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Surface induced dissociation of HD_2^+ – a non-statistical behavior in the H^+ and D^+ fragmentation channels

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Abstract

Surface induced dissociation (SID) of HD_2^+ upon impact on a Tore Supra tokamak graphite tile was studied in the collision energy range from 20 to 100 eV. SID of the projectile ion HD_2^+ on this graphite surface yields exclusively atomic fragment ions H^+ and D^+, whereas other possible fragment ions HD^+ and D_2^+ were completely absent. In contrast to the statistical ratio of 2:1 of D:H in the HD_2^+ ion, the relative abundances of the measured H^+ and D^+ fragment ions were about of equal magnitude over the whole collision energy range studied. This non-statistical decay can be accounted for by vibrational predissociation through a minimal centrifugal barrier at a total angular momentum of about $J \sim 27$–30.

1. Introduction

Collisions of slow ions with surfaces have been increasingly used to characterize both gaseous ions and the nature of surfaces [1–3]. Ion surface reactive collisions is a research area which has been rapidly growing the past 20 years in an effort to explore and develop new methods for characterizing the properties of gaseous ions, elucidating the nature of the surface under study and to investigate the basics of the ion/surface interaction. Besides physical and chemical sputtering, interest has been concentrated in particular on low energy (in the range of tens of eV) collisions involving reflection, surface-induced dissociation (SID), charge exchange reactions (CER) and surface-induced reactions (SIR). In addition, of being of fundamental importance, polyatomic ion–surface reactions are also relevant to a wide range of technological applications including such different fields as secondary mass spectrometry, surface modifications for the preparation of new materials (plasma processing) and quite importantly plasma–wall

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interactions in electrical discharges and fusion plasmas [4,5]. Much of the modeling and diagnostics of fusion plasmas relies on the understanding of the atomic and molecular processes which occur in the plasma and at the plasma wall. In particular the role of molecules and molecular ions is of utmost importance in the cold plasma edge and during plasma–wall interactions.

Energetic plasma particles strike solid surfaces such as tiles, limiters and divertors of a tokamak vessel, thereby eroding the surface material by sputtering processes. Sputtered particles are ionized in the plasma by electron impact and may hit the surface again. In fusion devices carbon is widely used as plasma facing material due to its high thermal resistivity and low Z value, although a disadvantage is the relatively large chemical sputtering yield by hydrogenic species. The use of low-Z materials such as carbon, boron and beryllium has been beneficial in present large tokamaks [6]. Whereas a large body of experimental data exists concerning physical sputtering, less is known about chemical sputtering and reactive collisions of ions at lower energies; the latter have so far been limited to laboratory studies mainly involving H^+ and O^+ projectiles and only recently extended to systems such as CH_3^+ and CH_4^+ but with conflicting results [7]. It is interesting to note in this context that in a recent workshop dedicated to the atomic and molecular data situation for tokamak fusion science [8] it transpired in a very clear fashion that many more data (i.e., more accurate and in a wider range than previously considered) are urgently needed in particular at the eve of starting the most challenging period in fusion research with the imminent construction of ITER [9].

Because of the urgent data need in fusion plasma technology (see also [10,11]) we started recently first systematic studies on surface-induced dissociation in the low collision energy range (<100 eV) of hydrocarbon and hydrogen molecular ions including in the later case H_2^+, H_3^+, D_2^+, D_3^+ and HD^+ projectile ions [12,13]. Whereas for most of these ions a number of gas phase studies has been carried and thus their properties are reasonably well understood (e.g., see the references given for the triatomic species in [14–18]), it appears that for HD_2^+ only a few studies are available in literature so far.

For instance, Alvarez et al. [19] measured total cross sections for the production of positive and negative ions by collision of HD_2^+ with a variety of target gases in the energy range from 40 to 600 keV. In addition, total cross sections for dissociative recombination of HD_2^+ were measured by Mitchell et al. [20] reporting that these cross sections were quite different from those for H_3^+ and D_3^+. Moreover, in a collision-induced dissociation study of HD_2^+ in the gas phase, Alvarez et al. [21,22] and Carrington et al. [23] observed the occurrence of all possible fragment ions, i.e., H^+, D^+, HD^+ and D_2^+. In contrast, in a photodissociation study of HD_2^+ also carried out by these authors [23,24], only two fragment ions, i.e., D^+ and H^+ were observed. They also noted that the intensity of the fragment ion D^+ was smaller (by a factor of 3) than that of H^+ and that the spectra leading to D^+ and H^+ fragments via the decay from long lived resonances were quite different. This immediately implies that a given resonance state populated in this photodissociation study will decay either into the D^+ or the H^+ channel.

