Electron collisions and rovibrational action spectroscopy of cold H$_3^+$ molecules

H Kreckel$^1$, A Petrignani$^1$, M Berg$^1$, D Bing$^1$, S Reinhardt$^1$, S Altevogt$^1$, H Buhr$^1$, M Froese$^1$, J Hoffmann$^1$, B Jordon-Thaden$^1$, C Krantz$^1$, M Lestinsky$^1$, M Mendes$^1$, O Novotny$^1$, S Novotny$^1$, H B Pedersen$^1$, D A Orlov$^1$, J Mikosch$^2$, R Wester$^2$, R Plašil$^3$, J Glosík, D Schwalm$^1$, D Zajfman$^1$, and A Wolf$^3$

$^1$Max-Planck-Institut für Kernphysik, D-69117 Heidelberg, Germany
$^2$Physikalisches Institut, Universität Freiburg, D-79104 Freiburg, Germany
$^3$Department of Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel
$^4$Faculty of Mathematics and Physics, Charles University Prague, Czech Republic

E-mail: holger@astro.columbia.edu

Abstract. Electron recombination of H$_3^+$ has found a lot of attention due to its outstanding relevance for the chemistry of the interstellar medium (ISM) and its role as a benchmark for the treatment of dissociative recombination (DR) of polyatomic ions. We report DR measurements performed at the TSR storage ring utilizing a cryogenic ion trap injector. Furthermore, a chemical probing spectroscopy technique is described that allows for a very sensitive monitoring of the populated states inside the ion injector. Since H$_3^+$ exists in two different nuclear spin modifications, a controlled manipulation of the ortho/para fraction is needed in order to perform state-selective measurements.

1. Introduction
The triatomic hydrogen ion H$_3^+$ is the simplest polyatomic molecule, consisting of two electrons and three protons forming an equilateral triangular configuration with 1.65 Bohr radii side length. H$_3^+$ is a stable molecule with a dissociation energy of 4.36 eV [1], while its neutral counterpart H$_3$ is unstable. Spectroscopy of H$_3^+$ is hindered by a vanishing electric dipole moment and the absence of stable electronically excited states. Therefore, one has to resort to vibrational spectroscopy in the infrared, an aggravation that lead to a decades-spanning quest for the first H$_3^+$ laboratory spectrum, which was finally observed in 1980 [2].

The pivotal role of H$_3^+$ for the chemistry of the interstellar medium (ISM) was already anticipated in the seventies [3], however, it took until 1996 until the first H$_3^+$ lines were found in interstellar space [4]. In recent years a multitude of molecules have been detected in molecular clouds, ranging from diatomics to alcohol and carbon-bearing molecules of up to 13 atoms. Since hydrogen is by far the most abundant element in the universe and the conditions in cold interstellar clouds (10-60 K) favour ion-neutral reactions, H$_3^+$ turns out to be the key reaction agent in these environments. Acting as an active proton donor, it facilitates the formation of many of the more complex molecules found in the ISM.

The H$_3^+$ column densities observed in dense and diffuse interstellar clouds are comparable and usually of the order of $1 \times 10^{14}$ cm$^{-2}$, a fact that is in stark contradiction with state-of-the-art
cloud models that predict a 2-3 orders of magnitude lower \( \text{H}_3^+ \) density in diffuse clouds [5]. While in dense clouds chemical reactions are the most effective pathway for the destruction of \( \text{H}_3^+ \), in diffuse clouds - due to trapping of heavier elements on dust grains - dissociative recombination (DR) with free electrons dominates. A slow electron recombination rate would explain the high abundance in diffuse clouds, therefore reliable DR experiments are crucial for unraveling this problem, especially since the results of \( \text{H}_3^+ \) DR rate measurements in the last four decades scattered over as much as four orders of magnitude [5].

1.1. Dissociative recombination of \( \text{H}_3^+ \)

The electron recombination of \( \text{H}_3^+ \) is somewhat of a cause célèbre. Not only have the experimental DR rates of the seemingly simple process

\[
\text{H}_3^+ + e^- \rightarrow \begin{cases} 
\text{H} + \text{H} + \text{H} & \text{(three-body channel),} \\
\text{H}_2 + \text{H} & \text{(two-body channel),}
\end{cases}
\]

