

# Towards state selective measurements of the $\text{H}_3^+$ dissociative recombination rate coefficient

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**Abstract.** Ion storage and trapping techniques in connection with efficient internal state control and diagnostic for molecular ions offer the potential of providing rate coefficients for the dissociative recombination of  $\text{H}_3^+$  for well-defined initial rotational states, required for understanding the role of this ion in the interstellar medium and other cold environments. Information on the vibrational and rotational excitation in stored  $\text{H}_3^+$  ion beams, as obtained from experiments at the ion storage ring TSR, is reviewed. In addition, the arrangement of the TSR injector trap, using buffer gas cooling in a cryogenic radiofrequency multipole structure to inject pulses of internally cold  $\text{H}_3^+$  ions into the TSR via a high-energy accelerator, is outlined. An account is given of tests towards the in-situ diagnostic of rotational level populations, where laser transitions between low-lying rovibrational levels could be detected in dilute  $\text{H}_3^+$  ion ensembles using chemical probing in the radiofrequency multipole ion trap.

## 1. Introduction

The dissociative recombination (DR) rate of the triatomic hydrogen molecular ion is still the most controversial issue in the field of molecular recombination. Since  $\text{H}_3^+$  is one of the main reaction agents in interstellar chemistry, its affinity to recombine with free electrons has decisive impact on models of the interstellar medium [1]. Beside the fact that for many years no proper theoretical description of the recombination mechanism for this particular ion was available, more than twenty published experimental values of the thermal DR rate coefficient – differing by two orders of magnitude – continue to raise questions [2]. Various experimental methods from flowing and stationary afterglows and infrared absorption spectroscopy to the more recent storage ring techniques were employed to pin down the DR rate needed for reliable astrochemical models. The situation was aggravated by the detection of  $\text{H}_3^+$  in dense [3] and diffuse [4] interstellar clouds that revealed similar column densities in both cases. This finding, contradicting practically all existing models of interstellar clouds, is still far from being understood.

As the symmetric structure of triatomic hydrogen can host infrared-inactive modes of vibrational excitation, it was conjectured that different amounts of vibrational energy might be responsible for the scatter of the experimental results, and more recently the influence of rotational excitation has been placed in the focus of interest. To shed more light on the role of internal excitations of  $\text{H}_3^+$  and its

isotopomers in the DR rate coefficients, a series of measurements has been carried out at the TSR storage ring in the past years.

## 2. What do we know about $\text{H}_3^+$ internal excitation in an ion storage ring?

For monitoring the vibrational excitation and cooling the Coulomb explosion imaging (CEI) technique was used [5]. In experiments of this type,  $\text{H}_3^+$  ions of 1.43 MeV energy from a conventional “hot” ion source were stored in the TSR and during storage a small fraction of the ions was continuously extracted and guided into a dedicated CEI beamline. Here the molecules (particle rate  $\sim 1$  kHz) were passed through a thin diamond like carbon (DLC) target foil of  $0.7 \mu\text{g}/\text{cm}^2$  thickness. In the foil the binding electrons are stripped off immediately (at a time scale of  $10^{-16}$  s) while the protons traverse the medium practically without energy loss. The protons repel each other due to their mutual Coulomb force and after a few centimeter of flight distance they have reached asymptotic velocities which they keep until they hit the particle detector located about 4.6 m downstream. Since the asymptotic velocities depend on the position of the protons relative to one another at the moment of stripping, the distance they have gained at detector impact carries information on the initial molecular conformation. To achieve a complete picture the relative distances have to be recorded in all three dimensions which is achieved by a 3D imaging detector.

The backward conversion of the measured asymptotic velocities into molecular wave functions is complicated by foil effects such as charge exchange and multiple scattering, which are hard to implement in a reconstruction process. Hence in a typical CEI analysis calculated molecular wave functions are used for a forward Monte Carlo simulation of the Coulomb explosion and the respective foil effects. The resulting velocity distributions are compared to the experimental results. Since the internuclear distance distributions depend on the degree of vibrational excitation, time-resolved CEI can be used to monitor the vibrational excitation during storage in the TSR.

The symmetric structure of  $\text{H}_3^+$  allows for two principally different vibrational modes. The symmetric stretch – or breathing-mode – oscillation preserves the equilateral triangular shape and is infrared-inactive; its radiative decay arises from anharmonic coupling to other modes and occurs over times of the order of a few seconds for the lowest excitation. The doubly degenerate bending mode on the other hand is associated with a time-dependent dipole moment and consequently decays radiatively on much shorter time scales [6].

