Isotope and Electric Field Effects in Dissociative Recombination of D_3^+

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The cross section for dissociative recombination of vibrationally cold D_3^+ has been measured at the ion storage ring CRYRING. The rate constant at 300 K, $\alpha = 2.7 \times 10^{-8}$ cm^3 s^{-1}, is a factor of 4.3 smaller than the corresponding value for H_3^+ measured earlier in CRYRING. An electric field of 30 V/cm was introduced in the electron-ion interaction region. This had no measurable effect on the dissociative recombination cross section. This suggests that the cross sections measured in storage rings for H_3^+ and its isotopic variants can be directly compared with theoretical results once such results become available. [S0031-9007(97)03562-X]

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The recent detection of H_3^+ in interstellar space [1] is a major discovery which supports the premise that H_3^+ plays the pivotal role in much of the chemistry in molecular clouds. Moreover, model calculations have shown that dark molecular clouds may have bistable solutions for which the chemical abundances differ by at least an order of magnitude [2–7]. The rate constant, α, for dissociative recombination (DR) of H_3^+ is of decisive importance in this scenario. If the 300 K rate constant is larger than 3×10^{-7} cm^3 s^{-1} or smaller than 7×10^{-8} cm^3 s^{-1}, only a single solution exists. The DR rate constant has for many years been a very controversial subject, as described in the review by Dalgarno [8], with experimental results ranging from a few times 10^{-7} cm^3 s^{-1} [9] to 10^{-11} cm^3 s^{-1} [10] published in the literature. Merged-beam experiments at the ion storage cooler ring CRYRING give an H_3^+ ($\nu = 0, 300$ K) rate constant of 1.15×10^{-7} cm^3 s^{-1} $\pm$ 15% [11,12], where ν is the vibrational quantum number, and the most recent flowing-afterglow Langmuir probe-mass spectrometer (FALP-MS) result [13] from Rowe's group essentially agrees with this result [the FALP-MS rate constant for H_3^+ ($\nu \leq 2, 300$ K) is 0.9×10^{-7} cm^3 s^{-1} $\pm$ 30% [13]].

The major problem in rationalizing a rate constant on the order of 10^{-7} cm^3 s^{-1} has been the lack of a favorable neutral-state curve crossing of H_3^+ ($\nu = 0$) [14] to drive dissociative recombination. This argument is now fading. HeH^+ shares with H_3^+ the lack of a curve crossing; nonetheless, storage ring experiments [15–20] have shown that its DR cross section is quite large. Theoretical calculations [21–23] corroborate this and suggest that DR of HeH^+ is driven by a new mechanism: nonadiabatic radial coupling between the electron-molecular ion system and noncrossing neutral Rydberg states that are close to the inner turning point of the zeroth vibrational level of the ion. It is plausible, but not proven, that DR of H_3^+ is driven by a similar, but more complex, mechanism [24,25]. The lack of an isotope effect implied by DR cross section data for H_3^+ [26] and D_3^+ [27] from single-pass merged-beam experiments has been used as an argument in favor of the so-called multistep mechanism [24] ("tunneling mode" recombination [25]). It has been argued [24] that the smaller reduced mass of H_3^+ and hence much higher tunneling probability, is completely compensated by the closer matching of energy levels in D_3^+, which enhances the multistep process.

Even if the CRYRING and FALP-MS results agree quite well, and a possible mechanism has been identified, the situation is more confusing than ever. There are three experimental observations that are difficult to reconcile with the CRYRING and FALP-MS results: (i) the new FALP experiment by Smith and Spanel [28] gives $\alpha(H_3^+, 300\ \text{K}) = (0.1\text{–}0.2) \times 10^{-7}$ cm^3 s^{-1}; (ii) the FALP experiment by Gougousi *et al.* [29] indicates that the deionization of the plasma does not occur by dissociative recombination, but rather by the formation of autoionizing H_3^{**} Rydberg states, which are stabilized by collisions or electric fields; and (iii) the single-pass merged-beam experiment by Mitchell's group [30,31], which indicates that long-lived H_3^{**} Rydberg states are formed in the electron-ion interaction region. If an electric field is applied in the postinteraction region, the Rydberg states are field ionized and a too small cross section is measured [30,31]. It has been speculated [29,30] that dissociative recombination of H_3^+ in the absence of collisions and electric fields (i.e., the conditions prevailing in the interstellar space) is very slow, something which would have far-reaching consequences for interstellar chemistry.

