Dissociative Recombination of Cold HD$^+$ at the Test Storage Ring

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The dissociative recombination cross section between HD$^+$ molecules and electrons at energies between 0.3 and 40 eV has been measured for the first time in an ion storage ring. The ion beam, stored with a mean lifetime of ~5 s, was observed to be vibrationally cold. In the measured cross section, theoretically predicted high-energy resonances appeared, which can be attributed to recombination via doubly excited Rydberg states of HD.

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Dissociative recombination is an important collision process in plasmas and one of the key processes to produce neutral atoms in the upper atmosphere [1]. The $H_2{}^+$ ion (and its isotopes), being the simplest molecular system, provides a good choice for direct comparison between theory and experiment. For HD$^+$, the dissociative recombination process can be depicted as

$$HD^+ + e \rightarrow HD^{**} \rightarrow H + D\,,$$

where the recombination proceeds via a repulsive doubly excited state HD**; see Fig. 1.

The theoretical papers devoted to the description of dissociative recombination in collisions with $H_2{}^+$ have been mainly restricted to slow (up to 1 eV) electrons and to the case when the repulsion term of the dissociative state, the lowest doubly excited state $(2p\sigma_u)^2\,{}^1\Sigma_g^+$, crosses low vibrational states of the molecular ion; see, e.g., Ref. [2]. At higher energies, where recombination is possible via the $(2p\sigma_u)(nl)$ states, some theoretical calculations have been made [3,4]. In this process one electron is raised to the repulsive $(2p\sigma_u)$ state of the ion and the other electron is captured into a Rydberg state with quantum numbers n and l.

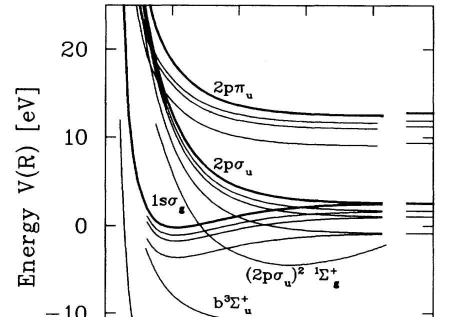

FIG. 1. Relevant potential energy curves for HD (thin lines) and HD$^+$ (thick lines). The Rydberg levels for HD were calculated for $N=2$, 3, and 4 by subtracting the hydrogen binding energy $E_n=\mathcal{R}/n^2$ from the ionic states. A more complete diagram is given in Ref. [5].

When $H_2{}^+$ or one of its isotopes is formed in an ion source by electron impact from the neutral species, most of the vibrational states v are populated, since the minima of the potential energy curves of the neutral and ionic molecule are displaced. The relative populations $P(v)$ given by the Franck-Condon principle are $P(0)=6\%$, $P(1)=13\%$, and $P(v\geq 2)=81\%$ [6]. Using such ion beams and an inclined—or merged—beam technique, measurements have been done for electron energies from 0.3 to 7.5 eV observing the total cross section [7] and the production of $D(n=2)$ and $D(n=4)$ [8]. For the energy range below 1.0 eV the cross section was measured precisely with ions in low vibrational states [9] and below 0.12 eV with ions in the vibrational ground state [10]. These single-pass experiments used cold ions produced by a reaction with He or Ne as buffer gas in an rf storage ion source. In this Letter we present a measurement of the dissociative recombination cross section for an intense beam of vibrationally cold, i.e., relaxed, HD$^+$ molecules with electrons up to an energy of 40 eV.

For molecular ions, storage rings provide an environment where a large number of cold ions (up to a few times 10^7 particles) can be maintained for a relatively long time (several seconds). For atomic ions, recombination measurements at variable electron energies were already demonstrated [11] using an electron cooler [12] as an electron target. In a similar fashion the dissociative recombination process and the related process of dissociative excitation can be studied by detecting the neutral fragments exiting the ring. Vibrational cooling of molecular ions with a static dipole moment is expected to occur within a time less than 1 s, because of spontaneous radiative transitions. For HD$^+$ the lifetimes $\tau_{\rm vib}(v')$ of the vibrational states are $\tau_{\rm vib}(1)=34$ ms, $\tau_{\rm vib}(2)=18$ ms, and $\tau_{\rm vib}(3\text{ to }5)\leq 10$ ms after averaging over rotational levels $N'\leq 4$ [13]. Thus, by storing a molecular ion beam for more than 1 s, an intense vibrationally cold beam can be produced. However, the molecules may still rotate as the decay time for a pure rotational transition of HD^+ is $\simeq 60$ s for the lowest rotational state and scales down approximately as $(N')^{-3}$. In contrast to cold ion sources this method to obtain vibrationally cold ions is independent of specific reactions and in principle is applicable to all infrared-active molecules.