Using a combination of an adiabatic (with respect to vibration) and sudden (with respect to the bending motion) transition state theory with semiclassical corrections Schlier and co-workers [25] were able to calculate corresponding branching ratios assuming that the trapping leading to long lived resonances is due to total angular momentum barriers. They showed that because of the narrow experimental window accessible in [23] low total angular momentum values ($J \leqslant 27$) will lead almost exclusively to formation of H^+ while high J values ($J \geqslant 30$) will lead almost exclusively to D^+ formation. The range of J values leading to both fragments is rather small and apparently not sampled in the photodissociation experiment of Carrington and Kennedy [23]. These conclusions, i.e., that vibrational predissociation of H_3^+ and its isotopomers occurs by tunneling through the lowest accessible centrifugal barrier at the available total angular momentum, have been confirmed by Chambers and Child [26] taking into account also parity considerations. They also showed that the observed strong preference of the $H^+ + D_2$ predissociation channel (over $D^+ + H_2$) in the experiment of [23,24] is consistent with an experimental preference for J values in the range $0 < J < 25$.

In this Letter we present the first results on surface-induced dissociations (SID) of HD_2^+ via impact on a graphite surface in the low collision energy range from 20 to 100 eV. The main result of this study is that surface-induced decomposition of the excited parent ion leads to practically the same amounts of H^+ and D^+ fragments over the whole collision energy range. This is in contrast to the statistical ratio expected of 1:2, as the parent molecular cation contains twice as much deuterium as hydrogen atoms. The present results are discussed in terms of the theoretical results obtained by Schlier and co-workers [25] and Chambers and Child [26]. Besides this non-statistical behavior in the formation of H^+ and D^+, another important finding is the complete absence of the diatomic HD^+ and D_2^+ fragment ions which were observed in experiments on collision induced dissociation (CID) of HD_2^+ in the gaseous phase [21–23].

2. Experimental

The present experiments were carried out with the tandem mass spectrometer apparatus BESTOF described in detail in our earlier papers [12,13,27]. It consists of a double focusing two-sector-field mass spectrometer (reversed BE geometry), a surface collision chamber connected to a linear time-of-flight mass spectrometer. Projectile ions were produced in a commercial Colutron dc plasma ion source. For the gas discharge we used a 3:7 mixture of H_2 and D_2 at a pressure of 0.2–0.5 Torr. The main process is evidently ionization of hydrogen and deuterium molecules and subsequent successive ion–molecule reactions leading to pure and mixed diatomic and triatomic molecular hydrogen isotopomer ions.

The produced ions were extracted by applying an electrical field between the anode and the first electrode of the focusing lens and accelerated to 3 keV for mass (and energy) analysis by the double-focusing two-sector-field mass spectrometer. After passing the mass spectrometer exit slit, the ions were refocused by an Einzel lens and decelerated to the required collision energy before interacting with the target surface. Shielding the target with conical shield plates minimized field penetration effects. The incident impact angle of the projectile ions was kept at 45° and the scattering angle (defined as a deflection from the incident beam direction) was fixed at 91°.

The collision energy of ions impacting on the surface is defined by the potential difference between the ion source and the surface and can be varied from about zero to about 2 keV with a typical projectile ion beam energy spread of about 1 eV in the case of the Colutron ion source [12,13]. A fraction of the product ions formed at the surface exited the shielded chamber through a 1 mm diameter orifice. The ions were then subjected to a pulsed extraction and acceleration field, which initiated the time-of-flight analysis of the ions. The second mass analyzer is a linear time-of-flight mass selector with a flight tube about 80 cm long. The mass selected ions were detected by a double-stage multi-channel plate connected to a multi-channel scaler (time resolution of 5 ns per channel) and a laboratory computer.

The surface used here was a graphite tile typically in use as a limiter surface in the fusion reactor Tore Supra in Cadarache/France. It was maintained under ultra high vacuum conditions (about 10^{-10} Torr) in the bakeable turbo-pump evacuated target collision chamber. However, even these conditions did not exclude deposition of multilayers of hydrocarbon contaminants on the surface, whenever the valve between the mass spectrometer and the target collision chamber was opened and the pressure in the target region increased to the 10^{-8} Torr range. The surface was thus a hydrocarbon-covered graphite surface as in our earlier studies [12,13], thereby mimicking a 'real' surface as occurring in many situations dealing with plasma–wall interactions.