The CEI measurement revealed the existence of both types of vibrational excitation at the beginning of storage and, as expected, the bending modes decayed within the first 50 ms while the population of the first excited state of the breathing mode,  $(1,0^0)$ , prevailed for the first two seconds of storage [7]. The measured velocity distribution for longer storage times agreed excellently with simulations based on theoretical wave functions for the ground state of  $\text{H}_3^+$ , indicating that the vibrational cooling is completed after 2 s. The decay observed by the CEI measurement in the storage ring is even considerably faster than expected from the calculated radiative lifetime [8] for non-rotating  $\text{H}_3^+$  molecules in the  $(1,0^0)$  state, which can be explained by substantial rotational excitation as discussed below. The conclusion that can be drawn from these measurements is that a waiting period of a few seconds, easily realized with electron cooler rings, will yield  $\text{H}_3^+$  ions in the vibrational ground state for subsequent DR measurements.

The situation is less clear regarding rotational excitation. In a DR imaging experiment at the TSR it was found that considerable excess energy ( $\sim 0.3$  eV) is set free in the DR process of  $\text{H}_3^+$  throughout the whole storage time interval of up to 30 s [9]. This energy has to be attributed to long-living highly excited rotational states since vibrations can be ruled out by the CEI results.

To back our findings theoretically, we have set up [7, 10] a rovibrational relaxation model based on existing linelist calculations for  $\text{H}_3^+$ . This model connects all  $\text{H}_3^+$  states below  $12000 \text{ cm}^{-1}$  with their respective dipole transitions (excluding those with Einstein coefficients  $< 10^{-7} \text{ s}^{-1}$ ). Radiative heating and induced emission are omitted at this stage because the starting temperature for the model of  $\sim 2700$  K is much higher than the temperature of the ambient 300 K radiation field. It turns out that this relaxation model reproduces the experimental findings very well: the model predicts that the decay of population

in the breathing-mode excited states is substantially faster as compared to the rotationless decay, and a detailed comparison between the experimental and the modeled decay curves for the population in the first excited breathing level shows good agreement.

Moreover, also the survival of highly excited rotational states is reproduced by the model. As a general trend, states with their axis of rotation perpendicular to the molecular plane ( $J = K$ ) are long-living since in this case the rotation does not disturb the symmetry of the triangular shape. If, on the other hand, the axis of rotation lies in the molecular plane the molecule can deform and develop a small dipole moment, which renders these states rather short-lived. As a result, for  $J > 7$  at least two states survive storage times even of minutes, namely those with  $J = K$  and  $J = K + 1$  [10].

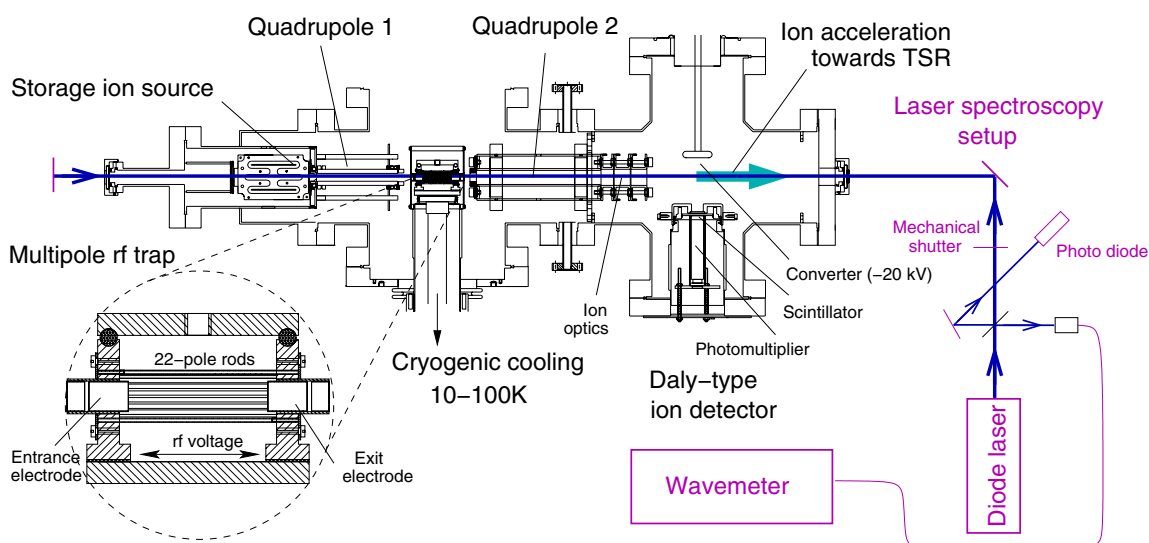
As a consequence, rotationally cold  $\text{H}_3^+$  cannot be created by simply extending the storage ring measurements to longer storage times; in fact, an active cooling mechanism is needed.

