3.1 Bericht Teilprojekt 5

3.1.1 Titel / Title

Reaktionen von gespeicherten kalten Ionen mit H Atomen und interstellar relevanten Molekülen

Reactions of stored cold ions with H atoms and molecules of interstellar relevance

3.1.2 Berichtszeitraum / reported period

01.07.2003 - 31.12.2006

3.1.3 Projektleiter / principle investigator

Gerlich, Dieter, Prof. Dr., Dipl.-Phys., Universitätsprofessor
Institut für Physik, Technische Universität, 09107 Chemnitz

Luca, Alfonz, Dr., wiss. Assistent
Institut für Physik, Technische Universität, 09107 Chemnitz

3.2 Zusammenfassung / Abstract

3.2.1 Wortlaut des Antrags / abstract of the proposal

Für viele **Gasphasenreaktionen** zwischen Ionen und Neutralen ist nach wie vor unbekannt, ob und wie schnell sie **bei tiefen Temperaturen** ablaufen, vor allem wenn es sich einerseits um Radikale wie z.B. das H-Atom oder andererseits um astrochemisch wichtige Moleküle wie CO, CO_2 oder H_2O handelt. Um die Wechselwirkung solcher Reaktanten mit gespeicherten Ionen zu untersuchen, wird in diesem Projekt die Multipolspeicherapparatur AB-22PT eingesetzt, die alternativ mit einem Atom- oder einem Düsenstrahl kombiniert werden kann. Typische Stoßpartner für die H-Atome werden Ionen von CH^+ bis $C_nH_m^+$ sein. Es soll auch untersucht werden, unter welchen Bedingungen das H-Atom einfach "stecken" bleibt, d.h. die Lebensdauer des Stoßkomplexes so lang ist, dass er sich durch Emission von Strahlung stabilisiert. Im Rahmen solcher Messungen wird auch nach Molekülen XY^+ gesucht, die über eine sequentielle Absorption von zwei H-Atomen **katalytisch H_2** produzieren. Eine wichtige, experimentell unbekannte Reaktionsklasse, die ebenfalls untersucht werden soll, ist die ein- bzw. mehrfache **Isotopenanreicherung** bei Stößen von Ionen wie H_3^+, $C_nH_m^+$ oder NH_n^+ mit D-Atomen. Ein weiterer Schwerpunkt der Experimente wird die **Strahlungsassoziation** von Ionen mit kondensierbaren Gasen sein. Von diesem Prozeß nimmt man an, dass er eine dominante Rolle bei der Bildung größerer Moleküle in dichten interstellaren Wolken spielt. Dazu wurden erste Ergebnisse mit der AB-22PT Apparatur erhalten. Die Bildung von protoniertem Methanol beim Stoß von CH_3^+ mit H_2O ist deutlich unwahrscheinlicher als bisher in den chemischen Modellen angenommen. Weitere Untersuchungen zur Wechselwirkung von CH_3^+ mit CO, HCN und CH_3OH oder von H_3O^+ mit C_2H_2 und H_2O sind geplant.

For many **gas phase reactions** between ions and neutrals it is still unknown whether at all and how fast they proceed **at low temperatures**, especially when the targets are radicals such as H-atoms or astrochemically important molecules such as CO, CO_2 or H_2O. In order to study the interaction of such reactants with stored ions, a 22-pole ion trap apparatus (AB-22PT) is used in this project, which can be combined with an effusive beam of slow atoms or a supersonic beam of molecules. Typical collision partners for the H-atoms are hydrocarbon ions ranging from CH^+ to larger $C_nH_m^+$. One (still) unsolved question is under which conditions an H-atom just "sticks", i.e., when the lifetime of the collision complex is so long that emission of radiation leads to its stabilization. In this context also molecules XY^+ are searched for, which may produce **H_2** in a **catalytic cycle** via sequential absorption of two H-atoms. An important experimentally unknown class of reactions, which also will be studied, is single or multiple **isotope enrichment** in collisions of ions such as H_3^+, $C_nH_m^+$ or NH_n^+ with D-atoms. Another subject of the project is **radiative association** of ions with condensable molecules. This process is assumed to be of significance for the formation of larger molecules in dense interstellar clouds. Results for the formation of protonated methanol in collisions of CH_3^+ with H_2O have been obtained and the rate coefficient is significantly smaller than assumed until now. Further systems include the interaction of CH_3^+ with CO, HCN and CH_3OH or reactions of H_3O^+ with C_2H_2 and H_2O.

