Threshold Effects and Ion-Pair Production in the Dissociative Recombination of HD$^+$

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Sharp thresholds are observed in the dissociative recombination cross section of vibrationally cold HD$^+$ in the energy range where new channels H($1s$) + D(n) [or D($1s$) + H(n)] with $n > 2$ open. The occurrence of these thresholds, not predicted by current theoretical calculations, contradicts the current assumption that the size of the total cross section can be calculated without accounting for the detailed branching ratios. An indirect signature of ion pair production is also found in the data, suggesting a significant branching into that channel.

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The dissociative recombination (DR) of molecular ions is a process of high importance in many environments such as astrophysical and planetary plasmas. During the last five years, a large effort has been made both experimentally and theoretically to understand the DR process. The advent of heavy-ion storage rings [1] has made possible the study of DR for vibrationally cold molecular ions. Also, the combination of storage ring techniques with the molecular fragment imaging method [2–4] has allowed light to be shed on the "reaction path" of DR, i.e., the dissociation path taken from the initial vibrational quantum state of the molecular ion to the final quantum state(s) of the fragment atoms. Absolute DR cross sections for a variety of important molecular ions have been measured [1], leading to the discovery of new recombination mechanisms [5–8], and making possible direct comparison between experiment and theory. A recent review of the field can be found in Ref. [1].

Being the simplest infrared-active molecular ion, HD$^+$ has been the subject of many experimental as well as theoretical investigations. For low kinetic energy electrons, the DR of vibrationally cold HD$^+$($v = 0$) proceeds [9] through the doubly excited autoionizing state $(2p\sigma_u)^2$ $^1\Sigma_g^+$, crossing the HD$^+$ ground state (see Fig. 1), according to

$$\mathrm{HD}^+(v = 0) + e^- \rightarrow \mathrm{HD}(^1\Sigma_g^+) \rightarrow \mathrm{H}(n) + \mathrm{D}(n'), \tag{1}$$

where n and n' are the final principal quantum numbers of H and D, respectively, and v is the initial vibrational state of the ion. The total DR cross section for HD$^+$($v = 0$) has been measured at various storage rings [10–12], and the final states n and n' have been identified both for low and high electron energies [2,4]. Also, a vibrational-state selective measurement ($0 < v < 7$) of the cross section at both low and high kinetic energies has been performed [13].

Since the doubly excited $(2p\sigma_u)^2$ $^1\Sigma_g^+$ state is located above the ground state of HD$^+$ at short internuclear distance, it can also autoionize, leaving an HD$^+$ molecular ion, possibly in a vibrationally excited state. During the dissociation process, nonadiabatic transitions occur [14] at the avoided crossings between the $(2p\sigma_u)^2$ state and the $^1\Sigma_g^+$ Rydberg states, leading to the population of various final states [4] of the type H($1s$) + D(n') or D($1s$) + H(n) as far as they are energetically accessible. For electron energies $E < 1.15$ eV, only the channels with $n = 1$ and 2 (or $n' = 1$ and 2) are energetically open and, lacking any efficient dissociation path from HD($^1\Sigma_g^+$)

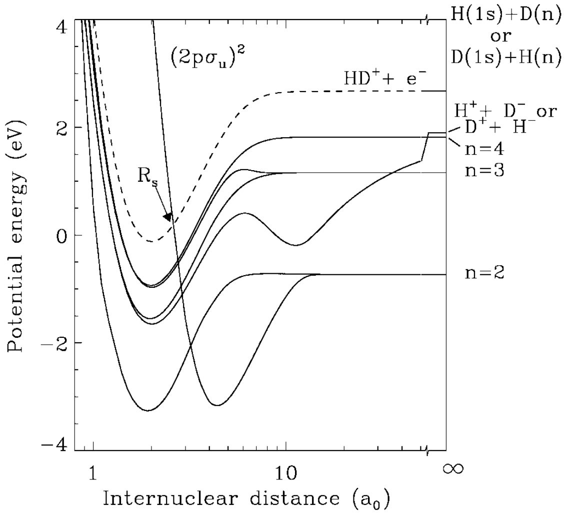

FIG. 1. Some of the relevant quasiadiabatic potential curves for HD and HD$^+$, showing the ground state of HD$^+$ (dashed line), Rydberg states of HD, and final asymptotic channels denoted by the principal quantum number n, including also the ionic channel. The autoionizing $(2p\sigma_u)^2$ state is also shown. The energy scale is relative to HD$^+$($v = 0$).