(1)

been the subject of long-standing controversies, also the theoretical picture has been unclear for many years. The traditional understanding of the DR process (the so-called direct DR) established by Bates [6] requires a dissociative neutral state to cross the ionic potential curve. However, for \( \text{H}_3^+ \) no such curve-crossing exists at low energy, a fact that led to the general notion that \( \text{H}_3^+ \) recombination at low temperatures must be very inefficient. This view was changed in the mid-nineties when it became clear that \( \text{HeH}^+ \), despite the lack of a favourable curve-crossing, has a high recombination rate. The successful theoretical treatment of \( \text{HeH}^+ \) DR employed a more complicated mechanism, the so-called indirect DR process [7]. Here, the electron is first captured into a non-dissociative resonance of a Rydberg state of the neutral molecule from where it couples to a dissociative state. The first full-dimensional theoretical calculation of the DR of \( \text{H}_3^+ \) was published in 2001 [8] (and refined later [9, 10]) identifying the Jahn-Teller effect as the driving mechanism for the coupling between Rydberg levels and dissociating channels.

The discrepancy among various experimental methods is still unresolved, however, it has been conjectured that different states of internal excitation in the experiments may be responsible for the spread in the measurements. Therefore, in a series of dedicated experiments at the TSR storage ring, we have been working on a better understanding of the influence of \( \text{H}_3^+ \) internal excitation on the DR process.

1.2. Storage ring experiments and internal excitation

Modern electron cooler storage rings provide a relatively clean environment for DR experiments. Typically the ion beam is coasting with a few percent of the speed of light (corresponding to energies in the MeV-range) in the ultra-high vacuum system of the ring where the internal excitations of the ions can decay by spontaneous emission of radiation. For translational cooling the ion beam is merged with a cold electron beam of the same velocity. In DR measurements the electrons also serve as reaction partners initiating the dissociation into atomic and molecular fragments, which are detected by neutral-particle detectors situated downstream of the electron cooler section.

Due to its symmetry \( \text{H}_3^+ \) can host metastable vibrational modes as well as long-lived rotations. To monitor these excitations in situ inside the storage ring, modern imaging techniques were employed at the TSR. A Coulomb explosion imaging (CEI) experiment revealed that the stored \( \text{H}_3^+ \) ions relax vibrationally within the first two seconds of storage, including the metastable symmetric-stretch mode. The CEI experiment has been described before [12], the results are in good agreement with theoretical calculations of vibrational lifetimes.

In order to obtain information on the rotational states, DR fragment imaging experiments were performed. In these experiments the impact positions of the neutral fragments resulting
Figure 1. (Colour online) Outcome of a new DR fragment imaging study performed in a TSR beamtime in July 2007 (preliminary analysis). Plotted are the transversal distance distributions of the three-body channel of $H^+_3$ DR measured with a “hot” Penning ion source (a) and the 22-pole injector (b).

In chart (a) the output of a Monte-Carlo simulation for 2300 K, 3500 K and 4600 K is plotted (lowest to highest lines). In chart (b) the results of a measurement with normal-$H_2$ and para-$H_2$ precursor gas are depicted along with the outcome of simulations for 12 K, 116 K, 232 K and 580 K (lowest to highest lines).

from the electron recombination of single molecular ions are recorded by an imaging detector consisting of an MCP stack with phosphor screen and a CCD-camera system. The distance distribution resulting from the three-body breakup reveals information on the initial internal energy of the $H^+_3$ ion prior to recombination. Since the CEI measurement showed that all vibrations decay within the first two seconds of storage, all remaining excess energy has to be attributed to rotational excitation. By comparing the measured distribution with a Monte-Carlo simulation of the breakup process, the rotational temperature of the stored ion sample can be inferred. Extensive studies [14, 15] revealed that standard “hot” ion sources typically produce $H^+_3$ beams with an average temperature of the order of 3000 K. (Fig. 1a) shows the upper endpoint of the transverse interparticle distribution of the three-body channel measured by DR fragment imaging with a Penning ion source. The rotational excess energy is most clearly seen in that region of the distribution, which does not change significantly even for storage times of up to 60 s. A model of the rovibrational relaxation of $H^+_3$ supports these findings [16] and shows that many of the rotational states have lifetimes of the orders of months or years.

Summing up the imaging studies on $H^+_3$ internal excitations that were carried out at the TSR, one can conclude that vibrations are of no concern in storage ring experiments since they decay rapidly while the rotations require active cooling due to their extremely long lifetimes.

