HD^+ . In the inset, we also show for comparison the same potential energy curves of HD^+ , calculated within the Born-Oppenheimer approximation.

one can still wonder if this effect results in a measurable asymmetry, because the energy gap is very small in comparison to the energy range spanned in GSD. The energy distribution of the dissociating $\text{HD}^+(1s\sigma)$ falls off, with increasing energy, from its maximum value at threshold and has a width of about 300 meV [1]. Furthermore, the asymmetry found by Carrington *et al.* [6] below the dissociation threshold was large for the $\nu = 21$ vibrational state which has a dissociation energy of 1.26 meV [7], i.e., less than the energy gap between the two dissociation limits. In contrast, the $\nu = 18$ state was found to be essentially symmetric. At 74.156 meV [7] below threshold its dissociation energy is much closer to threshold than the width of the GSD distribution. How fast the asymmetry disappears with increasing energy above the $\text{H}(1s)$ dissociation threshold and whether there is a measurable difference between the two dissociation limits is not immediately clear.

In addition to the basic interest in this process due to the breakdown of the Born-Oppenheimer approximation, it could also be relevant to astrophysics, where HD and HD^+ are among the molecules used to study the chemistry of the interstellar medium. In particular, these molecules are used to estimate the deuterium abundance in the universe, which sets limits on the primordial baryon density. If HD^+ preferentially dissociates into D and H^+ , then this process might play a role in estimates of the abundance of deuterons deduced from observations of D, HD, and other deuterated molecules [8–10].

Experimentally, HD molecules in their ground state were ionized by fast protons, which had been bunched and accelerated to 4 MeV. Recoil ions produced in the target region were extracted toward a microchannel plate detector by the weak electric fields of a time-of-flight spectrometer [11]. Typical time-of-flight spectra of single recoil ions measured with a weak extraction field are shown in Fig. 2(a). The H^+ and D^+ peaks in this figure have a similar structure with a narrow center peak containing the low energy fragments of interest in this work and a broad distribution of the fast fragments that is characterized by two shoulders and a central dip. When using such weak extraction fields, one has to be especially careful to satisfy the following constraints: (i) the detection efficiency must be the same for all recoil ions of interest, and (ii) the target density has to be very low to ensure that no chemical reactions forming H_2D^+ and HD_2^+ occur before the recoil ions leave the target region. The latter was verified by the absence of the $m/q = 5$ peak associated with HD_2^+ formation. The former was accomplished by accelerating the recoil ions to more than 3 keV just before hitting the detector, using a highly amplifying Z-stack microchannel plate detector, and by setting the discrimination level sufficiently low. The time-of-flight spectrum shown in Fig. 2(a) contains, in addition to the peaks of the molecular hydrogen target, some contributions from residual water. These contributions were removed to yield the background-free HD spectrum,

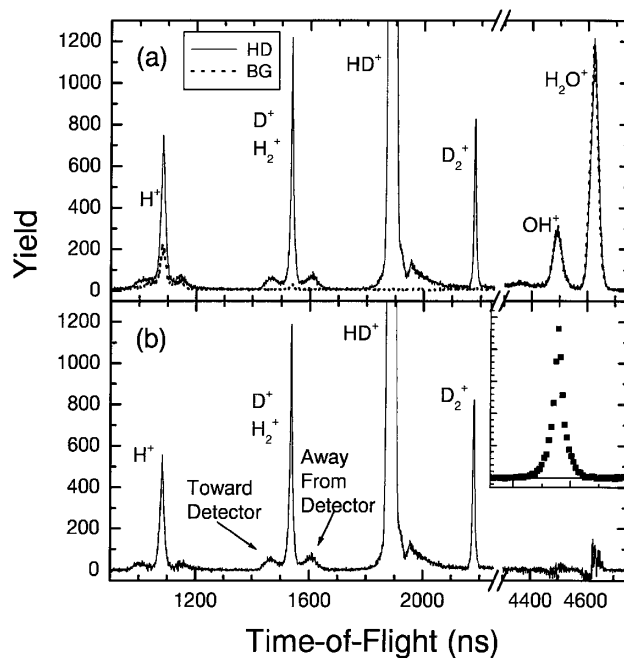


FIG. 2. (a) A typical time-of-flight spectrum of single recoil ions produced by 4 MeV proton impact on HD and background, measured with a 105 V/cm extraction field. (b) The same spectrum after background subtraction. In the inset, we show a magnified view of the $m/q = 2$ peak after baseline subtraction (see text and Ref. [12]). Note that the region around the center peak is flat.

shown in Fig. 2(b), by subtracting a water spectrum measured under the same conditions [12].