In recent experiments at the TSR it was shown that the degree of rotational excitation can be changed by intense electron cooling. For  $\text{D}_2\text{H}^+$  the creation of nonthermal ensembles could be demonstrated, using the thermalization by the 300 K background radiation as a temperature diagnostics [11]. This diagnostic method could not be extended to  $\text{H}_3^+$  because of its much weaker coupling to radiation. However, a dependence of the DR rate coefficient on the amount of electron cooling was also observed for  $\text{H}_3^+$  [12].

A more promising approach to prepare an  $\text{H}_3^+$  ensemble with well-defined temperatures is to use a cold inert buffer gas to collisionally quench the long-living rotations prior to injection into the ring. A supersonic expansion source was utilized for an  $\text{H}_3^+$  DR measurement at CRYRING and the rate coefficient that was obtained was lower by a factor of two compared to previous experiments with “hot” ion sources [13]. At the TSR a different approach was realized by constructing a cryogenic 22-pole radiofrequency (rf) ion trap from which ion pulses are then extracted and brought to MeV energies in the linear accelerator feeding the TSR. In the rf multipole ion trap, the  $\text{H}_3^+$  ions are stored by suitable radiofrequency fields while they are exposed to helium buffer gas at temperatures down to 10 K [14, 15]. The arrangement of this TSR injector trap will be described in section 3 and its operational status will be summarized in section 5.

Another aspect related to the internal excitation of  $\text{H}_3^+$  ions in merged-beams recombination measurements is the existence of heating processes acting on the ions while they circulate in a storage ring. In particular, once a cold (say, 10 K)  $\text{H}_3^+$  beam has been injected into the storage ring, is it safe to assume that the ions stay at low temperature during the storage? To investigate the radiative heating by the ambient 300 K radiation, the rovibrational model mentioned above was extended to include absorption and induced emission [10]. Test calculations revealed that heating by 300 K radiation is much too slow to have any influence on the population distribution, while stray light at higher temperatures produced, e.g., by hot filament ion gauges should be avoided. A further heating process more difficult to estimate may be caused by inelastic collisions of  $\text{H}_3^+$  ions with the residual gas in the storage ring. High excitation energies can in principle be reached by these collisions and, as discussed above,  $\text{H}_3^+$  hosts many metastable rotational levels which – once populated – will stay excited. Time-resolved DR rate coefficient measurements at the TSR indeed found evidence for a slow time dependence which is not caused by the electrons of the cooler [12].

It follows from these estimates and observations that, using cold ion sources, it might be necessary to avoid long storage times in DR measurements at ion storage rings. Also, this underlines once more the importance of direct in-situ monitoring of rotational level populations by spectroscopic measurements, which implies the development of suitable methods for rovibrational spectroscopy on  $\text{H}_3^+$  at low-density. For the low-lying rovibrational levels of interest here, there are presently no practical examples of ion beam spectroscopy. On the other hand, a laser experiment probing low-lying rovibrational levels of  $\text{H}_3^+$  ions in an rf multipole trap could be performed during the commissioning of the new TSR injector trap and will be described in section 4.



**Figure 1.** Setup of the TSR cryogenic injector trap. The acceleration of extracted  $\text{H}_3^+$  ions to keV energies for the beam transport to the TSR is indicated schematically by an arrow. Additionally shown is the arrangement for rovibrational laser spectroscopy using chemical probing.

### 3. The 22-pole injector ion trap

The operating principle of the 22-pole rf ion trap set up as an injector for the TSR will only be introduced briefly since details can be found in the literature [14]. The trap itself consists of 22 stainless steel rods that are alternately planted into two copper side-plates which are mounted electrically insulated on the cryogenically cooled ground plate of the trap. By applying a suitable radiofrequency field to the rods via the side-plates an effective potential is formed that traps the ions radially. The trapping principle is similar to that of the well-known Paul trap, but in the case of the 22-pole the radial dependence of the effective potential is closer to a hard-wall potential, which leaves the ions unaffected by the rf field over a large inner region of the trap.