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to the $n = 1$ final state, only the $n = 2$ state is populated [4]. At 1.15 eV the $n = 3$ channel opens, followed by the $n = 4$ channel at $E = 1.82$ eV, and so forth, for higher n. For electron energies $E > 1.91$ eV, the system can also dissociate into an ion pair $H^+ + D^-$ (or $H^- + D^+$).

It is usually assumed [15,16] that the size of the *total* cross section can be predicted independent of the distribution of flux at the avoided crossings, the cross section being mainly determined by the overlap between the initial vibrational wave function and the vibrational continuum of the dissociative state, as well as by its autoionization probability. In particular, ${H_2}^+$ and HD^+ are textbook examples for DR since the reaction proceeds in the "crossing mode" [16] via only one doubly excited potential curve that connects to all final states accessible at moderate electron energies; thus a smooth variation of the DR cross section without any changes related to the opening of new dissociation channels is expected within this description. First experimental evidence is presented in this Letter that the opening of new channels does significantly influence the total recombination rate. Also, the onset of ion-pair production is shown to affect the total recombination cross section. This result was deduced from a dedicated high-statistics measurement of the DR cross section, aiming at the detection of small variations, in the energy range of the higher final-state thresholds. Although the branching ratios among the neutral final channels have been measured previously by Zajfman *et al.* [4], these measurements were insensitive to variations of the total cross section and represent only the relative amounts of flux ending at the various asymptotes.

The experiment was carried out at the Test Storage Ring (TSR) located at the Max-Planck-Institut für Kernphysik, Heidelberg. A 2.0-MeV HD^+ beam was produced by a Van de Graaff accelerator, injected into the TSR, and allowed to vibrationally relax before the cross section measurement. Typically 10^7 HD^+ ions circulated in the ring with a lifetime of ≈30 s. The circulating beam was merged with the quasimonochromatic electron beam of the electron cooler over a length of 1.5 m; details about the experimental setup can be found in previous publications [3]. The electron beam diameter was adjusted to 1.9 cm, a much smaller value than usual [3] yielding a relatively high electron density (typically 2×10^7 cm^{-3}) and lower background from recombination events taking place in the merging regions of the electron and the ion beam, as discussed below.

The neutral fragments resulting from the DR of HD^+ were measured using an energy sensitive surface-barrier detector located ~6 m downstream from the electron cooler, after the next bending magnet of the ring. The DR events, where both an H and a D fragment reached the detector simultaneously, were separated from background events due to collisions with residual gas in the ring (yielding $H^+ + D$ or $H + D^+$) using energy discrimination [10]. The magnetic field of the bending magnet located in front of the detector prevented any charged particle (positive or negative) from reaching the detector.

The DR measurements were carried out by recording the associated rate as a function of the laboratory electron energy E_e, while the molecular beam energy E_i remained constant. For each injection, the ions were first stored to ensure vibrational deexcitation (about 400 ms for HD^+ [13]) and phase-space cooling of the ion beam was accomplished within 5 s by interaction with the velocity-matched electrons (energy E_0). After this cooling phase, the electron acceleration voltage was stepped up to an adjustable value of E_e and switched back and forth at a rate of 13 Hz between E_e and E_0. The measured DR rate at E_0 was on-line normalized to the DR rate at E_0. The high-energy DR peaks of HD^+ at 9 and 16 eV [10] were measured during the same energy scans and an overall normalization factor was applied to the DR spectrum to match the rate coefficient at these peaks to absolute values measured previously at the TSR [17].