The HD target is also contaminated by H_2 and D_2 from the HD recombination process, $\text{HD} + \text{HD} \rightarrow \text{H}_2 + \text{D}_2$, which proceeds slowly in any HD rich container. One has to determine the H_2^+ and D_2^+ contamination levels in order to evaluate the branching ratios for the two possible ground state dissociation channels of HD^+ . The D_2^+ contamination level was directly measured to be $0.476\% \pm 0.003\%$ from the time-of-flight spectrum shown in Fig. 2. In contrast, it is not trivial to determine the H_2^+ contamination level because this molecular ion has the same flight time as the D^+ fragment. A method for evaluating the H_2^+ fraction from the time-of-flight data has been suggested [12] that is based on theoretical calculations of the ground state dissociation fraction of each of the hydrogen isotopes. As a result of this procedure, however, the two dissociation channels of HD^+ are not measured independently. In this Letter, we present a direct observation of symmetry breakdown in ground state dissociation by comparing the two final channels.

To determine the H_2^+ contamination level directly, the momentum vector of each recoil ion was evaluated from the measured position of impact on the detector and its time of arrival. The position information was decoded by using a resistive anode with a resolution of about 0.18 mm. To achieve the needed experimental resolution in momentum, the target had to be localized and cooled. The HD

target gas was introduced into the interaction region as an effusive jet perpendicular to the beam. Such a target was still too large, however, and would have caused significant broadening, especially along the beam direction. We therefore used a weakly focusing lens as part of our spectrometer to focus the whole target volume into a spot smaller than the detector resolution both in time and position, a technique used in some cold target recoil ion momentum spectroscopy experiments [13,14]. Cooling of the target gas is necessary so that thermal motion is small in comparison with the kinetic energy of the fragments. The target gas was cooled in a small cell attached to a cryogenic head which was held at about 20 K. Some additional transverse cooling was accomplished by the flow of the effusive jet. See Refs. [1,11,12] for further details about the apparatus and the experimental technique.

The distributions of the momentum perpendicular to the extraction field are shown in Fig. 3 for the HD^+ molecular

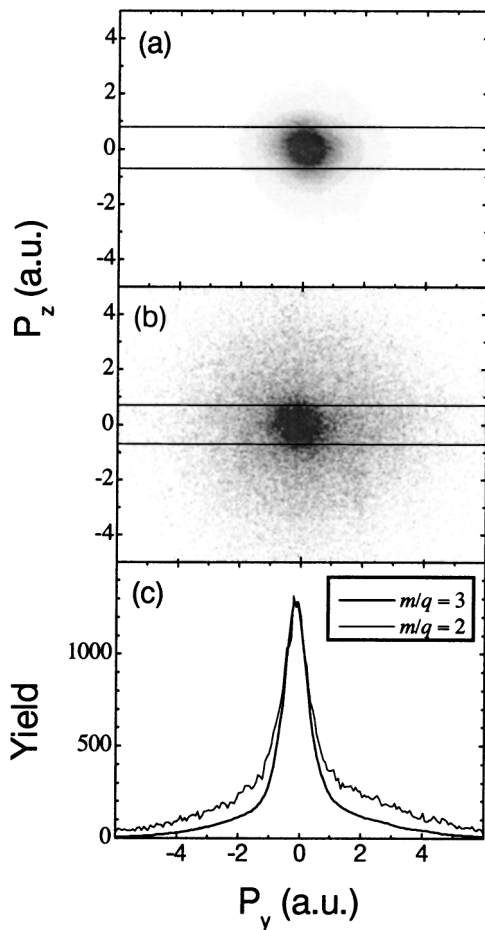


FIG. 3. The two-dimensional momentum distributions of (a) HD^+ and (b) D^+ and H_2^+ , i.e., $m/q = 2$ recoil ions measured with a 14 V/cm extraction field. The shades of gray represent the same percentage of the maximum in both distributions. (c) The one-dimensional momentum distribution along the direction perpendicular to the beam, produced by projecting the events within the marked slices of the 2D distributions onto the P_y axis.

ion and for the combined D^+ and H_2^+ peak (i.e., $m/q = 2$). The momentum distribution of the HD^+ peak is due to thermal motion for which a temperature of 22 ± 4 K was determined by fitting a Maxwell-Boltzmann distribution. The H_2^+ is expected to have a similar thermal distribution, resulting in a slightly narrower momentum distribution because of its lighter mass, $P_{\text{H}_2^+}/P_{\text{HD}^+} = \sqrt{m_{\text{H}_2^+}/m_{\text{HD}^+}}$. In contrast to the H_2^+ molecular ions, the D^+ fragments are expected to have a wider distribution due to the kinetic energy released upon dissociation and a minimum at $P_y = 0$ because of the threshold behavior. The expected sum of narrow and wide distributions can be easily seen in Fig. 3(b). To evaluate the H_2^+ fraction relative to the main HD^+ channel, we scaled the momentum of all HD^+ ions by the square root of the mass ratio, thus producing the distribution expected for H_2^+ shown in Fig. 3(a). Then, we projected the narrow slice marked on the figure of both 2D distributions onto the P_y axis, as shown in Fig. 3(c), and matched the center peaks of both as will be explained in detail in a forthcoming publication [11]. From this fit, the ratio of H_2^+ to HD^+ was determined to be $0.510\% \pm 0.015\%$. Using the procedure presented previously [12], we evaluated a similar ratio ($0.53\% \pm 0.02\%$). It is important to note, however, that this new method allows direct comparison between the two dissociation channels.

