

Study of Astrophysically Relevant Hydrogen Chemistry: combining an RF Ion Trap with a Cold Effusive Beam

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Abstract

This contribution presents recent progress made with an ion trapping instrument which is operated in the Department of Surface and Plasma Physics of Charles University. A special feature of the experimental setup is the combination of a low temperature 22-pole trap (22PT) with a cold effusive source for neutrals. This allows us to study the interaction of trapped ions with slow and cold neutrals. Using a discharge tube also radicals can be produced, especially H- or D-atoms. Recent experimental progress includes the extension of the temperature of the neutrals, T_{ACC} , down to 4 K and various improvements on the accommodator for getting stable dissociation degrees. Using an MCP detector, the chemistry of both cations and anions can be studied. The instrument is presently used to explore a variety of pure hydrogen reactions at low temperatures. As a typical result, the formation of H_3^+ via radiative and ternary association of H^+ an H_2 at 10 K will be discussed as well as the following formation of small hydrogen clusters. The conclusion and outlook give some hints to planned activities such as determination of state specific rate coefficients, the role of nuclear spin, and deuteration.

Keywords:

ion traps, interstellar chemistry, H-atom beam, radiative association, ortho and para- H_2 , deuteration

Introduction

Hydrogen is the most abundant baryonic species in the universe. It plays, both in its atomic and molecular form, a central role in many fields of natural science. Hydrogen plasmas can be found in laboratory discharges, flames, atmospheres, and astrophysical environments. Although pure hydrogen plasmas seem to be rather simple, the interactions of its components (H, H^+ , H^- , H_2 , H_2^+ , H_3^+ , electrons, and photons) are usually rather complex since many processes compete with each other. In order to model such a system, many relevant parameters are needed. The state of the knowledge, covering the energy range from thermal up to keV, has been reviewed recently [jan03]. This energy range is suitable for modeling the plasma physics of the solar corona and solar wind or technical applications, e.g. for describing the boundary region of a magnetically confined fusion plasma.

For questions raised in astrochemistry, the interactions of various forms of hydrogen, especially H and D atoms, need to be understood at low temperatures, down to a few K. At such cold conditions, other processes such as small barriers, isotope enrichment, nuclear spin restrictions, or cluster formation play a role [ger06b]. Recent publications emphasize that more experimental information on low temperature hydrogen chemistry is needed for tracing the chemical and physical processes occurring in the cosmic dark age of our universe [glo08a] or in dense interstellar clouds [wal04].

In addition to hydrogen, there is a small fraction of deuterium which plays a special role in low temperature chemistry. Despite a deuterium abundance of only 10^{-5} (relative to H), many deuterated molecules have been detected in the interstellar medium including doubly and even triply deuterated species. This phenomenon, called 'isotope fractionation' is due to a complex interplay between zero point energies, symmetry selection rules, and barriers. Many details of D-H exchange reactions must be known in order to correlate observed abundances of deuterated molecules with the cosmic D/H isotopic abundance ratio. An important experimentally unexplored class of reactions is isotope enrichment in collisions of ions or neutrals with D-atoms.

The instrument which is used in the detailed studies of hydrogen chemistry has been developed at the Technical University in Chemnitz [luc05], [bor09], [ger09a]. It is a "standard" rf trapping

instrument which are used today for a variety of applications in reaction dynamics, spectroscopy etc. A tutorial and more references can be found in [wes09], [ger08b], [yua11]. A special feature of our instrument is the integration of a temperature variable source for cold neutrals, especially hydrogen molecules or atoms. A recent series of measurements has concentrated on reactions between cold CH_n^+ with H and H_2 [ger11a]. Especially interesting is the dependence of the reaction of CH^+ with H on the rotational state of the molecular ion [pla11], [meh09].

This contribution summarizes the present status of our experimental activities to study various H_mD_n^+ ($m+n \leq 5$, also H_mD_n^-) collision systems, especially at the energies required for astrochemistry. Simple systems include the endothermic electron transfer from D to H^+ or the associative detachment in $\text{H}^+ + \text{H}$ collisions, more complex and experimentally unexplored is the deuteration of H_3^+ in collisions with D or the formation of ortho- H_3^+ in collisions of para- H_3^+ with para- H_2 .

Experimental

The modular design of the apparatus allows us to operate it in many different configurations. Fig. 1. shows the present version of the so-called CEB-22PT apparatus (Cold Effusive Beam – 22-Pole Trap). Primary ions are produced in a storage ion source which is capable of producing pulses of pre-cooled (350 K) molecular ions [ger92]. After selecting the desired ion mass using the QP mass filter, the ions are injected into the 22-pole trap. There they can be cooled down to 10 K via collisions with buffer gas. For reactions, the neutral target gas can be just leaked into the trap chamber; injected in a pulsed supersonic beam, or in a cold effusive beam. The gas can be dissociated using a discharge leading to a cold beam of radicals. The optical transparency of the trap on axis allows to perform spectroscopic measurements on the ions. The reaction products are analyzed using a second mass spectrometer. The MCP can detect as well positive as well negative ions.