In this Letter we address two issues that are of importance for understanding dissociative recombination of H_3^+ and its isotopic variants. First, we have investigated the isotope effect by measuring the DR cross section for D_3^+ using CRYRING. Second, we have applied an electric field in the *electron-ion interaction region* in

CRYRING in order to test whether this influences the DR cross section. Whereas electric fields have been shown to enhance dielectronic recombination of atomic ions [32], the effect of electric fields in the interaction region on dissociative recombination is not known.

The experiment was carried out at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory at Stockholm University [33]. The D_3^+ ions were produced in a plasma discharge source containing D_2 gas. The ions were extracted at an energy of 40 keV, mass selected, and injected into CRYRING. Immediately after injection, the beam energy was increased from 40 keV to 2.75 MeV/amu by means of a radio frequency acceleration system. Phase-space cooling of the 2.75 MeV/amu D_3^+ was applied by repeated passage of the stored ion beam through a velocity-matched electron beam, 85 cm in length and 4 cm in diameter. When the injection-cooling phase was completed after 12 s, an ion beam with small divergence, narrow momentum spread, and small cross-sectional area circulated in the ring system. The vibrational relaxation of molecules in storage rings, and the absence of repopulation mechanisms, have been most clearly demonstrated by a photodissociation experiment of CH^+ [34] and by imaging experiments of HD^+ [35], HeH^+ and its isotopic variants [19,20], and CH^+ [36].

Electron-molecular ion collisions at well-defined energies were obtained by changing the electron energy in the laboratory frame of reference from $E_{\rm cool}$ to $E_{\rm meas}$. This leads to a difference between the average longitudinal velocities of the electron and ion beams, $\nu_{\rm d}$, and a detuning energy $E_{\rm d} = m_e \nu_{\rm d}^2/2$ which is related to the laboratory electron energies through $\sqrt{E_{\rm d}} = \sqrt{E_{\rm meas}} - \sqrt{E_{\rm cool}}$.

The friction force between the two beams leads to an acceleration of the ion beam when $E_{\rm meas} > E_{\rm cool}$. The remedy for this was to rapidly switch the electron cooler back and forth between $E_{\rm cool}$ and $E_{\rm meas}$ using a time structure of $\tau(E_{\rm meas}) = 100$ ms and $\tau(E_{\rm cool}) = 200$ ms. Neutral particles formed in the electron cooler section were separated from the ion beam by the first dipole magnet following the cooler section, and detected by an ion-implanted-silicon surface barrier detector. The stored ion beam had a $1/e$ lifetime of 10 s; during each injection cycle, the electron cooler was switched ten times to $E_{\rm meas}$. The rate of dissociative recombination of D_3^+ per stored ion and unit time can be expressed as

$$R = n_e \langle v_{\rm d} \sigma \rangle \, l/C \,, \qquad (1)$$

where n_e is the electron density, l is the interaction length (85 cm), and C the circumference of the storage ring (51.6 m). The quantity $\langle \nu_{\rm d} \sigma \rangle$ (in units of $\rm cm^3\,s^{-1}$) is the rate coefficient *in the electron cooler*. An effective cross section is obtained by dividing $\langle \nu_d \sigma \rangle$ by ν_d. In order to correlated R with the number of counts in the neutral-particle detector, the number of ions in the ring must be determined. This was done with a current transformer which measures the magnetic field induced by the stored ion beam. More details on the ion storage ring technique can be found in Refs. [36–38].

In Fig. 1 we compare the rate coefficient, $\langle \nu_d \sigma \rangle$, measured in this experiment with our corresponding results for H_3^+ [11,12] and H_2D^+ [39]. The differences between H_3^+ and D_3^+ are striking. The cross section can be divided in three regions: the low-energy region ($<$0.1 eV), the intermediate-energy region (0.1–3 eV), and the high-energy region ($>$3 eV). The two latter regions are discussed in a forthcoming publication [40].

The cross section in the low-energy region determines the thermal rate constant. This requires a deconvolution of σ from the measured $\langle \nu_d \sigma \rangle$, as described in [18]. The result for D_3^+, $\alpha(T = 300\ {\rm K}) = 2.7 \times 10^{-8}\ {\rm cm^3\,s^{-1}}$, is considerably smaller than the corresponding results for H_3^+ ($1.15 \times 10^{-7}\ {\rm cm^3\,s^{-1}}$ [12]) and H_2D^+ ($6 \times 10^{-8}\ {\rm cm^3\,s^{-1}}$ [41]). Mitchell *et al.* [42] initially found a sizeable isotope effect; in a later paper, however, the same group ascribed the isotope effect as due to different vibrational populations in the D_3^+ and H_3^+ beams [27]. The results claimed for vibrationally cold ions showed no isotope effect [26,27]. The present results in combination with the previous storage ring experiments on H_3^+ [11,12] and H_2D^+ [39,41] suggest that there is indeed a strong isotope effect which decreases the DR cross section as a function of increased deuterium content. The cross section for D_3^+ measured in this work is in very good agreement with the single-pass result of Mitchell and coworkers [27] for the energies where the experiments overlap ($<$1 eV).

