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DR rate coefficient measurements using stored beams of H_3^+ and its isotopomers

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Abstract. In studies of the rate coefficient of the dissociative recombination of H_3^+ and its isotopomers, the rovibrational excitation of the molecular ions was found to play an important role, in particular when employing the technique of heavy-ion storage rings. The dependence of the DR rate on rotational excitation was investigated in recent experiments at the Test Storage Ring TSR in Heidelberg through time-resolved measurements on D_2H^+ and H_3^+ over long storage times. For both molecules, an influence of rotational excitation on the DR rate was observed. The level of excitation in turn was found to be dominated by radiative coupling to the surrounding 300 K background for D_2H^+ . In the case of H_3^+ , a strong influence of electron collisions on the excitation level was found, whereas an additional influence of collisions with residual gas in the storage ring cannot be excluded.

1. Introduction

Because of its astrophysical importance and its benchmark character for quantum chemical calculations, the dissociative recombination (DR) of H_3^+ with cold electrons has found great interest in both experiment and theory. Despite long standing research, measurements of the rate coefficient α of this reaction using different experimental techniques still differ significantly: While a recent storage ring experiment at CRYRING yields $\alpha = 7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ for 300 K electron temperature [1], supported by results from other storage rings [2, 3], measurements using the stationary afterglow technique result in $\alpha < 3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ [4]. To reveal the reason for this discrepancy, current investigations now focus on the detailed experimental conditions present in these measurements.

Heavy-ion storage rings with merged electron beam devices offer a clean environment for studies of DR reactions with precise control of the relative energy of the reactants and efficient detection of reaction products on a single molecule basis. Regarding the preparation of the molecular ions, internal excitations have to be considered. In the case of H_3^+ , the vibrational excitation is known to relax during storage in the ring [5], while a rotational excitation still has to be expected and indeed was observed in recent experiments [6, 7]. This situation has led to the development of ion sources for rotationally cold H_3^+ [8, 9]. However, also changes of the rotational state population during the storage of the ions may occur. Such changes, together with their effect on α , were observed in recent storage ring experiments at the TSR in Heidelberg for H_3^+ and its isotopomer D_2H^+ .

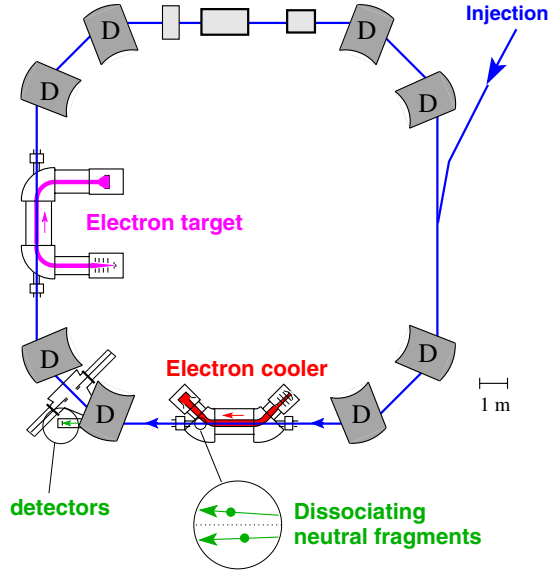


Figure 1. Overview of the TSR storage ring. Two electron beams can be overlapped with the ion beam using the *Electron Cooler* and *Electron Target* devices. The DR reactions described here were observed using the Electron Cooler and associated neutral fragment detectors. The new Electron Target was used only for excitation of H_3^+ (see section 3.2).

2. Experimental Setup

Figure 1 sketches the TSR storage ring with its electron cooler, neutral fragment detectors and the recently installed electron target. The molecular ions were accelerated to a total energy of 5.3 MeV, injected into the TSR and kept circulating there for up to 80 s. In the electron cooler, the ion beam was merged over a distance of 1.5 m with a beam of cold electrons. At matched velocities of the two beams, the electron beam had a density of $n_e = 1.1 \times 10^7 \text{ cm}^{-3}$ as well as temperatures of $kT_{\parallel} = 0.07 \text{ meV}$ in the longitudinal and $kT_{\perp} = 12 \text{ meV}$ in the transversal degree of freedom with respect to the beam direction.