In the present experiment a beam of 2.0-MeV HD^+ with impurities such as $H_3{}^+$ smaller than 1% was produced from a Van de Graaff accelerator using a standard Penning ion source and injected into the Test Storage Ring (TSR) [14] at the Max-Planck-Institut für Kernphysik, Heidelberg. After injection typically 10^7 particles circulated in the ring of 55.4-m circumference in an average vacuum of 7×10^{-11} mbar containing 90% of H_2. At each turn, the ion beam was merged with the electron beam of the electron cooler over a length of 1.5 m. The typical density of the electron beam was 5×10^6 cm^{-3}, and it was guided by a longitudinal magnetic field of 13 mT. A 50×50-mm Si surface barrier detector was mounted straight ahead of the cooler, at a distance of 6 m, to detect and energy analyze the neutral fragments produced in the interaction region. As the energy carried by the neutral products is different for the two types of dissociation processes, they can be discriminated: Events recorded with the full beam energy correspond to the simultaneous arrival of H and D and thus are due to the dissociative recombination process; the corresponding count rate is referred to as r_{HD}. Events recorded with $\frac{1}{3}$ or $\frac{2}{3}$ of the beam energy are due to the detection of H or D, respectively, and thus are associated with the dissociative excitation process; they are referred to as r_H and r_D. The detector is sensitive also to products from residual-gas reactions. In comparison to earlier merged-beam measurements of dissociative recombination [9,10], the higher beam velocity, the lower residual-gas pressure, and the higher electron current of this experiment yield a much better signal-to-noise ratio and thus a much shorter measuring time. The circulation of the molecules opens up the possibility of applying translational and internal cooling.

Figure 2 shows the count rate $r_H + r_D$ as a function of the time starting 20 ms after injection with the electron beam switched off. A rapid decay in the first 300 ms with a time constant of $\tau_{\rm short} \simeq 100$ ms is observed, followed by an exponential decay with a time constant of $\tau_{\rm long} \simeq 5$ s. We interpret this change in slope to be caused by a vibrational quenching of the molecular beam: When the beam is first injected in the ring, most of the vibrational states are populated. Since high vibrational states of HD^+ have a larger cross section for dissociation by residual-gas collisions due to their lower binding energy, the excited molecules dissociate faster than the cold ones. Thus we claim that, beside the radiative decay, vibrational quenching due to residual-gas collisions also contributes to the internal cooling of the stored ion beam. With a running electron cooler the structure of the rate curve was found to be unchanged for times shorter than 300 ms, but $\tau_{\rm long}$ was slightly reduced by 5% due to the additional recombination with electrons.

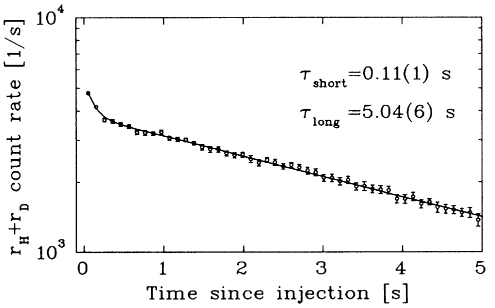

FIG. 2. Decay rate due to the dissociative excitation of HD^+ in residual-gas collisions as a function of time after injection. The time constants are from an exponential fit.

The dissociative recombination measurements were performed by recording the associated rate r_{HD} as a function of the laboratory electron energy E_e, while the molecular beam energy E_i remained constant. The energy E in the center-of-mass (c.m.) frame is therefore given by the relation

$$E = \{E_e^{1/2} - [(m_e/m_i)E_i]^{1/2}\}^2 ,$$

where m_e and m_i denote the electron and molecule mass, respectively. After each injection, the molecular ions were first stored for 4 s. During this time, they were electron cooled to ensure equal velocity of ions and electrons and to allow the deexcitation of the vibrational states. As a result of the relatively low electron density, transversal cooling of the stored beam is not expected to occur within 4 s. After the cooling phase the electron acceleration voltage was stepped up to an adjustable level E_e and switched back and forth between E_e and the cooling level (i.e., $E=0$) at a rate of 11 Hz to avoid shifts of the ion energy. Taking the difference between the count rates at these two levels allowed us to measure the reaction rate relative to that at $E=0$ and to eliminate the residual-gas-induced background. By varying the level E_e from one injection to the next, a scan over the c.m. energy range $E = 0.3$–40 eV has been performed.