The narrow center parts of the $m/q = 1, 2$ peaks in the time-of-flight spectrum shown in Fig. 2 were used to determine the yield of the $\text{H}^+ + \text{D}(1s)$ and $\text{H}(1s) + \text{D}^+$ dissociation channels, respectively. Note that the remaining low energy fragments are solely associated with the dissociation of the electronic ground state of HD^+ . These areas are evaluated after subtracting a second order polynomial base line which fits the peak's shoulders [12]. These areas have the following contributions:

$$A(1) = [\text{HD}^+ \rightarrow \text{H}^+] + [\text{H}_2^+ \rightarrow \text{H}^+], \quad (1)$$

$$A(2) = [\text{HD}^+ \rightarrow \text{D}^+] + [\text{D}_2^+ \rightarrow \text{D}^+] + [\text{H}_2^+]. \quad (2)$$

The GSD fractions, D^+/D_2^+ and H^+/H_2^+ , were determined previously to be 0.5206% and 1.4762%, respectively [1,12]. Using the evaluated contamination levels of H_2^+ and D_2^+ relative to HD^+ yields $[\text{D}_2^+ \rightarrow \text{D}^+]/[\text{HD}^+] = 0.00248\% \pm 0.00001\%$ and $[\text{H}_2^+ \rightarrow \text{H}^+]/[\text{HD}^+] = 0.00753\% \pm 0.00022\%$, respectively. Note that the subtraction of these contributions does not affect the accuracy of the measurement of either channel significantly. In contrast, the subtraction of the H_2^+ contamination itself from the $\text{H}(1s) + \text{D}^+$ dissociation channel is the main source of uncertainty in this experiment.

The main results of our measurements—the relative yields of the two ground state dissociation channels—are presented in Table I, both given relative to the bound HD^+ yield. $\text{H}^+ + \text{D}(1s)$ is clearly the favored dissociation channel. The difference between the two, though small, is significant (2.1σ), thus indicating a measurable symmetry breakdown in ground state dissociation of

TABLE I. The relative yields of $H^+ + D(1s)$ and $H(1s) + D^+$.

	$\frac{H^+ + D(1s)}{HD^+}$	$\frac{H(1s) + D^+}{HD^+}$
Experiment	$0.526\% \pm 0.009\%$	$0.488\% \pm 0.016\%$
Theory	0.544%	0.460%

HD^+ . The isotopic effect leading to the breakdown of the Born-Oppenheimer approximation for HD^+ causes not only small changes of the potential energy curves and localization of the electron density on the deuteron for highly excited vibrational states [6], but also is responsible for the measurable preference of $D(1s)$ over $H(1s)$ upon dissociation of $HD^+(1s\sigma)$. In other words, the localization of the electron density on the deuteron occurs also in the vibrational continuum.

We have also treated this dissociating system theoretically by employing a coupled channels method [11]. The adiabatic potential energy curves and the coupling between the two lowest electronic states were evaluated using prolate spheroidal coordinates with the origin at the nuclear center of mass [3]. The vibrational continuum wave functions of the final state of HD^+ and their overlap with the initial vibrational wave function of the HD ground state were then computed as a function of the energy above the dissociation threshold of HD^+ . Finally, these transition probabilities were integrated to yield the probability for each final dissociation product. The calculated values for $J = 0$, effectively the only state populated at the temperature of the HD target, are in good agreement with the measured values as shown in Table I.

To summarize, we have shown that ground state dissociation of heteronuclear hydrogen molecules leads to a measurable symmetry breakdown. Specifically, for HD^+ , the dissociation into $H^+ + D(1s)$ is more likely than that into $H(1s) + D^+$ by 7.5%. The measured ratio is in good agreement with our calculations of the $1s\sigma$ to $2p\sigma$ transition probability using coupled channels calculations. Furthermore, theory obtains the energy dependence of the $1s\sigma$ to $2p\sigma$ transition probability for such “half” collisions in the energy range of a few meV, i.e., collision energies that are beyond the experimental technology of regular collision methods. If the energy of the fragment can be measured to a precision of the order of 1 meV, which is experimentally challenging but feasible, then one

can compare the measured and theoretical transition probabilities as a function of energy directly. Finally, theoretical modeling of the chemistry in interstellar clouds including this asymmetry is needed to determine if, and to what extent, the preference of $D(1s)$ over $H(1s)$ formation upon dissociation of $HD^+(1s\sigma)$ by any mechanism contributes as a deuterium fractionation mechanism.

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