High-Resolution Dissociative Recombination of Cold H_3^+ and First Evidence for Nuclear Spin Effects

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The energy-resolved rate coefficient for the dissociative recombination (DR) of H_3^+ with slow electrons has been measured by the storage-ring method using an ion beam produced from a radio-frequency multipole ion trap, employing buffer-gas cooling at 13 K. The electron energy spread of the merged-beams measurement is reduced to 500 μeV by using a cryogenic GaAs photocathode. This and a previous cold-H_3^+ measurement jointly confirm the capability of ion storage rings, with suitable ion sources, to store and investigate H_3^+ in the two lowest, $(J, G) = (1, 1)$ and $(1, 0)$ rotational states prevailing also in cold interstellar matter. The use of para-H_2 in the ion source, expected to enhance para-H_3^+ in the stored ion beam, is found to increase the DR rate coefficient at meV electron energies.

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The triatomic hydrogen molecular ion H_3^+ is considered a key species for cold ion chemistry in different types of interstellar clouds [1]. Observations of H_3^+ in diffuse clouds with unexpectedly large absorption strength [2,3] have challenged gas phase astrochemistry models for these environments in which the H_3^+ abundance, among other parameters considered to be rather well constrained [4], depends on the dissociative recombination (DR) rate of H_3^+ with electrons at low (20–300 K) temperature. In this exothermic reaction [5,6] the incident electron is absorbed and neutral fragments (both atomic and molecular) are released, usually with substantial internal excitation and kinetic energy. The H_3^+ low-energy DR rate coefficient has been much debated over many years with laboratory results and theoretical predictions for the thermal rate coefficient considered uncertain over several orders of magnitude [7]. Owing to its high symmetry and simple structure as a polyatomic system amenable to a complete description of all electronic and nuclear degrees of freedom, H_3^+ also attracts great interest as a prototype system for fundamental molecular spectroscopy and dynamics [8,9].

Ion storage rings, offering high energy resolution using merged electron and molecular ion beams together with powerful tools for cooling and monitoring vibrational populations [10], have paved the way for reliable measurements of energy-resolved DR rate coefficients on a wide range of molecular ions. Results for H_3^+ from these instruments, first obtained [11] at the CRYRING facility, found a high DR rate coefficient (near 10^{-7} cm^3 s^{-1} for 300 K), which, however, is hard to reconcile [3] with the astrophysical H_3^+ observations. Moreover, results from the storage-ring facility TSR demonstrated that H_3^+ beams produced from standard ion sources remain rotationally excited over long storage times with temperatures of the order of 3000 K [12] (while being vibrationally cold [13]); for the more rapidly relaxing isotopomer D_2H^+, significant dependences of the DR rate coefficient on the rotational excitation were found [14].

Recently, substantial progress in this field was made on the experimental side by a first storage-ring DR cross section measurement [15,16] using an ion source capable of producing H_3^+ with rotational temperatures of 20–60 K, as well as on the theoretical side by calculations [9,17] accounting for the full dimensionality of the H_3^+ configuration space. The recent experiment at CRYRING used a supersonic expansion ion source characterized by infrared cavity ring-down spectroscopy of the H_3^+ ions in the high gas density region close to their creation zone [16]. A rotational temperature near 35 K is found in this region, from which the ions were extracted by a potential of ~800 V. The energy-resolved DR rate coefficient was obtained with a limiting electron energy spread of ~2 meV, using the CRYRING electron cooler. The good agreement between this experiment and the recent theory regarding the thermally averaged rate coefficient indicate a much improved understanding of the recombination mechanism while, interestingly, considerable discrepancies remain in the energy-resolved result, especially at 10–100 meV [17]. Thus, the theoretical energy dependence suggests better agreement for the $(J, G) = (2, 2)$ levels (Fig. 9 of Ref. [17]) that should not be populated at the estimated rotational temperature. This continues to nourish uncertainties [17] about the actual population dis-

tribution in the stored H_3^+ beam, which is not accessible to direct diagnostics. Several factors influencing the rotational population, whose perturbing effects cannot be ruled out in all cases, are thoroughly discussed in Ref. [16].