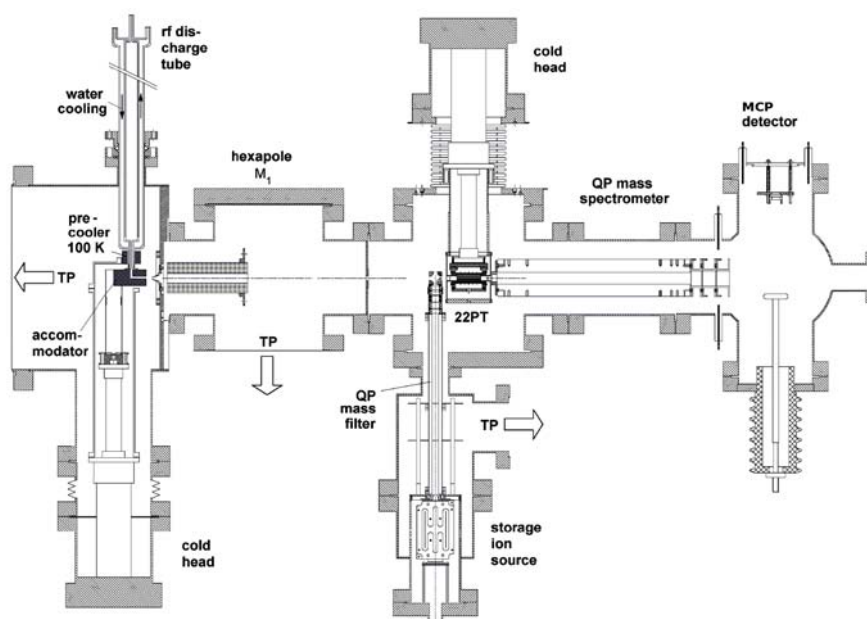


Fig. 1 Ion trapping instrument for studying the interaction of ions stored in the temperature variable 22-pole trap (22PT) with a cold effusive beam of H atoms, H_2 molecules or deuterated isotopologues [bor09]. Recent innovations on the cold effusive beam include the integration of a new cold head (Sumitomo RDK-101E, lowest temperature 3.6 K), a Teflon coated accommodator, and a rather weak hexapole magnet for focusing slow H-atoms.

Details of the design of the hydrogen atom source and many tests have been described in the PhD thesis of G. Borodi [bor08]. A short summary can be found in [bor09]. As indicated in the left part of Fig. 1, molecular hydrogen is dissociated in a discharge tube (Pyrex glass, inner diameter of 19 mm, length 330 mm, terminated with two capillaries, inner diameter 2 mm, length 5 cm). The exit capillary is cooled to 100 K (precooler), followed by an accommodator which is thermally connected to a cold

head (Sumitomo RDK-101E, lowest temperature 3.6 K). The gas leaves effusively the accommodator and the flow is formed into a beam by a skimmer and several apertures. The dissociation degree is influenced by the surface material and temperature. The literature contains many hints, recipes and tricks for delivering dissociation degrees up to 95% [sle81], [szc00]. Very efficient but not so stable is the coating with H₂O as described in [bor08]. In the current configuration we use a PTFE coated copper accommodator. Tests with a PTFE tube did not lead to full thermalization of the beam.

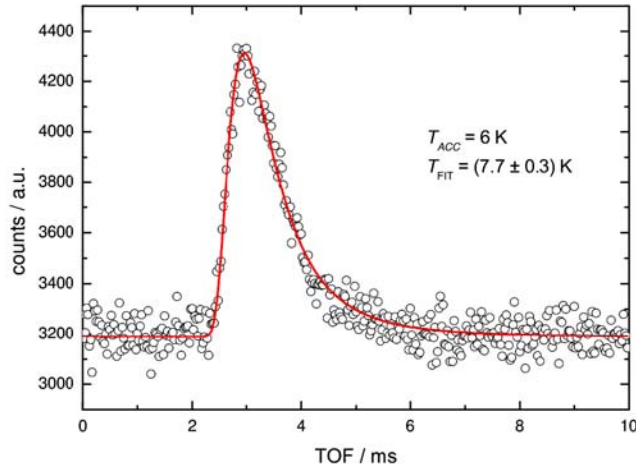


Fig. 2 TOF distribution of H atoms running the accommodator at 6 K. Comparison with the temperature, derived from the fit, reveals that the PTFE film is slightly warmer than the copper tube.