The observed energy dependence of the DR rate coefficient (essentially the DR cross section multiplied by the relative velocity) for vibrationally relaxed HD^+ ions is shown in Fig. 2; the absolute scale of the rate coefficient is estimated to be accurate within ±20%. The data contain a background due to DR events occurring in the regions where the electron and the ion beam are merged and demerged. The angular detuning between the electrons and the ions in the merging regions leads for these events to relative energies considerably higher than in the collinear overlap region; in particular, energies within the broad and strong neighboring 9-eV peak in the DR spectrum are reached, resulting in a relatively large contribution of this background when the nominal relative energy is set to 1–4 eV. The background can be determined [18] from the measured energy dependence of the DR rate coefficient and the known beam geometry; it is indicated in Fig. 2.

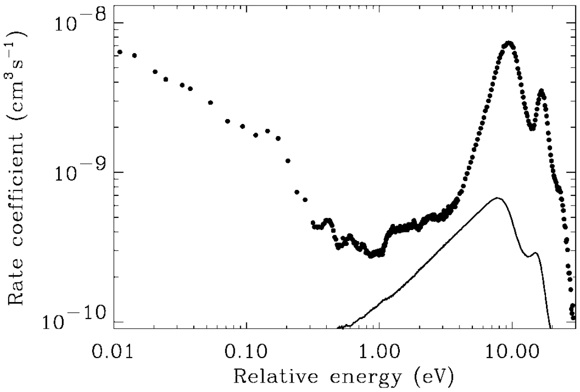

FIG. 2. Measured DR rate coefficient for HD^+ (dots), including the background from the merging regions as discussed in the text (full line). The systematic error on the absolute rate coefficient scale is ±20%.

The present high-statistics measurement reveals several features in the energy region of ≈0.7–2.5 eV, corresponding to the opening of the channels $H(1s) + D(n)$ [or $D(1s) + H(n)$] with $n \geq 3$, as shown in Fig. 3 after subtraction of the background. Although the DR cross section of HD^+ has been measured between 0 and 25 eV by several groups (see the review in Ref. [1]), the threshold energy region has never been carefully examined because of the small size of the rate coefficient in this region and the discussed background problems, characteristic of the merged beams geometry common to all storage ring experiments. For example, at TSR the background contribution with the usual electron beam diameter of 5.1 cm is found to be 70% of the measured rate in this energy range. Regarding the data shown in Fig. 3, the uncertainty introduced by the merging-region correction is estimated to be at most $\pm 0.5 \times 10^{-10}$ cm^3 s^{-1} at 1 eV and $\pm 1.0 \times 10^{-10}$ cm^3 s^{-1} at 2.5 eV. It is important to point out that the correction due to the merging regions is a smooth background which cannot introduce artificial steps in the data, and that the features of the cross section already occur in the uncorrected data (Fig. 2). The energy resolution is determined by the longitudinal electron velocity spread and amounts to ~50 meV (FWHM) at 1 eV and ~70 meV at 2.5 eV.

The rate coefficient shown in Fig. 3 exhibits a series of structures which through their energetic positions can be related to the opening of new channels for final states $n > 2$. The sharp threshold at ~1.15 eV coincides with the opening of the $n = 3$ channel and represents an increase of the DR rate coefficient by $(1.2 \pm 0.1) \times 10^{-10}$ cm^3 s^{-1}. The more complex structure seen between 1.7 and 2.0 eV can be understood as the effect of two competing, energetically very close thresholds. First, at 1.82 eV, the $n = 4$ channel becomes energetically accessible, yielding an increase in the rate coefficient (similar to $n = 3$ at 1.15 eV). However, at 1.91 eV the ion-pair channel ($H^+ + D^-$ or $H^- + D^+$) opens (see Fig. 1); part of the dissociating HD complexes then end up in this channel which, since the charged particles do not reach the detector, leads to a reduction of the measured rate coefficient. Additional smaller steps of the rate coefficient occur close to the next thresholds, 2.11 eV for $n = 5$ and ~2.3 eV for $n = 6$; no further steps are visible in our spectrum at the higher thresholds.