In order to clarify the situation we have performed DR cross section measurements on H_3^+ using an alternative approach for producing the rotationally cold ion beam. Unprecedented resolution is reached for the energetic dependence of the rate coefficient, and for the first time the effects of population changes among the two lowest rotational levels, as induced by modifying the abundance ratio of ortho and para nuclear-spin states in the stored ion beam, are verified. The experiment at the storage-ring facility TSR, Heidelberg, Germany, combines two instruments added recently in order to improve electron collision experiments with cold molecular ions: first, a cryogenic radiofrequency (rf) multipole ion trap, suitable for buffer-gas cooling of molecular ions, connected to the MeV accelerator feeding the storage-ring TSR; second, a cryogenic GaAs photocathode source yielding an electron beam with a limiting electron energy spread of only 500 μeV. The photocathode electron beam was overlapped with the circulating ion beam in a newly built, separate merged-beams electron target section, complementing the electron cooler whose function is now reduced to continuous phase-space cooling of the ion beam.

The cryogenic molecular ion injector at the TSR relies on collisional cooling of the rotational motion and additionally applies low-energy ion guiding and storage in order to minimize any accelerating fields in the high-pressure region needed for buffer-gas cooling. H_3^+ ions are produced in a rf storage ion source [18] operating at ~400–500 K, extracted by a potential of 10 V and then guided over 15 cm by an rf quadrupole to the 1 cm diam, 4 cm long rf multipole trap. This trap confines the H_3^+ ions within an essentially field-free region, achieved by the steep-wall effective potential of a cylindrical 22-pole rf ion cage [19] together with cylindrical dc end electrodes. The thick-walled ion trap block made of copper, serving also as the buffer-gas container, is cryogenically cooled to 13 ± 1 K. Helium buffer gas is continuously fed into the trap via precooled tubes at a typical number density of $(5–10) \times 10^{14}$ cm^{-3}. Assuming the Langevin rate coefficient of 1×10^{-9} cm^3 s^{-1} for He-H_3^+ collisions, the collision rate at this density is ~500/ms and the H_3^+ mean free path length of ~0.5 mm at 13 K is small versus the 10 mm trap diameter, so that the ions have several buffer-gas collisions between each radial reflection at the 22-pole rf cage. H_3^+ ions are pulsed into the trap, extracted by a -1 to 5 V pulse to the exit electrode after storage times of 1–100 ms synchronized with the accelerator and storage-ring timing cycle, and then transported over 18 cm at only 10–20 eV kinetic energy through a second rf quadrupole ion guide. At the exit of this quadrupole, where the residual gas pressure is $<10^{-5}$ mbar (density $<10^{11}$ cm^{-3}), the ion energy is increased to 12 keV for transporting them to the high-energy linear accelerator. Up to 2.5×10^6 H_3^+ ions per pulse were extracted from the trap and accelerated to $E_i = 5.25$ MeV for storage in the TSR with ion transmission factors of ~40%–50%. The buffer-gas interaction should ensure rotational cooling to <20 K temperatures [20], while vibrational relaxation is certainly achieved after >2 s storage in the ring [13].