3. Results and discussion

Fig. 1 shows secondary ion mass spectra after surface interaction of HD_2^+ primary ions at four

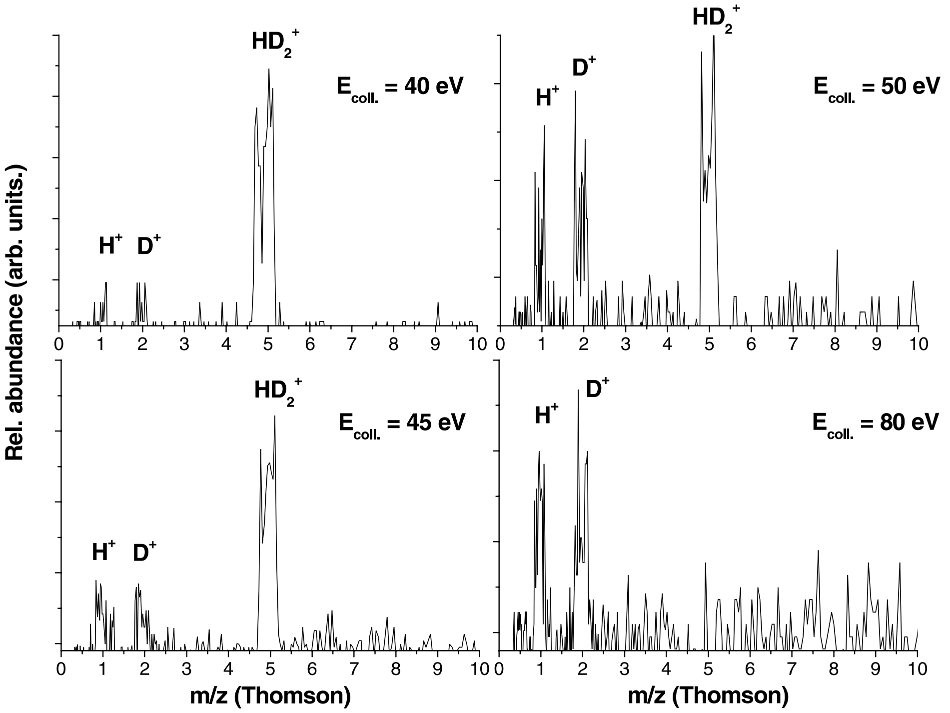

Fig. 1. Product ion mass spectra generated by the surface impact of the hydrogen molecular ion HD_2^+ at the collision energies of 40, 45, 50 and 80 eV interacting with graphite surface.

different collision energies. It can be clearly seen from these spectra, that HD_2^+ dissociates exclusively into H^+ and D^+, whereas HD^+ and D_2^+ are completely absent. This result is in contrast to gas phase studies of collision-induced dissociation of HD_2^+, where all possible fragment ions were detected [21–23]. Nevertheless, photodissociation studies on HD_2^+ resulted in similar break up channels as those reported here, with a complete absence of diatomic fragment ions [23]. It is interesting to note in this context that thermochemistry of the different reaction channels [28] (using for the enthalpy of formation of HD_2^+ the value of H_3^+) shows that the fragmentation channels leading to the diatomic product ions (reactions 1c,1d having an endothermicity of about 6.3 eV) require about 1.9 eV more energy than the channels leading to H^+ or D^+ formation (reactions (1a) and (1b) having an endothermicity of about 4.4 eV)

$$HD_2^+ \to H^+ + D_2 + 4.40\ \text{eV} \tag{1a}$$

$$HD_2^+ \to D^+ + HD + 4.45\ \text{eV} \tag{1b}$$

$$HD_2^+ \to HD^+ + D + 6.26\ \text{eV} \tag{1c}$$

$$HD_2^+ \to D_2^+ + H + 6.23\ \text{eV} \tag{1d}$$

It should be also mentioned in this context that upon dissociation of HD_2^+ into (i) HD^+ + D or (ii) H + D_2^+, the product ions HD^+ and D_2^+, while still in close contact with the surface, could capture an electron from the surface and thus get neutralized. Thereby ionization energy is released and the excited neutralized products dissociate further into (i) H + D or (ii) D + D, respectively. This process has already been observed in glancing incidence of H_2^+ on surfaces by Heiland and coworkers [29]. Since this electron capture is not likely to happen in CID experiments, the product ions HD^+ and D_2^+ produced would not be destroyed. Obviously, a similar neutralization reaction could also take place for atomic ions in the outgoing channel, but it is difficult to estimate whether in the atomic case neutralization is less likely than in the diatomic case.