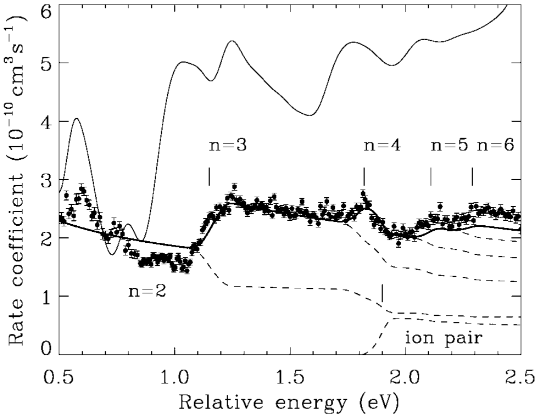

FIG. 3. DR rate coefficient for HD^+ in the region of the $n \geq 3$ dissociation thresholds after correction for the merging regions. The thin line shows the multichannel quantum defect theory (MQDT) calculation from Ref. [20] and the thick line shows the scaled result of a multistate curve-crossing (MSCC) model calculation, described in the text, together with the partial rate coefficients (dashed lines) for the different final channels. The calculated curves were convoluted with the present experimental energy spread.

It is interesting to compare the increase of the DR rate coefficient when surpassing the $n = 3$ threshold (i.e., between roughly 1.0 and 1.4 eV) to the branching ratio for the $n = 3$ state as measured by Zajfman *et al.* [4]. In the present case, the relative size of the step in the rate coefficient α (considering the uncertainty of the merging-region correction) amounts to $[\alpha(1.4\text{ eV}) - \alpha(1.0\text{ eV})]/\alpha(1.0\text{ eV}) = 0.7^{+0.4}_{-0.2}$, while the branching ratio from Ref. [4] above the $n = 3$ threshold yields $\alpha_3(1.4\text{ eV})/\alpha_2(1.4\text{ eV}) = 1.3 \pm 0.4$. This shows that a large part of the flux going into the $n = 3$ channel is an additional contribution to the total DR rate coefficient, but probably also some of this flux is taken from the $n = 2$ channel. Using the present data shown in Fig. 3 it is difficult to extend such a test to higher n states because of the presence of the ion-pair channel (as discussed above), the appearance of which almost coincides with the $n = 4$ onset. Direct observation of the ion-pair channel for vibrationally cold HD^+ has been reported, with a sharp onset of the associated partial cross section followed by a decrease with increasing electron energy [19]. The contribution of ion pair production to the total DR rate coefficient cannot be extracted directly from our data. However, the simple fact that this channel is seen as a dip in the measured rate coefficient indicates that the partial rate coefficient for ion-pair production is not completely balanced by an increase of the total recombination cross section at this channel threshold.

Theoretical calculations of the DR rate coefficient for HD^+, in particular, the recent one by Schneider *et al.* [20] using MQDT, have been found to be in reasonable agreement with the experimental results at low energy ($E < 0.3$ eV); they show, in particular, that the recombination rate is reduced with respect to the rate from direct DR by window resonances associated with vibrationally excited HD Rydberg states (indirect DR). At 1 eV the direct DR rate coefficient, which has a smooth energy dependence, is predicted [20] to be 1.1×10^{-9} cm^3 s^{-1}, but overlapping window resonances reduce the DR rate to much lower values (see Fig. 3) and cause the structure shown in the theoretical curve in Fig. 3 [20]. The variations seen in the theoretical model between 1.0 to 2.5 eV do not match the relatively simple structure present in the experimental data.

In order to obtain a better understanding of the mechanism that could cause the threshold behavior in the total recombination rate presented above, we have performed model calculations using a method similar to the MSCC of Cohen [21], where we treat all crossings of the dissociative state with the Rydberg series in a Landau-Zener approach. In the model a simple $1/E$ dependence for the electron capture cross section (consistent with the *direct* DR cross section given by Schneider *et al.* [20]) is assumed and the capture cross section is multiplied with the dissociation probability obtained by propagating flux coming from the capture region ($R < R_s$; see Fig. 1) outward along the avoided crossings with the Rydberg states and, from closed channels, back inward again, then repeating the propagation in an iterative process until all of the flux has either autoionized back or dissociated along the open channels at the given electron energy. For the closed channels, this can be regarded as a simplified time-dependent description of the autoionization caused by indirect DR, which does not account for its resonant or quantal character. The results, when normalized to the experimental data, turn out to reproduce well the observed spectral shape, including the relative sizes of the steps in the recombination rate coefficient. The total rate coefficient and the contributions of the different final states are shown in Fig. 3 after convolution with an energy distribution reflecting the approximate experimental energy spread (50 meV) and a rotational temperature of 500 K. Within the MSCC model, the increase of the total recombination rate when a final-channel threshold is surpassed can be understood as a reduction of the total autoionization rate following the initial capture by the amount that was due to the return flux from the closed channel below the dissociation threshold. The partial rate into previously open channels is reduced at the same time since some of the flux was also redirected to those channels below that threshold. The current calculation reproduces as well the branching ratios measured previously [4].