For measuring the energy dependence of the DR rate coefficient, a magnetically guided electron beam is produced from a 3 mm diam GaAs photocathode in an arrangement similar to that used in electron cooling [21] devices. This photocathode electron source [22,23] is operated at a temperature of 100–120 K and yields a space-charge limited current of the order of 250 μA. The electron beam is magnetically expanded (magnetic field ratio 20–40) in order to further reduce the electron energy spread in the direction parallel to the magnetic guiding field, accelerated to ~1 keV, and collinearly overlapped with the circulating ion beam using the newly constructed electron target [24]. The transverse and the longitudinal electron temperatures in the comoving frame of the accelerated photocathode electron beam were determined from a measurement of resonant structures in the HD^+ DR rate coefficient [25], directly preceding this experiment and using the same instrumental parameters, to be $kT_\perp = 500$ μeV and $kT_\parallel = 25$ μeV, respectively, the errors being estimated to $\pm 30\%$. The electron density in the 1.5 m long interaction region was $n_e = 4 \times 10^5$ cm^{-3}. Fully neutral fragmentation events from electron collisions with H_3^+ ions were identified and counted [6] using a surface barrier detector located in the neutral beam line downstream of the electron target. Before and during the recombination measurement the circulating H_3^+ beam was continuously phase-space cooled by the fixed-energy collinear electron beam of the TSR electron cooler, operated in another straight section of the ring ($n_e = 1.6 \times 10^7$ cm^{-3}, $kT_\perp = 10.5$ meV). Its velocity was matched to that of the injected ions (laboratory electron energy near 960 eV) and, after a precooling period of 2 s following the injection, defined the exact velocity of the circulating 5.25 MeV H_3^+ beam.

The electron target beam energy was scanned to measure the energy dependent DR rate coefficient. The result for detuning energies in the ranges of $E_d = 0–0.4$ eV and 6–20 eV is presented in Fig. 1. Data with H_3^+ storage times in the rf ion trap of 10 and 100 ms yielded the same result within statistical errors and were averaged. A scan for 1 ms trap storage time with lower statistics (not included in Fig. 1) also yielded results compatible within the statistical errors. The measurement covered H_3^+ storage times in the TSR between 2 and 10 s and no significant time dependence of the rate coefficient was observed over this range. The data were normalized to the electron density and to the DR signal on the high-energy peak at $E_d = 10$ eV, for which the absolute rate coefficient was taken from the previous CRYRING data [16]. In earlier studies at the

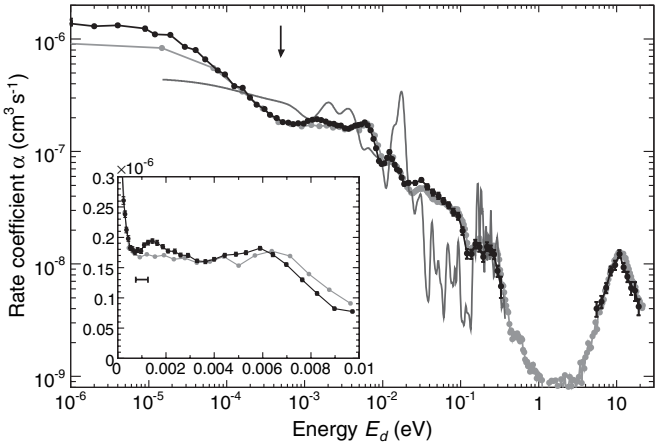

FIG. 1. Energy-resolved DR rate coefficient of H_3^+ measured with the injector ion trap at the TSR (interconnected black dots) and with the supersonic expansion source at CRYRING (interconnected gray dots). The TSR measurement is normalized to the CRYRING data near 10 eV. The arrow and the horizontal bar in the inset mark the limiting energy spread $kT_\perp$ at TSR. The continuous dark-gray line shows the theory of Kokoouline and Greene [17] including the toroidal averaging [27] for an ortho-para H_3^+ concentration ratio of 1:1 (see text), convoluted for $kT_\perp = 500$ μeV and $kT_\parallel = 25$ μeV.