The precise electron energy E_e was calculated from the acceleration voltage including the correction for the space charge potential, which can be derived from the measured current and the geometry of the electron beam. The energy resolution was limited to 5% at $E = 10$ eV and to 2.5% at $E = 40$ eV by three factors: the uncertainty of the applied voltages, the transverse energy spread of the electron beam ($k_B T_\perp \simeq 0.1$ eV), which is independent of the accelerator voltage, and the radial energy distribution of the 5.1-cm-diam electron beam due to the space charge potential together with the finite ion beam diameter of $\simeq 2.0$ cm.

The cross section for dissociative recombination was extracted by first taking the difference between the count rate $r_{\mathrm{HD}}(E)$ and the rate $r_{\mathrm{HD}}(0)$ observed at the cooling energy; with this subtraction the residual-gas contribution is eliminated, which amounts, e.g., to 40% of the total rate at 10 eV. The difference was then normalized to the count rate $r_{\mathrm{H}}(0)+r_{\mathrm{D}}(0)$ associated with dissociative excitation of the stored ions by residual-gas collisions. With the known electron density $n_e(E)$ the rate coefficient $\alpha(E)$ for the dissociative recombination of HD^+ can be determined from the relation

$$\alpha(E)=\frac{r_{\mathrm{HD}}(E)-r_{\mathrm{HD}}(0)}{A[r_{\mathrm{H}}(0)+r_{\mathrm{D}}(0)]}\frac{1}{n_e(E)}+\alpha(0)\frac{n_e(0)}{n_e(E)}\,.$$

The experimental cross section is given by

$$\sigma(E)=\frac{\alpha(E)}{(2E/m_e)^{1/2}}\,.$$

Using the characteristic electron energy distribution ($k_BT_\perp=0.1$ eV, $k_BT_\parallel=1$ meV) as observed in other experiments at the TSR [11], the rate coefficient $\alpha(0)$ at the relative energy $E=0$ and the normalization constant A were adjusted by comparing our result to the experimental cross section in the energy range $E\le 1$ eV obtained by Hus *et al.* [9], who measured the cross section for a $\mathrm{H}_2{}^+$ beam with comparable vibrational population. A factor of 0.7 from Ref. [2] was included to reflect the difference between $\mathrm{H}_2{}^+$ and HD^+. We estimated that this procedure leads to a systematic uncertainty in our absolute cross section of the order of 50%.

The resulting cross section $\sigma(E)$ for the dissociative recombination of HD^+ ions with electrons is shown in Fig. 3. The observed cross section first decreases approximately as E^{-1} with increasing energy ($E<1$ eV), but then levels off and displays a prominent peak at $E=8.6(4)$ eV as well as a weaker one at $E=15.8(4)$ eV. We have assigned these resonances to doubly excited HD^0 levels, namely, the $(2p\sigma_u)(nl)$ and $(2p\pi_u)(nl)$ states, respectively, with $n\ge 3$ (see Fig. 1). The first resonance had been predicted more than ten years ago by Zhdanov and Chibisov [3], who showed that only Rydberg states with $n\ge 3$ contribute, since for $n=2$ the autoionization probability is large. To our knowledge the second resonance has not yet been considered in the literature, but its energy agrees very well with that expected for dissociation via the $(2p\pi_u)(nl)$ states with $n\ge 3$.

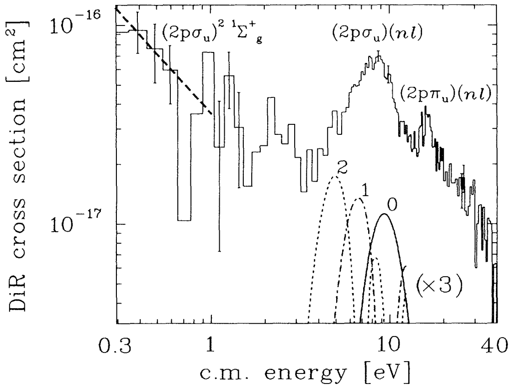

FIG. 3. Cross section for the dissociative recombination of HD^+ as a function of the center-of-mass energy for ions stored for times ≥ 4 s. Two resonances at 8.6 and 15.8 eV are visible; some characteristic error bars are drawn. For comparison, the theoretical cross sections up to 13.0 eV of Ref. [4] for the $(2p\sigma_u)(3s)\ {}^{1,3}\Sigma_u^+$ intermediate state and initial vibrational levels $v=0$ to 2 are shown (multiplied by 3). The dashed line for $E\le 1$ eV indicates the $1/E$ line through the data points of Hus *et al.* [9] scaled to HD^+ (see text).