With respect to the indirect DR process, the steps in the total dissociative recombination rate correspond to the disappearance of resonances associated with bound vibrational states within the correlated molecular Rydberg states, and the appearance of the very same Rydberg states as new dissociative channels indirectly populated through the doubly excited state. The MQDT calculation shown in Fig. 3 includes the bound vibrational levels associated with the HD Rydberg states [20] but neglects the related dissociative continua. This deficiency may explain the large discrepancies between the MQDT result and the experiment in the energy range of 1.0–2.5 eV. To extend the MQDT picture, one would have to include a series of continuum states besides the vibrational states, which implies the treatment of two simultaneously open continua (ionization and dissociation). An approximate formula was proposed by Giusti in her original paper [22] on the MQDT treatment of DR, where dissociative channels are included in the global K matrix to first order of perturbation. A qualitative analysis of this formula shows an increased survival factor due to the inclusion of this secondary dissociation channel, hence an increased DR cross section.

Altogether, the experimental result found here and its interpretation in comparison with the simple MSCC model underline the influence of secondary dissociation channels on the magnitude of the cross section, as Rydberg states may hinder the dissociation below their dissociation limit, and contribute to the total DR rate above it. This observation calls for an improved, unified description of both the inner and the outer molecular region in the theory of DR, possibly using an extended MQDT calculation or a wave-packet treatment of the dissociation dynamics, which would incorporate the different time scales in a more natural way.

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[1] M. Larsson, Annu. Rev. Phys. Chem. **48**, 151 (1997), and references therein.
[2] D. Zajfman *et al.*, Phys. Rev. Lett. **75**, 814 (1995).
[3] Z. Amitay *et al.*, Phys. Rev. A **54**, 4032 (1996).
[4] D. Zajfman *et al.*, Phys. Rev. Lett. **79**, 1829 (1997).
[5] T. Tanabe *et al.*, Phys. Rev. Lett. **70**, 422 (1993).
[6] G. Sundström *et al.*, Phys. Rev. A **50**, R2806 (1994).
[7] S. L. Guberman, Phys. Rev. A **49**, R4277 (1994).
[8] J. Semaniak *et al.*, Phys. Rev. A **54**, R4617 (1996).
[9] C. Bottcher, J. Phys. B **9**, 2899 (1976).
[10] P. Forck *et al.*, Phys. Rev. Lett. **70**, 426 (1993).
[11] C. Strömholm *et al.*, Phys. Rev. A **52**, R4320 (1995).
[12] L. H. Andersen *et al.*, Phys. Rev. A **55**, 2799 (1997).
[13] Z. Amitay *et al.*, Science **281**, 75 (1998).
[14] T. F. O'Malley, Phys. Rev. **162**, 98 (1967).
[15] D. R. Bates, Phys. Rev. **78**, 492 (1950).
[16] M. R. Flannery, Adv. At. Mol. Phys. **32**, 117 (1994).
[17] M. Lange *et al.* (unpublished).
[18] A. Lampert *et al.*, Phys. Rev. A **53**, 1413 (1996).
[19] G. Dunn (private communication).
[20] I. F. Schneider *et al.*, J. Phys. B **30**, 2687 (1997).
[21] J. S. Cohen, Phys. Rev. A **13**, 99 (1976).
[22] A. Giusti, J. Phys. B **13**, 3867 (1980) [Eq. (26), p. 3879].