Direct High-Energy Neutral-Channel Dissociative Recombination of Cold H_3^+ in an Ion Storage Ring

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The cross section for neutral-channel dissociative recombination of vibrationally cooled H_3^+ at energies between 0.0025 and 30 eV has been measured by utilizing the electron cooler at the storage ring CRYRING. The molecular ions were stored at an energy of 32.6 MeV and phase-space cooled by the electron cooler for about 8 s prior to data taking. A peak in the cross section at 9.5 eV is interpreted as a direct adiabatic neutral-channel recombination through the $^2A_1$ resonant state. The cross section below 1 eV is in rather good agreement with single-pass data.

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Few cross sections in molecular physics have received such attention as that for the process of dissociative recombination (DR) of H_3^+ (cf. Ref. 1). The reason for this is twofold. First, H_3^+ is the most important molecular ion for the chemistry in interstellar clouds, where it is formed from reactions between neutral and ionized hydrogen and can readily protonize oxygen, carbon, and other heavy atoms. This is the beginning of the formation of nearly one hundred different molecules. The dominant loss process of H_3^+ in this environment is dissociative recombination with low-energy electrons. H_3^+ has also been observed in other astrophysical objects such as the Jovian atmosphere [2] and supernova 1987A [3]. The H_3^+ abundance in these sources depends critically on the DR cross section. Second, there is a 4 orders of magnitude spread between different laboratory measurements of the DR destruction rate [4–15]. Theoretical calculations favor a small recombination rate [16,17]. Figure 1 shows potential curves of H_3^+ and H_3 relevant for the process of dissociative recombination.

The merged-beam technique used by Mitchell and coworkers [1,6,7,12] offers the cleanest conditions so far for studying collisions between electrons and H_3^+ at well-defined, low center-of-mass energies (0.01–1.0 eV). There is clear experimental and theoretical evidence that the DR cross section of H_3^+ depends critically on the initial vibrational state distribution [1,12,17,18]. In the most recent merged-beam work the ions were therefore produced in an ion-trap source with a residence time of several milliseconds before extraction [12,18]. Calculations of Einstein A coefficients of low vibrational levels of H_3^+ show that lifetimes in the range 100–1000 ms are expected for some levels [19]. It would therefore seem that a confinement time of milliseconds [12] may be insufficient to guarantee a complete vibrational relaxation; however, provided that the source pressure is sufficient, collisional deexcitation is the dominant mechanism.

Heavy-ion storage rings have been used extensively during recent years for atomic physics experiments. The applicability of these facilities for studies of DR of molecular ions was recently pointed out [20] and investigated quantitatively in a case study [21]. It was shown that the main advantages with the storage ring technique for DR measurements are control over internal modes of excitation due to long storage times, and much higher luminosity compared to single-pass experiments [21]. The high luminosity allows studies over a wider range of collision energies than normally accessed in single-pass experiments (≤ 1 eV).

In this work we present measurements of the dissociative recombination cross section of vibrationally relaxed H_3^+ ($v=0$) for collision energies in the range 0.0025–30 eV. The experiment was conducted at CRYRING [22]

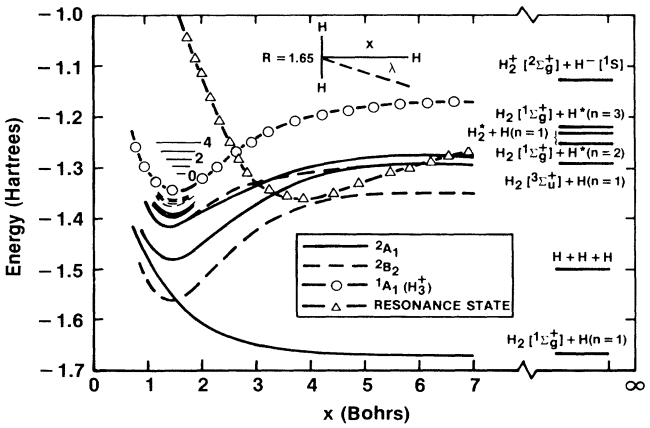

FIG. 1. Potential energy curves for H_3^+ and H_3 in C_{2v} symmetry (i.e., $\lambda=0°$). Coordinates are shown in the diagram at the top of the figure (reproduced with permission from Ref. [17]). The resonance state of neutral H_3 is denoted —Δ—Δ—.