In order to study field effects on dissociative recombination, a controlled electric field must be applied to the electron-ion interaction region. The electron beam is guided through the 85 cm interaction region by a magnetic field which is parallel to the beam and produced by the cooler solenoid. The stored and translationally cooled

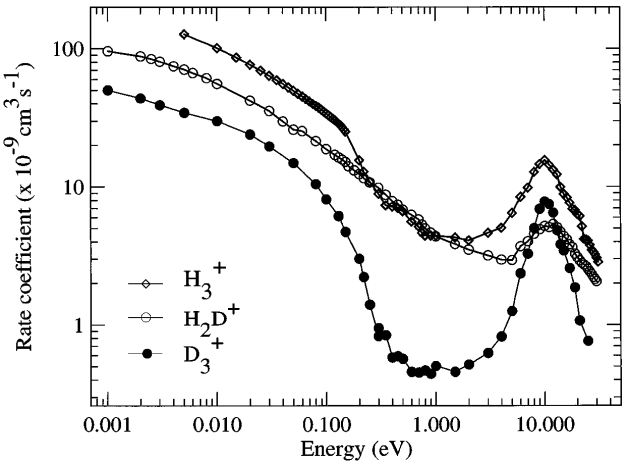

FIG. 1. The rate coefficient measured in the CRYRING electron cooler, $\langle \nu_d \sigma \rangle$, as a function of detuning energy. The data for D_3^+ are from the present work and the data for H_2D^+ are taken from Ref. [39]. The data below 0.2 eV for H_3^+ have been modified by folding the cross section from Ref. [12] with an electron-velocity distribution with $kT_\perp = 0.01$ eV.

ion beam has a small divergence, and it is merged with the electron beam at zero angle. This results in a very small $\vec{\nu} \times \vec{B}$ motional electric field. The space-charge potential of the electrons gives rise to an electric field across the ion beam. In the present experiment the ion beam was cooled, which lead to a small beam diameter, and the number of ions stored during the data taking phase was no more than 10^5. The electron current was 46 mA. The electron and ion beams were aligned such that the ion beam travelled in the minimum of the space charge potential; thus the electric field across the ion beam was very small.

A precisely known electric field in the interaction region can be introduced by letting the two beams interact at a finite angle θ. Since the solenoid magnetic field is parallel to the electron beam, the ion beam will cross the magnetic field at the angle θ. The magnetic field component perpendicular to the ion beam, $B_\perp$, gives rise to a motional electric field in the interaction region. The deliberate misalignment of the electron beam was achieved by means of two pairs of correction coils available in the CRYRING electron cooler. These coils are usually used for aligning the electron beam with respect to the ion beam. They are mounted symmetrically along the solenoid of the electron cooling region (i.e., the interaction region), providing a small, almost constant $B_\perp$ along the merging beams region. This technique of adding an electric field in the interaction region was introduced in an experiment at CRYRING concerning the influence of field effects in dielectronic recombination of Si^{11+} [43].

Figure 2 shows the electron cooler from above, a time-axis with its origin where the ions enter the merged-beams interaction region, and a diagram showing the electric fields experienced by the ions and neutral recombination products. The electron and ion beams were misaligned so that the electric $\nu B_\perp$ field was 30 V/cm. The misalignment was only effective during the 100 ms time slots, τ_{meas}, where data were taken.

The misalignment of the beams at a finite angle θ introduces a correction to Eq. (1). This correction has been taken into account in Fig. 3, which shows the result for an electric field of 30 V/cm in comparison with nominally 0 V/cm (it is difficult to estimate the field at $\theta = 0°$; reasonable numbers are probably a few V/cm). It would seem as if the electric field slightly decreases the rate coefficient; however, if the errors in the measured points are taken into account, we cannot claim a measurable effect. More importantly, the rate coefficient does *not* increase.

The absence of a measured electric field effect can be interpreted in three different ways. The most likely explanation is that 30 V/cm is too small a field to enhance the dissociative recombination process. This implies that no corrections for field effects are needed under normal experimental conditions in a storage ring. This conclusion has been reached for the atomic process dielectronic recombination [43].