For loading and unloading the trap and for axial confinement, two cylindrical end-electrodes are located in the side-plates. The complete device is attached to the low-temperature stage of a 10 K cold head and special care is taken for good thermal conductivity between all parts of the trap and the cryohead. In order to cool the ions collisionally, pre-cooled buffer gas is let into the trap volume.

The complete arrangement, as set up during test experiments before the installation at the TSR, is shown in figure 1. An rf storage ion source [16] is used to produce  $\text{H}_3^+$  ions which are transported into the trap by rf-quadrupole ion guides at energies of few eV. After the trap, where the pressure can be locally raised for buffer gas cooling, the ions are guided by a second rf quadrupole into a region of low background gas pressure and finally accelerated to keV energies, suitable for injection into the linear accelerator coupled to the TSR. The ions extracted from the trap can be counted with near-unity efficiency on a Daly-type scintillation detector [17]. The rf quadrupoles can also be used for ion mass selection.

Before the setup was installed at the TSR, the feasibility of rovibrational laser spectroscopy of  $\text{H}_3^+$  ions confined in the rf ion trap was investigated. In particular, the method of chemical probing, previously demonstrated [18, 19] for other molecular ion species in rf traps of the same type, could be successfully applied to  $\text{H}_3^+$  [22].

#### 4. Laser spectroscopy of $\text{H}_3^+$ in an rf ion trap by chemical probing

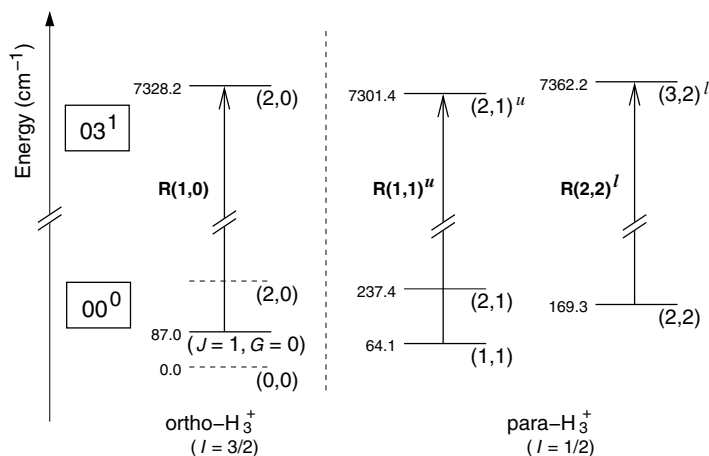
Laser spectroscopy of  $\text{H}_3^+$  is complicated by the vanishing electric dipole moment for many rovibrational transitions and by the absence of stable electronically excited states. Consequently, for regular infrared absorption spectroscopy a long light integration path and high  $\text{H}_3^+$  densities are required [23]. The number of ions that can be stored in the present rf ion trap, however, is too low by many orders of magnitude for this technique.

A more sensitive way to observe infrared transitions is to use a chemical reaction that is endoenergetic for the vibrational ground state and hence proceeds only for vibrationally excited ions [18, 19]. In the present investigation we chose the reaction