The data from the secondary ion mass spectra as shown in Fig. 1 can be re-plotted into so called collision-energy-resolved-mass-spectra (CERMS). In a CERMS plot the relative abundances of the different ions (parent as well as product ions) are shown as a function of the collision energy (see Fig. 2 lower panel). Interestingly, the abundances of H^+ and D^+ are nearly the same over the whole collision energy range. This 1:1 ratio of the atomic hydrogen isotopes is in contrast to the expected statistical ratio of 1:2 and also different from the ratio 3:1 observed in the photodissociation experiment by Carrington and Kennedy [23]. It is interesting to note that due to results also shown in Fig. 2 (upper panel) for similar studies concerning the surface induced dissociation of HD^+ it can be excluded that this result (the 1:1 ratio for the abundances of H^+ and D^+ for decaying HD_2^+) is due to any discrimination occurring in the mass spectrometric detection system for ions with different kinetic energies. Because of momentum conservation the two dissociation products of decaying HD^+ should have quite different kinetic energies (coming from kinetic energy release in the decay reaction) and thus if discrimination plays a role the abundances of H^+ and D^+ for decaying HD^+ should be different. Moreover, it is also interesting to point out that the onset for SID occurs for HD^+ at a collision energy of about 30 eV, whereas the onset for SID for HD_2^+ sets in at about 40 eV. This difference can be attributed to the slightly higher dissociation energy for HD_2^+ (4.4 eV for reaction channel (1a) and (1b), see above) as compared to the dissociation energy for HD^+ with an energy of about 2.74 eV. Using the well established [30,31] average value of translational-to-internal energy transfer on hydrocarbon-covered metal or carbon surfaces of about 6–8% we find that the difference of about 10 eV in collision energy amounts to about 0.7 eV in internal energy, not enough to gap the difference in dissociation energies of about 1.7 eV. It is well conceivable that the missing 1 eV could already be present in the diatomic ion coming from the Colutron source as these ions are very likely produced via direct electron impact ionization reactions, whereas the triatomic ions are rather produced via ion molecule reactions and thus will be in a thermalized state (for more information on this question see a discussion of internal energies and their influence on surface induced dissociations in [7]).

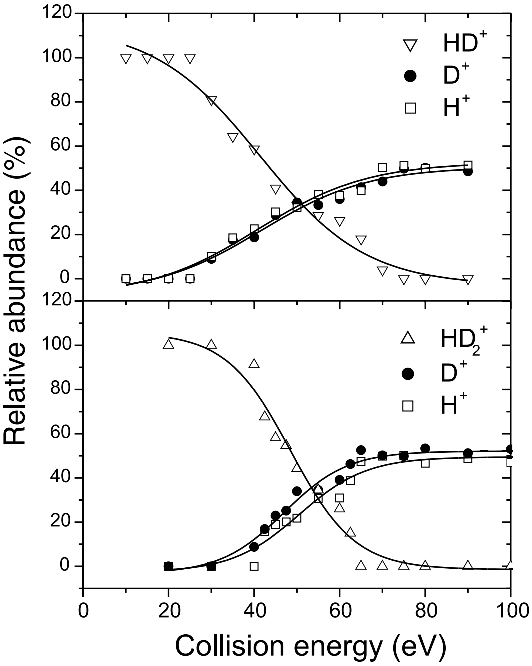

Fig. 2. Collision energy resolved mass spectrum (CERMS) for surface induced dissociation of HD^+ (upper panel) and HD_2^+ (lower panel) at a graphite surface in the collision energy range from 20 to 100 eV. Lines drawn through the data points are only given to guide the eye.