2. Experimental setup and techniques

2.1. The 22-pole injector trap at TSR

The 22-pole injector trap was built in order to prepare and inject cold $H^+_3$ ions into the TSR storage ring (see Fig. 2). Active cooling of the stored ions is achieved by collisions with Helium buffer gas. The trap consists of 22 stainless steel rods of 1 mm diameter and 40 mm length that are alternatingly planted into two copper sideplates [17]. By applying appropriate radiofrequency signals to the sideplates a radially confining potential is created. The trapping principle is similar to that of the well-known Paul trap with the significant difference that the effective potential has a large field-free region in the trap center, hence RF heating is strongly suppressed. The entire
device is mounted on a cryogenic head that cools the trap to 12 K. Up to $2 \times 10^6$ H$_3^+$ ions can be stored inside the trap and depending on the final energy needed and the accelerator settings, 5% to 40% of the ions can be transferred to the storage ring in a single injection.

2.2. Chemical probing spectroscopy inside the 22-pole trap
To verify the buffer-gas cooling inside the 22-pole trap and to probe the population of single rotational states, an action spectroscopy scheme was developed. The number densities inside the trap are too low by far to do conventional absorption spectroscopy, therefore a laser-induced chemical reaction is used as a sensitive probe of vibrational transitions. The ArH$^+$ formation reaction

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{ArH}^+ + \text{H}$$

is endothermic by 0.57 eV for ground state H$_3^+$, while it becomes exothermic for H$_3^+$ ions with at least two vibrational quanta. In the experiment, a few hundred H$_3^+$ ions are stored inside the trap into which Helium and Argon are blend continuously. The trap temperature is kept at 55 K to prevent Argon from freezing to the trap walls and electrodes. A tunable diode laser of (1.38-1.4) $\mu$m wavelength is used to trigger transitions from the three lowest rotational states of H$_3^+$ to the third harmonic of the bending mode vibration. Laser-excited H$_3^+$ immediately reacts to form ArH$^+$ ions, which are also captured by the RF potential until the contents of the trap are extracted and analyzed by a quadrupole mass spectrometer. Depending on the transition strength, typically 1-15 ArH$^+$ ions per trap filling are detected when the laser wavelength coincides with a transition. Details on the spectroscopy procedure are given elsewhere [13]. As compared to previous measurements [13] higher laser power (15 mW) and a longer laser interaction time are employed to increase sensitivity and reproducability of the experiment. Systematic studies were carried out to determine the optimal Helium and Argon number densities inside the trap.

3. Results
3.1. Dissociative recombination of rovibrationally cold H$_3^+$
The H$_3^+$ ions were produced in a storage ion source and transferred to the ion trap where they were stored in Helium ($n_{\text{He}} \sim 10^{14} \text{ cm}^{-3}$) buffer gas at 12 K. After storage times of typically 10-100 ms the ions were extracted from the trap and guided through an RF quadrupole at low
energy (0.5 eV) in order to transport them out of the high pressure region where there is still a potential risk of reexciting them in collisions with background gas. After the quadrupole they were preaccelerated to 10 keV and injected into the RFQ accelerator where they reach an energy of 4 MeV prior to injection into the TSR. The ions were stored for 10 s and during the entire storage time they were cooled by the electron cooler. The measurements were done with the ultracold electron beam of the electron target utilizing a liquid nitrogen cooled photocathode [18]. The relative energy was varied between 0 eV and 20 eV, while the transversal and longitudinal resolution were $T_{\perp} = 1$ meV and $T_{\parallel} = 30 \mu$eV, respectively.

Fig. 3 shows the measured rate coefficients obtained with the 22-pole ion trap in comparison to a standard Penning ion source. It can be seen that structures in the measured rate coefficient are much more pronounced for the cold ion beam. Furthermore a significant reduction of the rate is observed at low energies. The outcome of the 22-pole measurement is in excellent agreement with a previously published Cryring result that was achieved using a supersonic expansion source [19].

The comparison with theory reveals good overall agreement, while there are still pronounced differences at certain energies. In general the theoretical calculation shows much more structure, although it has been convolved with the appropriate TSR resolution and ion temperature. It is not clear yet whether the structures are washed out in the experiments due to effects that are not taken into account yet, or whether the resonance widths are underestimated in the calculation. Between 20 meV and 100 meV the measured rates are higher by an order of magnitude than the theory for a rotational temperature $T_{\text{rot}} = 60$ K and $T_{\text{rot}} = 100$ K. The discrepancy is greatly reduced when even higher temperatures are assumed [10]. This might be a hint that heating effects inside the storage ring exist that raise the ion temperature during storage. In a recent fragment imaging measurement at TSR (Fig. 1 b), beamtime in July 2007, preliminary analysis), however, a fragment distribution was measured that is compatible with a cold ion beam. Nevertheless further measurements are needed since the experimental method

Figure 3. (Colour online) Scans of the DR rate coefficient from a recent beamtime (July 2007) showing a direct comparison of data from a standard Penning ion source (stars) and the 22-pole injector trap (diamonds). Theoretical calculations are plotted for rotational temperatures of 60 K and 100 K [10, 11].
is not sensitive to temperature changes below 200 K, a temperature rise that might already be sufficient to cause changes in the aforementioned energy range. Also a small tail is visible for $R > 580 \text{mm}^2$ that is not seen in the simulations and thus appears to be “non-thermal”. Considering the full distribution – which is not plotted here – this section accounts only for a very small fraction ($\sim 10^{-3}$) of the events.