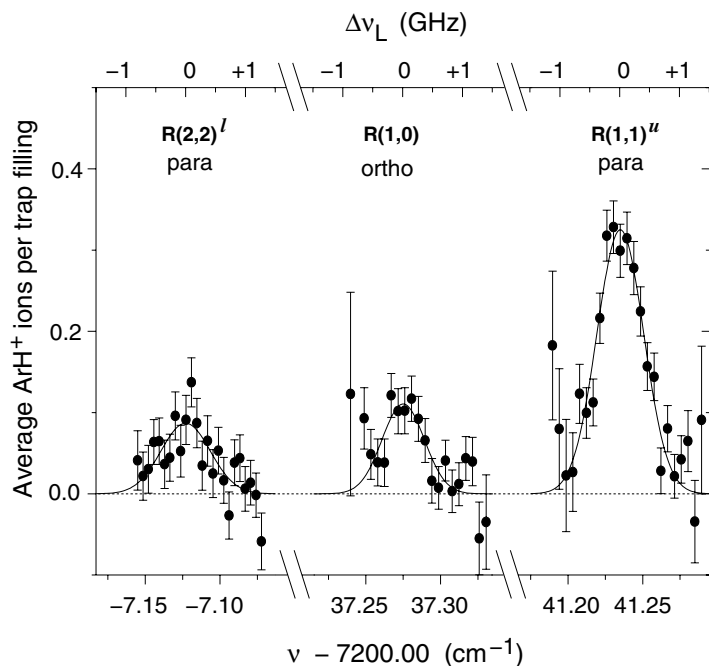


which is endothermic by 0.57 eV for ground-state  $\text{H}_3^+$  and hence suppressed at the given temperature. However, as soon as the internal energy of the  $\text{H}_3^+$  reaction partner exceeds the given amount of energy – which is the case for all  $\text{H}_3^+$  states that are carrying two or more vibrational quanta – this ion-neutral reaction can be supposed to proceed very fast. Consequently, the formation of  $\text{ArH}^+$  from  $\text{H}_3^+$  stored in Ar buffer gas can be regarded as a marker for vibrational excitation and thus for the occurrence of laser-induced rovibrational transitions.

The implementation of the laser experiment in the TSR injector trap is indicated in figure 1. At the 10-K operating temperature intended for the injector trap, the argon vapor pressure is extremely low; hence, the trap temperature was stabilized at  $55 \pm 5$  K. A commercial infrared diode laser was used to produce about 2 mW of radiation with wavelengths between 1.38 and 1.39  $\mu\text{m}$ . To measure absorption profiles the laser wavelength was swept over  $\sim 2$  GHz near the expected resonances [20, 21] by the use of a piezo actuator and monitored by a commercial wavemeter with an absolute accuracy of  $\pm 500$  MHz. In the experiment about 300  $\text{H}_3^+$  ions were injected into the trap per filling. Helium buffer gas at a number density of  $4 \times 10^{11} \text{ cm}^{-3}$  and argon at  $2 \times 10^{11} \text{ cm}^{-3}$  were let into the trap volume. To avoid the leakage of hydrogen – which drives the backward reaction of Equation (1) and diminishes the  $\text{ArH}^+$  lifetime – from the rf ion source into the trap, the ion source had to be operated at very low hydrogen pressure. As a consequence the  $\text{H}_3^+$  ions were not thermalized to the ion source temperature and a noticeable fraction of them was vibrationally excited when entering the trap. This led to the formation of  $\text{ArH}^+$  within the first few milliseconds, before the  $\text{H}_3^+$  ions were cooled by the buffer gas within the trap. The  $\text{ArH}^+$  ions decay with a time constant of  $\sim 20$  ms through the inverse reaction of Equation (1). To ensure the complete decay of the initial  $\text{ArH}^+$  signal before starting the laser excitation measurement, a delay of 220 ms after injection had to be introduced. Following this delay, the laser was activated for 20 ms, the ions were extracted from the trap and the laser-induced  $\text{ArH}^+$  ion signal, selected by the second rf quadrupole operating as a mass filter, was counted by the Daly detector.



**Figure 2.** Level scheme of the lowest rotational states of  $\text{H}_3^+$  and the investigated transitions to excited states within the  $0,3^1$  vibrational level.



**Figure 3.** Laser-induced  $\text{ArH}^+$  signals observed on transitions starting from the three lowest  $\text{H}_3^+$  rotational states. The upper scale denotes the laser frequency detuning  $\Delta\nu_L$  from the line centers, as monitored by the wavemeter, while the lower scale indicates the absolute frequency (wave number) which is accurate to  $\pm 0.017 \text{ cm}^{-1}$ .

This procedure allowed us to observe three rovibrational transitions in  $\text{H}_3^+$ , starting from the three lowest rotational levels, up to the third vibrational bending level ( $0,3^1$ ). The level scheme for these transitions is depicted in figure 2 while the observed absorption profiles are shown in figure 3. The  $\text{ArH}^+$  signal count rate was typically 0.1 ions per trap filling. From the line profiles, the frequencies (wave numbers) of the three transitions can be derived [22] with experimental errors of  $\pm 0.017 \text{ cm}^{-1}$ . The results are more accurate than previous measurements [20, 21] by about a factor of 4 and consistent with the earlier results within their experimental errors.