TSR for D_2H^+ [14] the high-energy DR rate was indeed found to be insensitive to changes of the rotational excitation. Over the entire range of $E_d > 3$ meV, the energy dependence agrees within $<12\%$ with that seen by CRYRING with the supersonic expansion source. The thermal rate coefficient at 20 K obtained from the normalized TSR data agrees with the CRYRING result of 2.6×10^{-7} cm^3 s^{-1} [16] within the systematic error of $\pm 20\%$. Toroidal averaging effects (not corrected in the TSR data because of their small size of $<6 \times 10^{-10}$ cm^3 s^{-1} for the <9 mm radius electron beam) affect the low-energy comparison (<0.3 eV) by at most 10%. At lower energies (see inset of Fig. 1) the present data are more strongly modulated as expected from the lower limiting electron energy spread ($kT_\perp = 500$ μeV) at the TSR, and a new structure is observed at 1.4 meV. The rise near 500 μeV occurring in both data sets indicates a strong low-energy structure in the DR cross section at <100 μeV.

The agreement of the TSR and CRYRING data sets on the energy-resolved DR rate coefficient indicates that individual H_3^+ levels contribute to the total signal with very similar weights in both cases. This is supported by the recent theoretical results [17], which for several low-lying rotational levels of H_3^+, show similar overall sizes, but very clear differences in the energy dependence of the DR rate coefficient. Since both experiments start with cold (<60 K) ion sources, any excited state population (excitation energy >151 K) must be built up by the ion extraction, the beam acceleration, or in the storage ring, and thereby becomes sensitive to the individual experimental parameters. Since, in particular, the beam energies and the electron densities differ substantially ($E_i = 12.1$ MeV, $n_e = 6.3 \times 10^6$ cm^{-3} at CRYRING [16]), it is highly unlikely that excited state contributions occur with the same weight in both experiments. Hence, the observed consistency gives a very strong indication that the data of both measurements indeed represent the DR rate coefficient from H_3^+ ions in the two lowest, i.e., the (1, 1) and (1, 0) levels only.

Since significant contributions of excited rotational levels to the experimental DR rates can be ruled out with high certainty according to the present results, there is now strong evidence that theory significantly underestimates the DR cross section in the range of 30–200 meV; it also does not reproduce the strong low-energy structure found experimentally at ~ 100 μeV, lifting the rate coefficient at these energies up by a factor of 3 in comparision to theory.

An essential parameter for the DR rate coefficient of rotationally cold H_3^+ ions is the relative population of the two $J = 1$ levels, differing by the nuclear spin configuration of the three protons. The exchange symmetry of the molecular wave function implies that the lowest H_3^+ level (1, 1) has the para nuclear-spin symmetry (total nuclear spin $I = 1/2$), while the (1, 0) level, energetically higher by 32.8 K, has the ortho symmetry ($I = 3/2$). Selection rules for nuclear spin modifications in ion-neutral reactions involving H_3^+, H_2, and H_2^+ are discussed in the literature [26]. Both the CRYRING and the present cold-H_3^+ experiments have used normal H_2 to produce these ions. In the present work, the production in the rf storage ion source at >400 K should yield an ortho-para population ratio close to the "high temperature" [26] value of 1:1. On the other hand, for the colder formation temperatures at CRYRING the state populations were analyzed by laser spectroscopy (Fig. 2 of Ref. [16]) and also found to lie near 1:1. The good agreement between the two experiments can hence be rationalized on the basis that the respective ortho- and para-H_3^+ ratios were rather similar to each other, so that the ratio of 1:1 is chosen in the calculated curve of Fig. 1.

To probe the sensitivity of the DR rate coefficient on the ortho-para H_3^+ ratio, in particular at ~ 10 meV where significant differences of ~ 2 are predicted [17], we performed a second measurement supplying alternately normal H_2 and para-H_2 to the rf ion source. As we presently cannot measure [ortho-H_3^+]/[para-H_3^+] for our rf storage ion source, we assume that this ratio shows a reduction to $\lesssim 0.8$ when using para-H_2 instead of normal H_2, guided by previous results from self-sustained plasma discharges using pure para-H_2 [26]. Here the steady-state concentration ratios [ortho-H_3^+]/[para-H_3^+] ranged between 0.66 and 0.8 (down to 0.12 in pulsed discharges). The ortho-H_3^+ component arises in spite of the use of para-H_2 through the reaction of para-H_3^+ with para-H_2, that partly produces ortho-H_3^+ and leads to a nonzero [ortho-H_3^+]/[para-H_3^+] ratio depending on the experimental parameters [26]. Subsequent spin symmetry changes of H_3^+ in the cryogenic rf ion trap are expected to be negligible as He buffer gas is used for cooling.