(see Fig. 2), a 1.44-Tm heavy-ion synchrotron and storage ring located at the Manne Siegbahn Institute of Physics. H_3^+ ions are extracted at 30 keV from an electron-impact ion source (MINIS), accelerated to 900 keV in a four-rod radiofrequency quadrupole, injected into CRYRING, accelerated to 32.6 MeV, and stored and cooled. Storage mean life is limited by the as-yet unbaked vacuum ($p=50$ pTorr). A current transformer [23] measures the absolute circulating current. A typical value immediately after acceleration is 3 μA, which corresponds at this energy to 2×10^7 stored H_3^+ ions.

After reaching full energy the ions make successive passages through a collinear beam of velocity-matched electrons. Schottky noise spectra show that the relative velocity spread is reduced from 8×10^{-4} to 6×10^{-5}. This external cooling proceeds for 8 s, which is more than sufficient for the spontaneous decay of all excited vibrational levels by cascading through bending vibrations [19,24]. Recombination occurs at maximal rate during electron cooling, and all neutral recombination products exit through the first ring dipole following the electron cooler. These products impinge on a surface barrier detector which easily resolves three peaks associated with the arrival of one, two, or three hydrogen atoms, respectively. The one (1H) and two (2H) atom peaks (i.e., $\frac{1}{3}$ and $\frac{2}{3}$ full pulse height) arise from neutral fragments formed by collisions of H_3^+ with background gas (bg), i.e., $H_3^+ + bg \rightarrow H + H_2^+$ or $H^+ + H_2$. The peak at full pulse height (i.e., H_2+H or $H+H+H$) appears only when the merged electron beam is present.

Following this initial cooling period the electron beam energy is switched alternatively from the cooling energy E_{cool}, where $v_e = v_I$, to the measuring energy $E_{meas}^{1/2} \sim E_{cool}^{1/2} \pm E_{rel}^{1/2}$, corresponding to the value of the relative energy E_{rel} at which the cross section is to be determined. Fully relativistic kinematics [25] are used to obtain the interaction energy E_{rel} from the electron and ion laboratory energies E_e and E_I. Figure 3 is a plot showing the intensity of the 3H peak during 32 injection cycles with the sudden decrease in intensity when the cooler energy is switched. The measurement and cooling time intervals were chosen to be 0.5 and 1.0 s, respectively, after a careful measurement of the cooling and heating times and the electron drag force. The measurements were found to be insensitive to small variations in this timing scheme. The slope μ of this plot yields a storage lifetime $\tau = 1/\mu$ of 2.2 s, and an effective total beam destruction cross section $\mu kT/v_I p = 6.2\times10^{-17}$ cm^2 assuming an average ring vacuum of 50 pTorr. Lifetimes measured at various occasions during the data taking varied by no more than 4%.

The rate of the reaction $H_3^+ + e \rightarrow H+H+H$ or $\rightarrow H+H_2$ in the storage ring is given by $R = \rho_e v_{rel} \sigma_{DR} l / L$ ion^{-1}s^{-1}, where ρ_e is the electron density in the merged-beam region, v_{rel} is the relative collision velocity, σ_{DR} is the dissociative recombination cross section, l is the length of the interaction region, and L is the circumference of the ring. For CRYRING, $l=0.9$ m and $L=51.6$ m. The absolute cross section was determined for a few values of relative collision energies by combining the measured count rate in the 3H peak with the measured beam lifetime, filling factor, and electron and ion currents. At other relative energies the cross sections were extracted by normalizing to the H peak, which provides a direct measure of the circulating beam. The measured cross section as a function of E_{rel} is shown in Fig. 4 for the region 0.0025–30 eV.

The most conspicuous new feature in the cross section is the peak at 9.5 eV. It has not been observed previously and has not been predicted theoretically. There is, however, a prediction that the production of H^- in $H_3^+ + e$ collisions should peak at around 9 eV provided that only vibrationally relaxed H_3^+ participates in the collisions [16]. The production of H^- proceeds via electron cap-

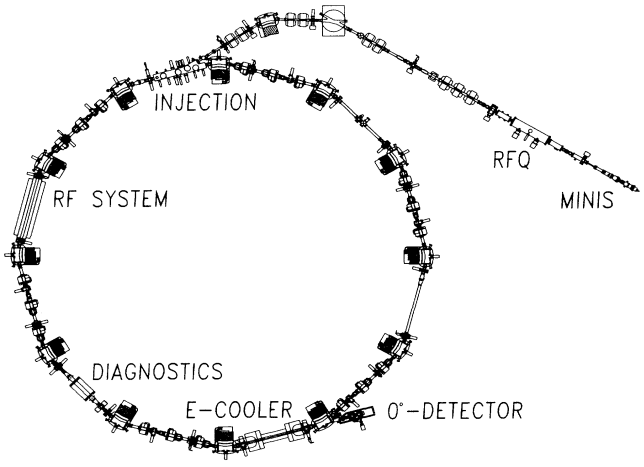

FIG. 2. Schematic diagram of CRYRING. Neutral particles produced in the electron cooler are detected by the 0° detector.