Velocity matching is used for phase-space cooling of the ion beam, resulting in a narrow distribution of ion velocities and orbits in the storage ring. In addition the recombination at small collision energies, determined by the electron temperature, can be observed at this setting. For measuring the recombination rate at higher relative energies, the electron beam was set to a velocity different from the ion velocity, corresponding to a detuning energy E_d in the co-moving frame of reference. The neutral fragments emerging from DR reactions leave the storage ring at the next dipole magnet and are recorded by a solid state detector mounted straight ahead of the electron cooler section (see figure 1).

At the very low ion beam currents used in order to avoid damage to the neutral fragment detector, the total current of the ion beam cannot be measured simultaneously. Therefore the recombination rate at a fixed relative energy of 10 eV was used for normalization to the ion beam current. An absolute scale can then be obtained by additional measurements comparing this DR rate subsequently to the rate of residual gas induced dissociative excitation events and to the standard diagnostic devices of the storage ring. To record the DR rate coefficient α as a function of the electron detuning energy E_d , the following timing scheme was applied: In the first seconds after injection of the ions into the ring the electron cooler was kept constantly at cooling energy ($E_d = 0$) to achieve phase-space cooling. After this, the detuning energy was switched in a fast, repeating cycle between three values. In a *measurement* step, the rate at the desired energy was recorded. Second, a *reference* step at $E_d = 10 \text{ eV}$ was applied for normalization to the ion current, followed by a *cooling* step to maintain phase-space cooling. The duration of one full cycle was about 300 ms. To obtain the full spectrum $\alpha(E_d)$, the energy of the measurement step was changed for each new injection.

To study changes in the internal excitation of the molecular ions, the measured DR rate coefficient can be analyzed as a function of the storage time t_{store} . Additionally, an influence of the electron beam on this excitation can be investigated by appropriate changes in the timing scheme applied to the electron energies.

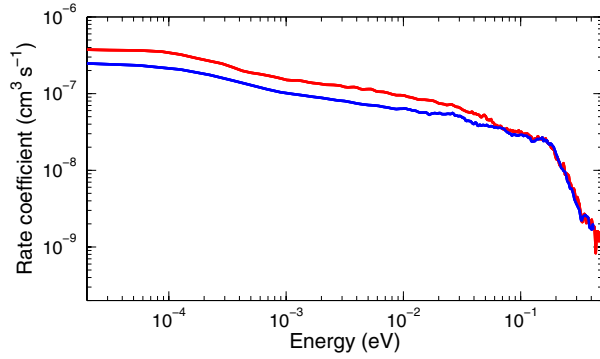


Figure 2. DR rate coefficient α of D_2H^+ as a function of the electron energy E_d . Upper curve: For storage times $5 < t_{\text{store}} < 16$ s, lower curve: For $30 < t_{\text{store}} < 61$ s.

3. Results

3.1. Observations for D_2H^+

The DR rate coefficient measured for D_2H^+ (figure 2) shows a considerable change at energies below ~ 0.1 eV when comparing two different storage time intervals. Since vibrational cooling was completed in both intervals and all external settings were kept constant, this can only be explained by a change in the rotational state distribution of the ions together with a significant dependence of the rate coefficient on this distribution.

This change in the DR rate can now be followed in more detail as a function of storage time, as shown in figure 3. In these measurements, the electron energy was switched between two values only (*cooling*, $E_d = 0$ and *reference*, $E_d = 10$ eV). Depending on the fraction of time spent at cooling or reference energy, the DR rate coefficient α shows different behavior: With a strong cooling cycle (that is, the electron beam set to $E_d = 0$ most of the time, filled circles in figure 3) α is strongly reduced on a timescale of several tens of seconds, as observed already in figure 2. Using a weak cooling cycle (triangles in figure 3) the reduction of α is much weaker, and the same result is obtained for even weaker cooling cycles (not shown). This suggests that the development of the rotational state distribution is already dominated by radiative coupling to the 300 K background for these weak cooling cycles and electron interactions have no significant influence on α . This result is in agreement with the theoretical expectation of a thermalization to the environment within some tens of seconds [10].

The results for the strong cooling cycle on the other hand show that interactions with the cold electron beam can be used to further reduce α , suggesting that a non-thermal population of rotational states was prepared here. The data represented by diamonds in figure 3 demonstrate that the same blackbody-dominated level of α is reached by switching to the weak cooling cycle after 30 s of constant cooling.