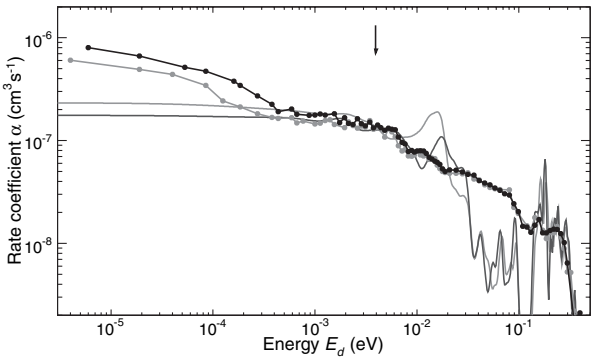

FIG. 2. Energy-resolved, high-energy normalized DR rate coefficient using normal H_2 (interconnected gray dots) and para-H_2 (interconnected black dots). The arrow indicates the limiting energy spread of $kT_\perp = 4$ meV. The theory [17,27] is shown for an ortho-para H_3^+ concentration ratio of 1:1 (continuous gray line) and for pure para-H_3^+ (continuous black line), convoluted for $kT_\perp = 4$ meV and $kT_\parallel = 30$ μeV.

The para-H_2 gas was produced separately using a paramagnetic catalyst at <23 K, filled into a teflon-coated container under ~ 1.8 bar at room temperature, and used within <30 h. It was fed into the ion source under the same conditions as normal H_2. To release any adsorbed H_2, all cryogenic surfaces of the ion trap setup were warmed up to >120 K and pumped before switching the source gas. The ortho-H_2 admixture in the supplied gas is estimated to be $<1\%$. The effect of traces of ortho-H_2 leaking into the ion trap was minimized by low ion source pressure, short storage (0.5 ms) and high He density (10^{15} cm^{-3}). Since the expected differences in the DR rate at ~ 10 meV should be visible even at a more limited energy resolution, we here used the electron target with a thermal cathode yielding increased $n_e \sim 1 \times 10^7$ cm^{-3} together with $kT_\perp \sim 4$ meV. Apart from changing the ion source gas, all running conditions were kept identical.

The results for normal H_2 and para-H_2, respectively, are shown in Fig. 2; they are independently normalized as in Fig. 1. For para-H_2 source gas, the DR rate coefficient is seen to increase by up to 25% at $E_d < 3$ meV as compared to normal H_2, while at higher energies the two measured curves coincide within $\sim 10\%$. This is in strong contrast to the theoretical expectation. In particular, theory mainly predicts a decrease of the data for para-H_2, just opposite to experiment; moreover, while the observed difference at the lowest energies is relatively large, the predicted stronger difference at 10–30 meV cannot be observed.

To summarize, detailed experimental results are provided for the energy dependence of the DR rate coefficient of cold H_3^+ clearly shown to be in the (1, 0) and (1, 1) states only. Significant low-energy resonances suitable as a reference for future theory are pointed out. Moreover, only moderate differences between the DR rates for the two remaining states, distinguished only by their nuclear spin symmetry, are found experimentally except at low energies, in contrast to the theoretical predictions; in fact, experiment finds the DR rate to increase for para-H_3^+ at low energies, opposite to the theoretically predicted trend. The experiment clearly demonstrates the need of further theoretical work to understand the DR process of this triatomic prototype system as well of the need of laser spectroscopic schemes for *in situ* monitoring of the rotational level populations in stored H_3^+ ion beams.

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