From the intensities and widths of the three line profiles, three important parameters could be inferred. Firstly, the width of each observed line is governed by the Doppler spread of the ion absorption frequencies, as given by the translational temperature. Secondly, the intensity ratio between the two lines for para- $\text{H}_3^+$  (see figure 3) can be used to calculate the rotational temperature. Finally the relative strength of the  $R(1,0)$  (ortho) and the  $R(1,1)^u$  (para) lines gives the “ortho-to-para” temperature describing the relative abundance of the two nuclear-spin species of  $\text{H}_3^+$ . The latter parameter does not necessarily have to be related to the temperature, since in the absence of a catalyst nuclear spin conversion is forbidden. The Doppler widths of  $\sim 470 \text{ MHz}$  in all three cases indicate a translational temperature of  $170 \pm 20 \text{ K}$ ; the rotational temperature derived from the intensity ratio of the two para-transitions amounts to  $150 \pm 20 \text{ K}$  and the ortho-para ratio results in a “nuclear-spin temperature” of  $140 \pm 20 \text{ K}$ .

All temperatures are considerably higher than the trap wall temperature. This is probably caused by the specific conditions of the laser probing experiment, which strongly differed from the operating conditions envisaged for ion injection into the TSR. In particular, the buffer gas densities during the laser spectroscopic experiment had to be kept lower by a factor of about 200 and, moreover, surface contaminations are likely to have been present in the 22-pole trap during this experiment. The combination of both factors can strongly affect the efficiency of buffer gas cooling and appears to have contributed to ion temperatures considerably above the level of  $55 \text{ K}$  expected for thermalization with the cryogenic walls of the ion trap.

Laser measurements at higher buffer gas densities, approaching the level of  $10^{14} \text{ cm}^{-3}$  used for thermalization in the TSR injector trap, may become possible after further improvements of the purity regarding the gas supplies and the inner surfaces of the trap. The purity of the buffer gas is particularly critical at the elevated operation temperatures ( $\sim 55 \text{ K}$ ) required by the use of argon as a reactant for

the laser spectroscopic detection scheme. Moreover, the laser experiments can be improved by a better vacuum separation between the ion source and the ion trap. Further spectroscopic experiments might also clarify the effect of collisions with H<sub>2</sub> (in particular ortho-H<sub>2</sub>) on the temperature of the stored H<sub>3</sub><sup>+</sup> ions.

## 5. Perspectives

The operation of the TSR injector trap in comparison to the laser experiment is facilitated by the operating temperature of <12 K, which freezes out most residual gas molecules (such as H<sub>2</sub>O and N<sub>2</sub>) that limit the H<sub>3</sub><sup>+</sup> lifetime. Hence, much higher buffer gas densities can be applied while keeping the H<sub>3</sub><sup>+</sup> storage time sufficiently high. The usable densities of  $\sim 10^{14}$  cm<sup>-3</sup> imply collision rates of  $\sim 100$  per millisecond, which ensure buffer gas cooling of the ions over flight paths small compared to the trap dimensions.

The cryogenic multipole ion trap is presently installed at the Radiofrequency Quadrupole (RFQ) accelerator of the TSR facility. A crucial aspect is the transport efficiency of the trapped ions into the TSR. First tests of the transport efficiency were performed without trapping, using a continuous beam from the rf ion source. It was found that the transmission from the source through the accelerator into the TSR at optimal setting can be as high as 50%. Furthermore the maximum number of ions that could be extracted from the trap and detected at the scintillation detector was found to be  $5 \times 10^5$  ions. Combining these two values it seems possible to inject more than  $10^5$  ions per trap filling into the TSR, enough for a detailed investigation of the DR cross section of rotationally cold H<sub>3</sub><sup>+</sup> ions.

Beside the application as a source for cold ions, multipole rf ion traps for H<sub>3</sub><sup>+</sup> offer attractive possibilities for further measurements employing chemical probing or similar techniques; e.g., the use of para-hydrogen in a laser spectroscopic experiment might reveal information on the ortho-para thermalization of H<sub>3</sub><sup>+</sup> at very low temperatures. Another interesting topic is the deuteration of H<sub>3</sub><sup>+</sup> in reactions with HD. Measurements of the rate for this reaction may provide a useful diagnostic of the H<sub>3</sub><sup>+</sup> temperature in the trap. In addition, many further aspects can be studied for this process, which is believed to be responsible for a wealth of deuterated molecules detected in the interstellar medium.

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