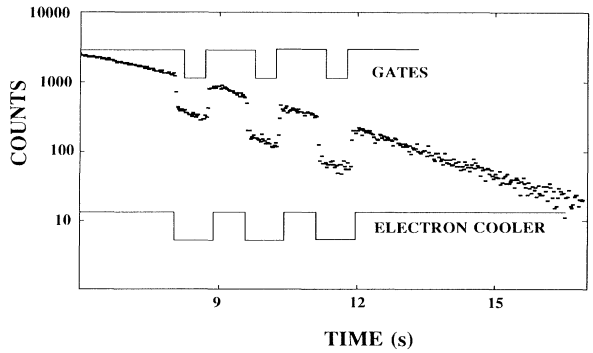

FIG. 3. Intensity of 3H peak vs time after injection for a particular negative value of v_{rel} ($=v_e - v_I$). Data gate openings are delayed to allow stabilization of electron energy. The slight nonlinearity in the beginning of the decay curve is due to pulse pileup.

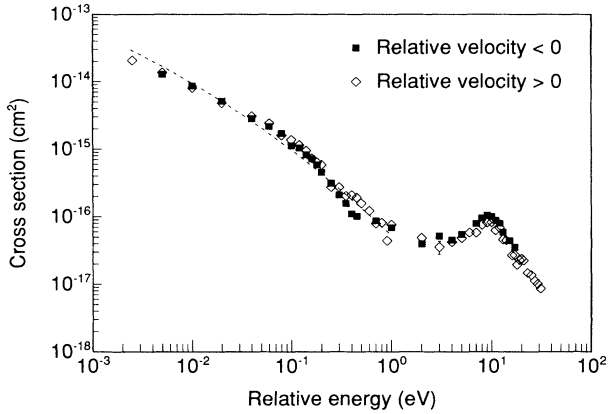

FIG. 4. Total cross section for forming H+H+H and H+H_2 vs interaction energy. Diamonds, $v_e > v_I$ ($v_{rel} = v_e - v_I > 0$); squares, $v_e < v_I$ ($v_{rel} < 0$). The dashed curve is a fit by an $E_{rel}^{-1.44}$-dependent cross section averaged over a flattened electron-velocity distribution.

ture to the resonant $^2A_1$ state (see Fig. 1), which dissociates diabatically to $H^- + H_2^+$. At 9 eV there is sufficient energy in the nuclear coordinate that one would expect the diabatic resonance state to be followed during the complete dissociation process [16]. This process has been experimentally confirmed and it has been shown that the cross section for production of H^- in $H_3^+ + e$ collisions peaks at 7.5 eV for vibrationally excited H_3^+ [26]. The appearance of a peak at 9.5 eV in the neutral channel provides information on three important points: (i) The shape of the peak allows an estimate of the internal state distribution of the H_3^+ ions, (ii) the measured neutral-channel cross section combined with the cross section for H^- [26] gives the branching ratio for the two decay channels, and (iii) it provides a means to determine the strength of the capture process. Each point is discussed further below.

The cross section for the direct DR process can be described as $\sigma = (\Gamma/E)(\mathrm{FC})(S)$ [1], where Γ is the strength of the capture process, E is the center-of-mass collision energy, FC is a Franck-Condon density describing the vibrational overlap between the initial ion state and the repulsive neutral state, and S is called the survival factor and describes the likelihood for dissociation instead of autoionization. A full calculation of the DR cross section curve for H_3^+ has never been carried out. It is instructive, though, to consider the cross sections calculated by Guberman [27] for a number of model potentials for diatomic molecules. The situation for H_3 and H_3^+ resembles the potential curve crossing case B of Guberman [27]. The cross section for this crossing case—a large internuclear distance (R) crossing above $v=0$—falls as $1/E$ for small collision energies, increases at higher energies, reaches a maximum and finally decreases. This peaking is a distinct signature of a large-R potential curve crossing. The shape of the peak depends sensitively on the initial state distribution. We have used the potential curves shown in Fig. 1 in a Franck-Condon analysis [28]. The Franck-Condon densities between the lowest bound vibrational levels of the ion and the continuum levels of the $^2A_1$ resonant state were calculated in a simplified diatomic model of H_3^+. This analysis shows that the best description of the 9.5-eV peak is obtained when only $v=0$ is included and hence only vibrational cool ions were present in our experiment.