It is obvious from Fig. 1 that these resonances can only lead to peaks in the dissociative recombination cross section if the variance of the internuclear distance of the HD^+ molecule is small; that is, if they are in low vibrational states. Based on theoretical calculations for different vibrational states, it should be possible to derive the vibrational distribution of the HD^+ beam from the measured spectrum. However, a theory accounting for autoionization was presented by Derkits, Bardsley, and Wadehra [4] only for the specific intermediate $(2p\sigma_u)\times(3s)\ {}^{1,3}\Sigma_u^+$ state with initial vibrational quantum numbers $v=0$ to 2. The calculation of Zhdanov and Chibisov [3] indicates that for higher angular momenta l and main quantum number $n=4$ the energy dependence and the relative amplitudes of the cross section for different v are similar to those for $n=3$ and $l=0$. Furthermore, only small shifts in energy occur for the different isotopic modifications and low vibrational levels. But, as Guberman [5] pointed out by *ab initio* calculation for some of the involved potential energy curves, shifts of the order of 0.5 eV may occur relative to the potential curves used for the theoretical cross section, where the hydrogen binding energy was subtracted from the ionic level. This leads to an additional uncertainty of the deduced vibrational population. Lacking better calculations we used the result of Ref. [4] (see Fig. 3) to estimate the vibrational population in the stored beam. These results are available only for energies below 13.0 eV; for $v=1$ (2) two (three) maxima of the cross section appear, corresponding to the maxima of the vibrational wave functions. The cross section for the individual vibrational states was multiplied by adjustable parameters representing the relative population of the vibrational states in the HD^+ beam. Together with an overall normalization factor they were then adjusted to the shape and height of the 8.6-eV peak. The result indicates that the dominant fraction of molecules ($\simeq 60\%$) is found to be in the lowest vibrational state, but higher states must also be populated with a certain fraction ($v=1$ with $\simeq 30\%$ and $v=2$ with $\simeq 10\%$) in order to explain the observed low-energy tail of the resonance (see Fig. 3). A normalization factor of $\simeq 25$ between the measured cross section and the specific $(2p\sigma_u)(3s)$ state was found by this procedure, indicating the importance of the higher Rydberg states nl. That the dominant fraction is in the $v=0$ state after a storage time of 4 s is also supported by the observed threshold behavior of the dissociative excitation as deduced from the $r_H(E)$ and $r_D(E)$ rates; but an analysis in terms of population parameters is not yet possible, as a theoretical treatment of this process has not been performed so far.

The observation that not all HD^+ molecules are in their vibrational ground state seems to be in contradiction with the expected fast decay of all excited vibrational states. However, the observed population of vibrational states may represent an equilibrium between vibrational excitation, caused by collisions of the stored molecules in the residual gas, and radiative relaxation. Moreover, we would like to point out that so far the theoretical calculations of the dissociative recombination cross section did not take into account the rotation of the molecule. For a comparison to single-pass experiments this may be tolerated, because one can assume that the rotational population of the ionic molecule is the same as for the neutral species [15], given by the temperature and some conditions of the ion source (maximum population at $N\simeq 3$). Because of the decay cascades and residual-gas collisions, we can expect to have enriched our beam with molecules in low vibrational but higher rotational states. An evaluation of the dissociative recombination cross section including rotation is felt to be necessary for a precise interpretation of our data.

To conclude, using stored molecular ions we have measured the dissociative recombination cross section of HD^+ with electrons between 0.3 and 40 eV and observed two resonances, which we attributed to electron capture into doubly excited states of the neutral molecule. For the first time, a detailed comparison of theoretical predictions for such processes with experimental data becomes possible. Moreover, this experiment clearly demonstrates that the storage ring technique enables the production of vibrationally cold molecular ion beams. Further experiments using this technique are presently planned to investigate the interaction of internally cold molecular ions with electrons and photons.

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