3.2. Nuclear spin manipulation
The lowest rotational state of $\text{H}_3^+$ is the $(J=1,K=1)$ state, the next lowest state $(J=1,K=0)$ lies 32 K higher. However, the rotational quantum numbers are not the only difference between these two levels, they also belong to different nuclear spin modifications. In $\text{H}_3^+$ the three proton spins can either align to a total spin of $3/2$ (ortho-$\text{H}_3^+$) or $1/2$ (para-$\text{H}_3^+$). The lowest state is a para-$\text{H}_3^+$ state, the next lowest state is of ortho symmetry. Nuclear spin flips are strongly suppressed and therefore buffer-gas cooling of normal-$\text{H}_3^+$ with Helium down to 12 K will not result in a pure para-$\text{H}_3^+$ ensemble but in a mixture of the two lowest states. The nuclear spin configuration can be changed in proton-exchange collisions with $\text{H}_2$, hence the final ortho/para ratio will be determined by collisions of $\text{H}_3^+$ with $\text{H}_2$ molecules leaking out of the source into the 22-pole ion trap. To manipulate the ortho/para ratio in a DR measurement, the normal-$\text{H}_2$ bottle of the ion source was replaced by para-$\text{H}_2$ (purity $> 99\%$). It is unclear how much the ortho/para ratio will be altered by this procedure, however, the use of para-$\text{H}_2$ should increase the para-$\text{H}_3^+$ fraction in any case. Some conclusions supporting this assumption can be drawn from the spectroscopy results described in the next section. Fig. 4 shows the comparison of two DR measurements utilizing normal-$\text{H}_2$ or para-$\text{H}_2$ as a precursor gas in the source. The experiments were performed at a somewhat lower resolution ($T_\perp = 3 \text{meV}, T_\parallel = 30 \mu\text{eV}$) to allow for faster data acquisition at a higher electron density. The two measurements do not differ much, but the para-enhanced curve (black dots) shows a faster DR rate at low energies. The theoretical rate coefficients for an ortho/para-$\text{H}_3^+$ ratio of 1:1 and pure para-$\text{H}_3^+$ are also plotted and show the opposite trend, here para-$\text{H}_3^+$ recombines slower. Nevertheless, it has to be noted that the
Figure 5. Results of the improved chemical probing spectroscopy study. The relative ArH\(^+\) signal is plotted for laser-induced transitions from the three lowest rotational states of H\(_3^+\) to the third vibrational bending mode harmonic. The upper panel was obtained using normal-H\(_2\), for the lower panel para-H\(_2\) was let into the ion source.

Rate-coefficient calculation at very low energies depends on the exact positions of vibrational levels in Rydberg states which have a significant uncertainty. Furthermore, a new calculation with more accurate vibrational energies reveals faster recombination for para-H\(_3^+\) in accordance with the experiment [10].

3.3. Chemical probing spectroscopy

For the spectroscopy measurements the trap temperature is fixed at 55 K, and 100-300 H\(_3^+\) ions are stored. Helium is let into the trap (n\(_{He}\) \sim 4 \times 10^{13} \text{cm}^{-3}\) for cooling and Argon is used as the probe gas (n\(_{Ar}\) \sim 10^{12} \text{cm}^{-3}\)). Furthermore, a certain amount of H\(_2\) is leaking out of the ion source into the trap. These hydrogen molecules limit the lifetime of ArH\(^+\) inside the trap since they induce the backward process of reaction 2, which is exothermic. Typical ArH\(^+\) lifetimes during the measurement are in the order of 30 ms.

After injection into the trap H\(_3^+\) ions are stored for 200 ms before the laser is activated. This time is needed because H\(_3^+\) ions coming from the ion source are highly excited and form ArH\(^+\) immediately. During this 200 ms cooling period the initial ArH\(^+\) ions decay in collisions with H\(_2\) and H\(_2^+\) ions are cooled in collisions with Helium. The laser is switched on for 100 ms saturating the ArH\(^+\) yield against the 25 ms decay constant of the backward reaction. After the laser interaction the trap contents are guided through a mass selecting RF quadrupole onto a Daly type ion detector that allows for the detection of single ArH\(^+\) ions.