As mentioned in the introduction using a combination of an adiabatic (with respect to vibration) and sudden (with respect to the bending motion) transition state theory with semiclassical corrections Schlier and co-workers [25] were able to calculate corresponding branching ratios assuming that the trapping leading to long lived resonances is due to total angular momentum barriers. The unimolecular dissociation rate then depends on the structure of the total angular momentum barrier in each of these dissociation channels. Classically, for a given J the centrifugal term will be always lower for the D^+ channel than the H^+ channel (due to the larger reduced mass of the former channel) and this leads to a lower centrifugal barrier height in the D^+-forming channel. On the other hand, tunneling through the H^+ barrier is easier, but this is not enough to compensate for the lower barrier height in the D^+ case. Nevertheless, as argued by [25] and later by Chambers and Child [26] using also parity considerations it is also necessary to take into account the zero-point energy, because the zero-point energy of D_2 is by 341 cm^{-1} lower than that of HD. As a result of this only the H^+ channel will be open as long as the total energy is lower than the asymptotic HD zero-point energy. When the total angular moment barriers are plotted relative to the zero-point energy of D_2 (with the relevant zero-point energies added for each channel) one notes (see in Fig. 3 taken from [25]) that for low J the H^+ barrier is always lower than the D^+ barrier. With increasing J the H^+ barrier increases faster and compensates for the difference in the zero-point energies. This means that at lower J values HD_2^+ will dissociate into $H^+ + D_2$, while at higher J values the D^+ + HD channel opens up. In a more quantitative manner using sudden transition state theory with tunneling corrections [32] Schlier and co-workers showed that low total angular momentum values ($J \leqslant 27$) lead almost exclusively to formation of H^+ while high J values ($J \geqslant 30$) lead almost exclusively to D^+ formation. The range of J values leading to both fragments is rather small and apparently not sampled in the photodissociation experiment of Carrington and Kennedy [23]. Moreover, both models [25,26] predict kinetic energy release values consistent with the experimental findings [23].

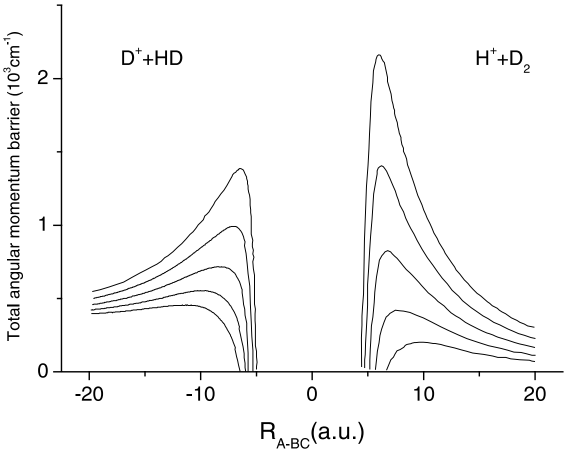

Fig. 3. Quantal total angular momentum barrier for the HD_2^+ system as given by Schlier and co-workers [25]. The energies are plotted relative to the D_2 zero-point energy and barriers are given for values of J = 20, 25, 30, 35 and 40.

Therefore, these models can account for the deviation of measured H^+/D^+ ratios in the previous photodissociation results and also in the present SID study as compared to the statistical prediction of a 1:2 ratio for the H^+/D^+ intensity. Nevertheless, the measured H^+/D^+ ratios are different in the two experiments. One reason might be a different internal energy population in the two experiments. Moreover, it is quite interesting to note that the H^+/D^+ ratio is constant over the whole collision energy range in the present surface-dissociation experiments. According to the earlier work of Kleyn et al. [33] about the rotational energy transfer in direct inelastic surface scattering of NO on Ag (111) in the energy range below 1.7 eV the rotational temperature scales with the normal component of the incident energy. Thus one might expect to see such a dependence also in the present surface collision experiment, i.e., at higher energies the D^+ channel should dominate according to the discussion given above. However, the constancy of the ratio D^+/H^+ in the present experiment suggests that the total J value does not change with increasing collision energy which is not too surprising taking into account the quite different experimental situations. The present conclusion about conservation of the J number during the surface collision is actually in line with a recent observation concerning hydrocarbon ion surface reactions [7]. In this recent study we could demonstrate that different internal energy in a hydrocarbon projectile ion is not equilibrated during the surface collision but leads to different unimolecular dissociation rates in surface induced collisions. In the present case this would suggest that ions coming from the Colutron ion source have a certain amount of total angular momentum (approximately $J \sim 27$–30 due to the fact that we observe about equal abundances for H^+ and D^+ product ions) which is not changed significantly by varying the collision energy, all what is changed is the overall efficiency (see the decrease of the parent ion matched by an increase of the product ions in Fig. 2) of the fragmentation due to the different vibrational excitation induced by the ion surface interaction at different collision energies. Comparing the present experiment with the earlier photo-ionization experiment one would have to conclude that the total J value is slightly higher in the present one.

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