The cross section falls off slower than would be expected on the high-energy side of the 9.5-eV peak. The reason for this is probably that other channels open up at about 15 eV. At this energy capture into a Rydberg orbital by promotion of a bonding electron to an antibonding orbital becomes energetically possible. This process has been observed more clearly in HD^+ [29].

Electron recombination branching ratios have only rarely been measured for H_3^+. Mitchell *et al.* [30] measured the three-body (H+H+H)/two-body(H_2+H) ratio for DR with vibrationally excited H_3^+ ions. More recently Peterson *et al.* [31] have measured the same ratio for near-resonant electron capture by 3-keV H_3^+ in Cs vapor. The three-body/two-body ratio increases with increasing internal ion energy [31]. DR branching-ratio experiments with relatively cool H_3^+ ($v=0,1$) indicate that the channel $H_3^+ + e \rightarrow H_3^*$ play an important role [32]. The high-energy neutral-channel cross section in combination with the data for H^- production [26] gives directly the neutral-channel/($H^- + H_2^+$) ratio. Despite the rather high energy which goes into the nuclear coordinate at 9.5 eV, less than 2% of the neutralized H_3 molecules dissociate diabatically along the $^2A_1$ resonant state potential curve all the way to $H^- + H_2^+$.

Theoretical calculations of molecular electronic capture widths (Γ) are rare [27]. The cross section at high energy should be useful for theorists since (a) it has been recorded for state-selected ions, and (b) only the direct process is operative and no interference from indirect capture via Rydberg states needs to be taken into account.

The cross section below 1 eV is the part of the curve which is most pertinent for astrophysical applications. It was analyzed by assuming the electron-velocity distribution $f(v)$ in the center-of-mass system to be a product of two Maxwell distributions (see Ref. [33]). The transverse electron temperature ($T_\perp$) has not been measured directly, but $kT_\perp = 0.1$ eV is a reasonable assumption (cf. [33]). The longitudinal electron temperature ($T_\parallel$) is much smaller ($kT_\parallel \leq 10^{-4}$ eV). The dashed line in Fig. 4 was obtained by integrating a model cross section $\sigma = 5.3 \times 10^{-17} E_{rel}^{-1.44}$ cm^2 over the flattened electron-velocity distribution. Uncertainties in the measured cross sections consist of statistical errors, indicated by error bars for the worst case in Fig. 4, and uncertainties in the interaction length and in the measurements of the circulating ion beam currents. We estimate the systematic errors to be 10%. The cross sections measured in the present work are approximately a factor of 2.7 larger

than those measured by Hus *et al.* [12] for $E_{rel} \leq 0.1$ eV. Considering the enormous spread among various laboratory measurements of H_3^+ DR rates, the agreement between the cross sections from this work and the earlier merged-beam experiment [12] must be characterized as satisfactory. The very low rates obtained with the flowing-afterglow–Langmuir-probe technique [11] can now be ruled out. The merged-beam results (this work and Ref. [12]) are between a factor of 3 and 10 lower than several other laboratory measurements including other flowing-afterglow measurements (see Ref. [15] for a compilation). It has been argued that if H_3^* is formed in long-lived high-n Rydberg states, they may be ionized in the electric field used to separate the ions from the neutrals in the merged-beam single-pass experiment [12,15], thus giving rise to a too low cross section. This argument is weakened by the present results. In the single-pass experiment Rydberg states above $n=18$ would be field ionized. In CRYRING, at 32.6 MeV, Rydberg states of $n=6$ or higher would be lost by field ionization on passing the first dipole after the electron cooler section. The fact that we measure higher cross sections than obtained in the single-pass experiment [12], where neutral losses due to field ionization should be less important, suggests that high-n states play a less significant role.

In conclusion, this work shows that ion storage ring technology, including electron cooling, is a very powerful tool for studies of dissociative recombination of molecular ions. Vibrationally fully relaxed ions are easily obtained by ion storage. The electron cooler increases the phase-space density of the molecular ion beam and also provides a target for high-luminosity DR measurements. Time requirements for data taking are down by a factor of 100 compared to single-pass experiments.

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