The thermalization of the atomic beam was verified by determining its velocity distribution via time-of-flight (TOF) measurements. For this purpose, a chopper wheel with 2 slits interrupts periodically the beam (time resolution $\sim 20 \mu\text{s}$). The neutrals are detected using an electron impact ionizer at a distance of 58 cm. The data shown in Fig. 2. have been recorded at $T_{\text{ACC}} = 6 \text{ K}$ for H-atoms. The measured distribution was fitted with a convolution of a Maxwellian with the instrument function calculated from the shape of the atomic beam and the chopper aperture and frequency. Comparison with the fit, $T_{\text{FIT}} = 7.7 \text{ K}$, reveals that there is still a slight temperature gradient in the teflon layer. It is also possible that thermalizing collisions with the PTFE surface are not so efficient as the layer of water ice [bor08].

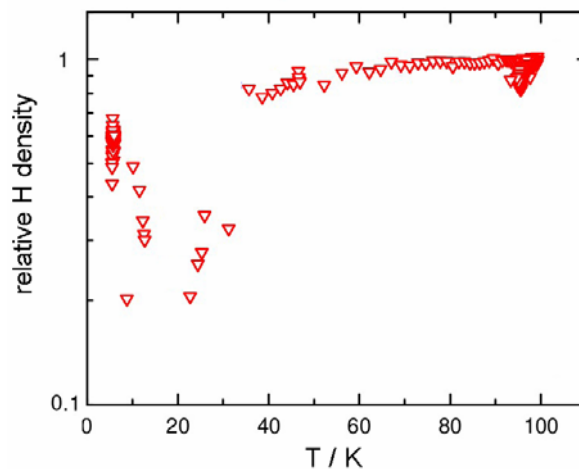


Fig. 3 Relative H-atom density (\sim dissociation degree) of the H atom source as a function of the accommodator temperature. The accommodator has been coated with a thin PTFE film. Between 10 and 30 K, fast recombination reduces the flux of atoms.

As explained in detail in [bor09] the number density of hydrogen atoms at the location of the trap can be determined using an electron bombardment ionizer or, directly in the trap, using chemical probing. In both cases measurements are performed with the discharge switched ON and OFF and using a shutter for blocking or passing the direct beam. A typical result (in relative units) is plotted in Fig. 3.

Below 30 K, the H atoms are lost due to efficient recombination on the surface of the accommodator. Going further down in temperature, the situation becomes again better. Most probably this is due to coating with H atoms or reduced mobility. For a detailed understanding, more tests are needed. The overall flux of H atoms is sensitive to changes in experimental conditions. Therefore the hydrogen atom density is routinely calibrated in situ using CO_2^+ as probing ion [bor09].

Results and discussion

The capabilities of the instrument are demonstrated by extending previous measurements of H_3^+ formation towards lower temperatures. As described in detail in [ger92c], two processes contribute, the stabilization of the collision complex via emission of a photon (radiative association) or via the collision with a third body (ternary association),

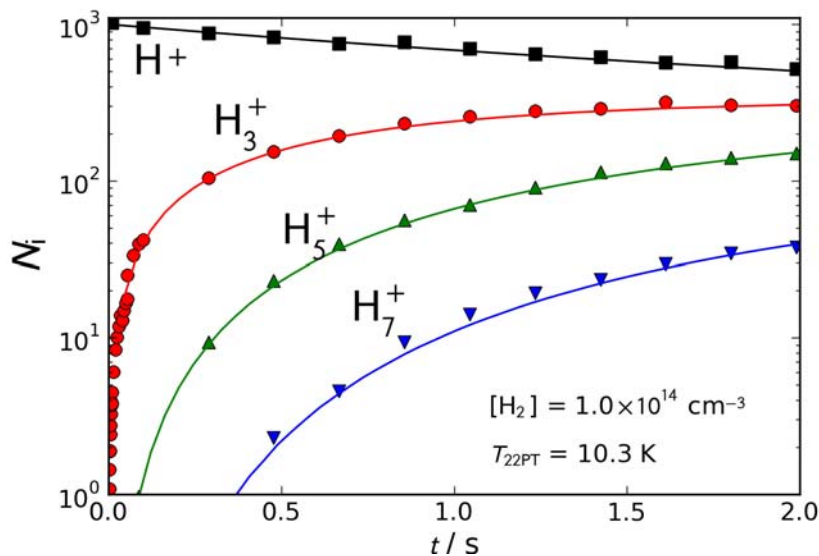


Fig. 4. Reactions of H^+ ions with H_2 at $T_{22\text{PT}} = 10.3$ K. Plotted is the number of primary and product ions per filling, N_i , as a function of the storage time t . Solid lines represent a solution of chemical kinetic equations.