Fig. 5 shows the relative ArH\(^+\) signal obtained by the improved spectroscopy setup for three transitions starting from the lowest three H\(_3^+\) states (1,1), (1,0) and (2,2) to the third harmonic of the bending mode vibration. From the Doppler width of the distributions the translational temperature of the ions inside the trap can be derived. For all the depicted lines a temperature of 67 \pm 2 K was found, slightly higher than the nominal wall temperature of 55 K. The upper and lower chart show the signal when normal-H\(_2\) and para-H\(_2\) gas is used in the ion source, respectively.
In both cases the rotational temperature – inferred from the signal ratio of the two para states (1,1) and (2,2) and the Einstein coefficients of the respective transitions – is consistent with the translational temperature. The ratio between ortho- and para H$_3^+$ states, however, changes significantly. Using normal-H$_2$, a para-H$_3^+$ fraction of 40% is found, increasing to 60% when para-H$_2$ is used as the precursor gas. Unfortunately the conditions that have to be employed for the spectroscopy experiment differ largely from the operation of the trap at the TSR, therefore no direct conclusion can be drawn on the ortho/para-H$_3^+$ fraction in the DR measurements. Nevertheless the measurement shows that the ortho/para ratio of H$_3^+$ can be modified in a controlled fashion on the one hand, but on the other hand that it is unlikely that a pure para-H$_3^+$ sample can be prepared in collisions with para-H$_2$ – in agreement with earlier experiments and nuclear spin selection rule considerations [21].

4. Summary
The electron recombination rate coefficient of cold H$_3^+$ ions was measured with high resolution using the 22-pole ion trap setup at the TSR. The outcome of the experiment shows excellent agreement with previous Cryring measurements despite largely different experimental parameters. Overall agreement with the latest theoretical treatment is reached, however, the calculations yield a much more structured cross section than the experimental curves. Reasons for these deviations are still under discussion.

The recombination rate for para-enhanced H$_3^+$ appears to be higher at low energies, a result that was reconciled with theory in the most recent treatment [10].

In order to confirm the buffer-gas cooling inside the ion trap and to probe nuclear-spin changing collisions with para-H$_2$, a chemical probing scheme was developed. It could be shown that a controlled manipulation of the ortho/para fraction of H$_3^+$ is possible.

5. Acknowledgement
HK was supported in part by the NASA Astronomy and Physics Research and Analysis (APRA) program.

References
[1] Cosby P C, Helm H, Chem. Phys. Lett. 152 (1998), 71
[2] Oka T, Phys. Rev. Lett. 45 (1980), 531
[3] Herbst E, Klemperer W, Astrophys. J. 186 (1973), 505
[4] Geballe T R, Oka T, Nature 384 (1996), 334
[5] Oka T, Dissociative recombination: theory, experiment and applications IV, edited by Larsson M, Mitchell J B A, Schneider I F, (World Scientific, Singapore 2000), 13
[6] Bates D R, Phys. Rev. 78 (1950), 492
[7] Guberman S L, Phys. Rev. A 49 (1994), R4277
[8] Kokoouline V, Greene C H, Esry B D, Nature 412 (2001), 891
[9] Kokoouline V, Greene C H, Phys. Rev. A 68 (2003), 012703
[10] Fonseca dos Santos S, Kokoouline V, Greene C H, J. Chem. Phys. 127 (2007), 124309
[11] Fonseca dos Santos S, Kokoouline V, Greene C H, private communication
[12] Kreckel H, et al., Phys. Rev. A 66 (2002), 052509
[13] Mikosch J, et al, J. Chem. Phys. 121 (2004), 11030
[14] Strasser D, et al, Phys. Rev. Lett 86 (2001), 779
[15] Strasser D, et al, Phys. Rev A 66 (2002), 032719
[16] Kreckel H, Tennyson J, Schwalm D, Zajfman D, Wolf A, New J. Phys. 6 (2004), 151
[17] Gerlich D, Physica Scripta T59 (1995), 256
[18] Orlov D, Weigel U, Schwalm D, Terekhov A, Wolf A, Nucl. Instrum. Methods Phys. Res. Sect. A 532 (2004), 41
[19] McCall B J, et al, Nature 422 (2003), 500
[20] Kreckel H, et al, Phys. Rev. Lett. 95 (2005), 263201
[21] Cordonnier M, Uy D, Dickson R M, Kerr K E, Zhang Y, Oka T, J. Chem. Phys. 113 (2000), 3181