The comparison of two sets of data with intermediate cooling shows that the electrons with $E_d = 10$ eV

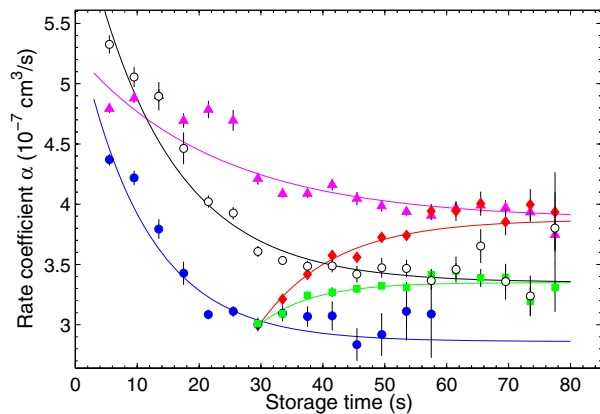


Figure 3. DR rate coefficient $\alpha(E_d = 0 \text{ eV})$ of D_2H^+ as a function of storage time. Triangles: Weak cooling cycle ($\leq 17\%$ cooling time), filled circles: Strong cooling cycle (92% cooling time). Diamonds: Switching from constant cooling to weak cooling cycle after 30 s of storage, squares: Switching to intermediate cooling cycle (50% cooling time) after 30 s, open circles: Strong cooling cycle but electron density reduced to 50%.

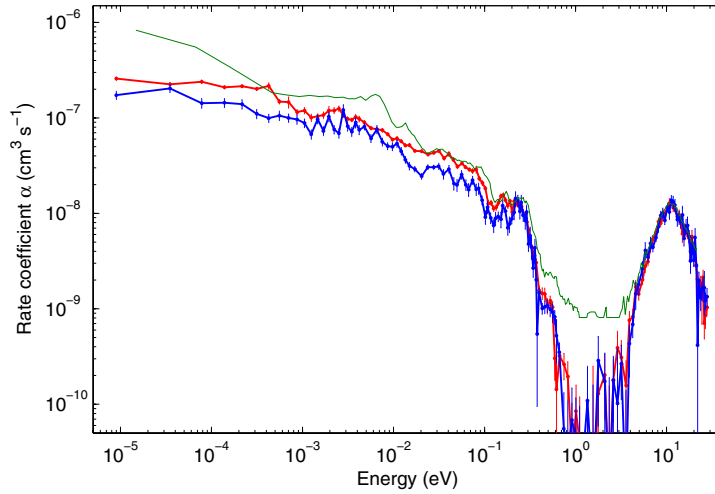


Figure 4. DR rate coefficient α of H_3^+ as a function of the electron energy E_d . Upper thick curve: For storage times $5 < t_{\text{store}} < 20$ s, lower thick curve: For $30 < t_{\text{store}} < 50$ s, thin curve: The spectrum obtained at CRYRING [1].

present during the reference step of the cooling cycle do not influence the measurement: The same intermediate level of α is reached by applying an intermediate cooling cycle (squares) and by using the strong cooling cycle with the electron density reduced by a factor of 2 (open circles). In these two cases, the number of electrons with $E_d = 10$ eV differs by an order of magnitude, but no difference in the final DR rate coefficient is observed.

The observed cooling of the rotational excitation by low-energy electrons can be explained by selective depletion of molecules in states with high α through the DR process. Assuming e.g. a linear increase of α with rotational energy, the experimental data can be reproduced qualitatively by a model taking into account radiative cooling and selective depletion as mechanisms changing the rotational excitation [11]. However, also other dependencies of α on the rotational energy as well as other mechanisms like (de-)excitation of individual ions in inelastic collisions with electrons or residual gas present in the storage ring cannot be excluded at this point.

3.2. Observations for H_3^+

Figure 4 shows the energy spectrum of the DR rate coefficient α of H_3^+ , comparing again two different storage time intervals (thick curves). As in the case of D_2H^+ , a reduction of α with storage time is found at small energies. In addition the spectrum taken after a long time of electron cooling appears somewhat more structured, thus supporting the assumption of a cooling of rotational excitations. The thin curve shows in comparison the data obtained at CRYRING with a lower electron temperature of $kT_{\perp} = 2$ meV and using a supersonic expansion ion source producing H_3^+ at a rotational temperature measured to be 20–60 K [1].