Fig. 4 shows a typical set of data measured at $T_{22\text{PT}} = 10.3$ K and at a hydrogen number density of $1 \times 10^{14} \text{ cm}^{-3}$. The number of injected protons (typically 1000 per filling) decays exponentially. They are directly converted into H_3^+ followed by subsequent collisions leading to larger hydrogen clusters. The formation of clusters has been discussed in detail in [pau95]. The ternary rate coefficients for cluster formation have been obtained from least squares fits of measured data resulting in $k_3(\text{H}^+) = (4.3 \pm 0.1) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$, $k_3(\text{H}_3^+) = (6.4 \pm 0.5) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$, $k_3(\text{H}_5^+) = (6 \pm 2) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$. Association of H_7^+ and fragmentation of all clusters were also included in the model, but their rates could not be reliably determined from the fit. The rate coefficients of H_3^+ and H_5^+ formation via ternary association are a factor 0.4 smaller in comparison with [pau95]; this may be due to differences in the actual temperature or in the number density.

Evaluating such measurements performed at different number densities of $[\text{H}_2]$, one obtains the effective rate coefficients k^* , shown in Fig. 5. The observed behavior is typical for the combination of ternary association, prevailing at higher densities and radiative association which plays only a role at

low densities. This dependence can be described by the equation

$$k^* = k_3 [\text{H}_2] + k_r \quad (3)$$

Fitting the data with Eq. (3) leads to a radiative association rate coefficient of $2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. This result is 2 times higher than the value measured previously at 80 K while a simple RRKM based theory predicts a much steeper temperature dependence [ger92c]. In order to clarify this unexpected result, more measurements will be made, including studies with para- H_2 .

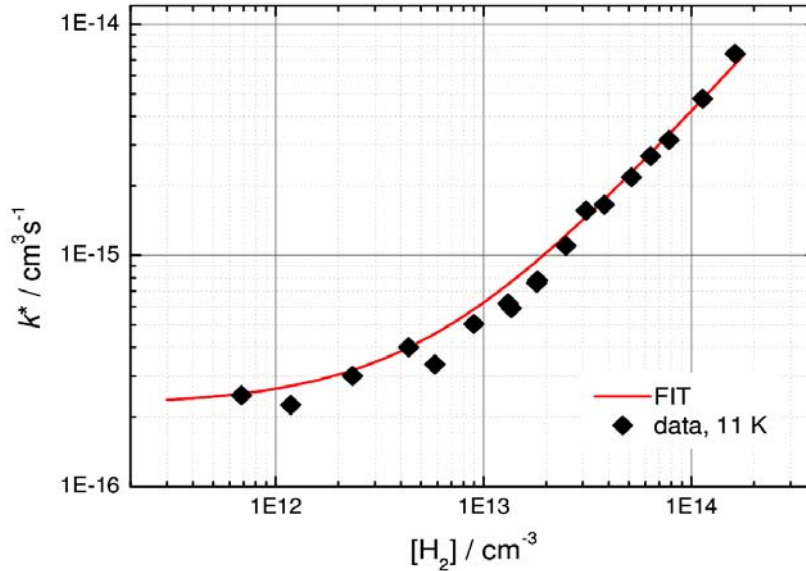


Fig. 5. Dependence of the effective rate coefficient for $\text{H}^+ + \text{H}_2$ association as a function of the H_2 number density. The ion trap was operated at 11 K. The measured values have been approximated by the function $k^* = k_3 [\text{H}_2] + k_r$ (red line) leading to $k_r = 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$.

Conclusions and outlook

The goal of our present activities is to study in detail various elementary steps of the hydrogen chemistry at low temperatures using the combination of a linear rf multipole ion trap with an effusive source of hydrogen molecules and atoms. This contribution describes recent improvements: the H-atom beam velocity and density has been characterized using TOF and chemical probing, respectively. New results are reported for ternary and radiative association of H^+ with H_2 at 11 K proving the high sensitivity of the instrument. A critical test for the apparatus will be the 3.6 meV endothermic electron transfer from D to H^+ since the threshold behavior is well characterized by theory [esr00]. Other challenges in hydrogen chemistry are the associative electron detachment reaction $\text{H}^+ + \text{H} \rightarrow \text{H}_2 + \text{e}^-$ (see separate contribution) and all the other H_mD_n^+ collision systems such as $\text{H}_3^+ + \text{D}$. Unique in our approach is not only the atomic beam but also the combination trap - effusive molecular beam. The possibility to vary independently T_{ACC} and $T_{22\text{PT}}$ and the use of normal- H_2 and para- H_2 makes it possible to measure state specific rate coefficients, e.g. for $\text{H}^+ + \text{D}_2$.

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