A second explanation one can conceive of is that the field effects have saturated already at "0" V/cm ($\theta = 0°$) conditions. It is known from CRYRING branching ratio measurements of H_3^+ [44] and H_2D^+ [39] that *no* long-lived H_3^* (H_2D^*) Rydberg molecules arrive at the detector. Field-induced or not, the signal measured in the detector derives from dissociative recombination. Moreover, imaging data from the storage ring TARN II were best fitted assuming the D_3^+ recombination signal derived from D + D + D in their lowest state [45]. This is a radically different scenario from the one proposed by Gougousi *et al.* [27], who suggest that small electric fields stabilize the formation of long-lived H_3^* Rydberg

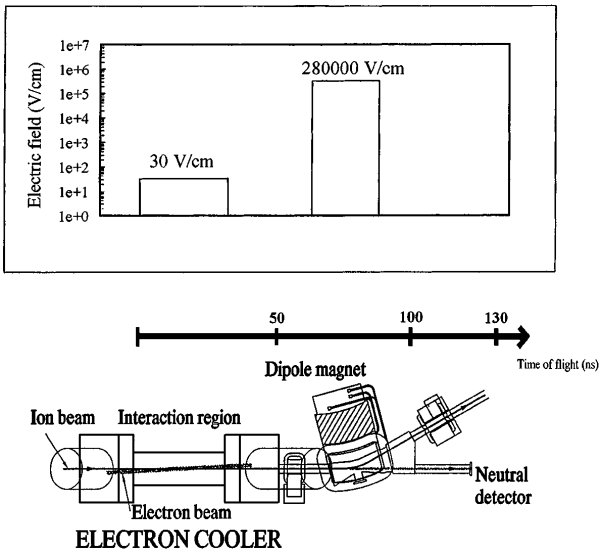

FIG. 2. The electron cooler schematically shown from above. The origin of the time scale is chosen where the ions enter the interaction region. The upper part of the figure shows the electric fields in the interaction region and the dipole magnet.

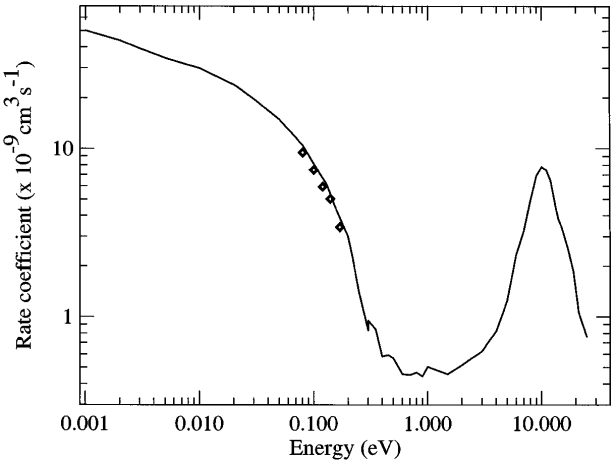

FIG. 3. The rate coefficient with (◇) and without (—) an electric field applied in the interaction region. A thin line has been chosen to represent the rate coefficient at zero electric field in order to make the slight difference visible. If the errors in the measured points are taken into account, the effect of a 30 V/cm electric field is negligible.

molecules. Whether these Rydberg molecules are formed in the CRYRING electron cooler and then subsequently field ionized by the strong motional electric field in the dipole magnet (see Fig. 2), or whether they are not formed at all, could be debated. The important point is that they do not contribute to the measured cross section since no neutral H_3 (H_2D) was detected [39,44]. Thus, the only reasonable conclusion following the saturation hypothesis is that the H_3^+ dissociative recombination process itself is extremely sensitive to electric fields. As long as there is no experimental evidence (storage ring, flowing afterglow, etc.) to support this sensitivity, it remains purely speculative.

A third possibility is that the 30 V/cm field increases the formation of D_3^* Rydberg molecules, which are then field ionized in the dipole magnet. This possibility is not contradicted by the experimental observations. On the other hand, it is of no concern for the interpretation of the "0" V/cm ($\theta = 0°$) experimental results.

In conclusion, we have measured a sizeable isotope effect on the cross section for dissociative recombination of D_3^+. The rate constant derived from the measured cross section, $\alpha(300\ \mathrm{K}) = 2.7 \times 10^{-8}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$, is a factor 4.3 smaller than the value for H_3^+ measured at CRYRING [12]. An electric field of 30 V/cm was added to the interaction region. This had not measurable effect on the cross section.

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