The strong increase of the CRYRING curve with respect to the TSR data at electron energies below 1 meV can be explained by the different electron temperatures: Due to the higher electron temperature, the TSR data is averaged over a larger energy range, leading to a reduction of the measured α value in this low energy region. An up to now unexplained feature is the behavior in the region between 10 and 200 meV. Here the rate coefficient measured at CRYRING is higher than the TSR results in particular when comparing to the data obtained at long storage times. This is in contradiction to the assumption that the molecular ions were rotationally colder in the CRYRING experiment *and* that low rotational excitations correspond to smaller rate coefficients. Possible explanations of this observation could be (i) unknown heating mechanisms, which affect the ions during storage in the ring and which were counteracted by the extended electron cooling procedure applied in the TSR experiment, and (ii) a non-monotonic dependence of α on the rotational energy.

As for D_2H^+ , also the H_3^+ rate coefficient was now followed as a function of storage time at the TSR (see figure 5). Again one observes a reduction of α with storage time when applying a strong electron

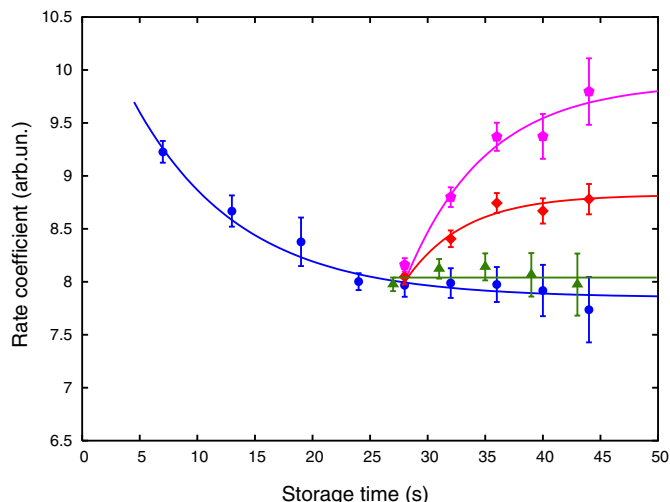


Figure 5. DR rate coefficient $\alpha(E_d = 0\text{ eV})$ of H_3^+ as a function of storage time. Circles: Strong cooling cycle (83% cooling time), diamonds: Switching from strong to weak (33%) cooling cycle after 28 s of storage, triangles: Adding electrons with $E_d = 10\text{ eV}$ after 28 s, pentagons: Adding electrons with $E_d = 116\text{ meV}$ after 28 s,

cooling cycle (circles in figure 5). When switching to a weaker cooling cycle after 28 s (diamonds), α changes again to a significantly higher level. In the case of H_3^+ , this cannot be explained by coupling to the 300 K background superseding the now weaker electron cooling. Thus, the observed rate increase must have its origin either in a heating mechanism not taken into account yet (like inelastic collisions with residual gas particles), or in an influence of the electrons at *reference* energy which are applied for 67% of the time in the weak cooling cycle, but had no effect in the case of D_2H^+ (see above).

To check for an effect of these 10 eV electrons on H_3^+ , the same experiment was repeated using the new *electron target* device (see figure 1) to supply an additional electron beam merged with the ion beam at a certain relative energy. A possible excitation of the molecular ions by electron collisions should then be visible as an increase of α at the time the additional, pumping electron beam is switched on. As seen in figure 5 (triangles), electron pumping at 10 eV has only a minor influence on α , whereas a strong effect is observable when pumping at 116 meV. The experiment was designed to have equal electron density in both electron beams, but the density of the pumping beam was not accurately known in this early experiment with the electron target. Thus, heating of rotational excitations by electrons at 10 eV appears unlikely, but cannot be excluded completely at the current stage of experiments.

To learn more about the influence of electron collisions on the rotational excitation of the molecules, as manifested in the value of α , the same pump-probe experiment was repeated at several different settings regarding the energy of the pumping electrons. As seen in figure 6 the effect of electron pumping sets in at $\sim 80\text{ meV}$, that is well below the energy of the first vibrational excitation, showing again that the observed changes of α are due to changes in the *rotational* excitation. For higher electron energies the pumping effect decreases until at $\sim 10\text{ eV}$ a significant change of α is no longer found.

4. Conclusions

The experiments described here show that the rotational state distribution of H_3^+ and its heteronuclear isotopomer D_2H^+ can be influenced by several mechanisms in storage ring experiments. For both species such variations of the rotational excitation result in changes of the DR rate coefficient α .

For D_2H^+ , the radiative coupling to the 300 K background became obvious, and strong indications were found for the preparation of a non-thermal ensemble of molecules by interaction with the cold electron beam. In the case of H_3^+ , the influence of electron collisions on the properties of the molecular ions could be mapped out in more detail by simultaneous operation of two electron beams. Here an additional effect of residual gas collisions on the molecular state distribution could not be excluded, which would be superseded by the radiative coupling for the infrared-active D_2H^+ .

In conclusion, the interaction with both electrons and residual gas during acceleration and storage

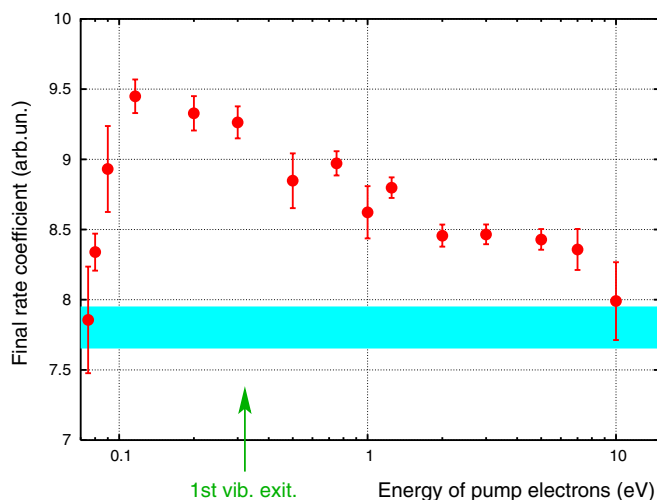


Figure 6. Final level of the DR rate coefficient α of H_3^+ (averaged over $37 < t_{\text{store}} < 47$ s) as a function of the energy of the additional electron beam. The shaded band marks the level reached without adding electrons. The arrow marks the energy of the first vibrationally excited state (313 meV).

of the molecular ions is found to be an important issue in the interpretation of storage ring experiments on dissociative recombination, in particular when aiming at a good control of the internal states of the molecules. However, the DR rate coefficients studied in the present experiments, while clearly varying with experimental conditions, did not exhibit changes larger than a factor of two. Thus it appears unlikely that internal excitations of the ions in storage ring experiments bear the reason for the large difference still separating the results of DR rate coefficient measurements obtained using the different experimental approaches.

Acknowledgments

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References

- [1] McCall B J *et al.* 2003 *Nature* **422** 500–2
- [2] Jensen M J, Pedersen H B, Safvan C P, Seiersen K, Urbain X and Andersen L H 2001 *Phys. Rev. A* **63** 052701
- [3] Tanabe T *et al.* 2000 *Dissociative Recombination: Theory, Experiment and Applications IV* ed Larsson M, Mitchell J B A and Schneider I F (Singapore: World Scientific) p 170
- [4] Plašil R, Glosík J, Poterya V, Kudrna P, Rusz J, Tichý M and Pysanenko A 2002 *Int. J. Mass Spec.* **218** 105–30
- [5] Kreckel H *et al.* 2002 *Phys. Rev. A* **66** 052509
- [6] Strasser D, Lammich L, Kreckel H, Krohn S, Lange M, Naaman A, Schwalm D, Wolf A and Zajfman D 2002 *Phys. Rev. A* **66** 32719
- [7] Lammich L, Kreckel H, Krohn S, Lange M, Schwalm D, Strasser D, Wolf A and Zajfman D 2003 *Rad. Phys. Chem.* **68** 175–9
- [8] Kreckel H *et al.* 2005 *J. Phys.: Conf. Series* this volume
- [9] McCall B J *et al.* 2005 *J. Phys.: Conf. Series* this volume
- [10] Miller S, Tennyson J and Sutcliffe B T 1989 *Mol. Phys.* **66** 429
- [11] Lammich L *et al.* 2003 *Phys. Rev. Lett.* **91** 143201