3.2.2 Zusammenfassung des Berichts / abstract of the report

One of the aims of the *FGLA* was to simulate in the laboratory astrochemical gas phase processes occurring under inter or circumstellar conditions. In TP 5 a rather complicated ultrahigh vacuum apparatus has been developed and characterized which allows to study collisions between cold ions confined in a trap and a neutral beam of atoms, molecules or radicals traversing the trapped ion cloud with a controllable velocity distribution. Special attention has been given to the interaction of H and D atoms with simple molecular ions at temperatures down to 10 K; however, also first experiments with condensable targets have been started.

This report describes briefly the present status of the complex molecular beam - ion trap machine with emphasis on the progress made with the integration of the hydrogen atom beam. This new instrument has been used for measuring rate coefficients for a variety of ions colliding with H- or D-atoms. A general observation is that, in the case of hydrocarbons, collisions with H_2 generally lead to hydrogenation while collisions with H atoms often cause dehydrogenation. Recent models of cold clouds have revealed the importance of deuteration of molecules. Therefore more weight than originally planned has been put onto H - D exchange reactions using deuterium in the discharge source.

Initially it was planned to reach a technical level which allows to operate the machine as a flexible user facility. This goal included not only two traps for gas phase and nanoparticle work, but also several beams of neutral radicals and molecules. Such a universal experimental setup would have allowed to study many different systems, especially with the help and initiatives from guest researchers. In several test arrangements, the potential of the combination of individual modules has been demonstrated. For example, a pulsed supersonic H_2O beam was successfully used for producing protonated methanol from CH_3^+ via association. However, the last years have shown that much more engineering work and another scientific environment would have been necessary for getting the required technical reliability of achieving the aims of the ambitious research plan. In order to continue all the initiatives started in the FGLA, several new collaborative projects have been started. They are mentioned in the outlook. In Tucson, for example, the construction of the next generation of trapping apparatus for astrochemical applications is under construction, supported by an NSF grant.

3.3 Ausgangsfragen, neuster Stand der Forschung / Initial goals, current status of the field

Hydrogen is the most abundant baryonic species in the universe. Therefore, many astrophysical and -chemical processes involve H and H_2. For improving our quantitative understanding of gas phase and surface mediated processes with H radicals, the initial proposal of TP 5 contained an ambitious experimental program. Since both gas phase processes and grain surfaces play a central role in the chemistry of cold clouds, it was planned to construct a versatile atomic or molecular beam machine and to utilize alternatively two modules, a temperature variable 22pole trap and a quadrupole trap for charged nanoparticles.

The research program was quite ambitions as well. One class of astrochemically relevant reactions involves just three atoms in total, e.g., $AH^+ + H$ or $AB^+ + H$. Such systems are simple enough that theoretical methods are capable, at least in principle, to predict reactive cross sections from first principles including all degrees of freedom. The very basic collision system $H_2^+ + H$ has not yet been studied because of parasitic reactions with the H_2 background. Another class of reactions refers to polyatomic systems such as $CH_5^+ + H$, $C_2H_3^+ + H$, $C_3H_2^+ + H$. Basic questions included the role of small barriers in low temperature ion molecule reactions, radiative and ternary association, cyclic and linear isomers, etc. A specific project was the search for complex molecular ions, XY^+, which allow for an efficient catalytic production of H_2 molecules via two sequential association processes, i.e., $XY^+ + H \rightarrow XYH^+ + H \rightarrow XY^+ + H_2$. Finally, deuterium fractionation via collisions with D atoms became an additional weight in the research program. The importance of deuterium enrichment in hydrogen bearing molecules has been discussed for example by Gerlich *et al.* (2002). So far interesting results have been obtained for $XH^+ + D \rightarrow XD^+ + H$ with X=C and CH_4.

As already outlined in the original proposal, there have been very few experiments studying the interaction between ions and H or D atoms under conditions relevant for astrochemistry. The early ICR studies and those using the SIFDT technique have been operated at 300 K or at higher effective temperatures. In gas phase studies, the overall situation has not changed in the last years, while there have been many theoretical and experimental activities aiming at understanding interactions of H atoms with surfaces and ice layers. To our knowledge, there is, besides ours, no low temperatures ion chemistry experiment involving hydrogen atoms. One gas phase result, the interaction of C_n^- or C_nH^- anions with H, has been reported from the Boulder ion group (Barckholtz *et al.* 2001). Another related activity are beam experiments with H atoms, exited to Rydberg states. A joint study has on the state-to-state dynamics of high-n Rydberg H-atom scattering with D_2 has been published recently (Dai *et al.* 2005, Song *et al.* 2005).

Originally it was thought, that a special quadrupole trap for confining and monitoring single nanoparticles could be used in the TP 5 beam machine in exchange with the 22PT. The initial progress (Schlemmer *et al.* 2001, Gerlich 2003) made in our laboratory with the development of the *ultra high precision nanoparticle mass spectrometry* method has stimulated this optimistic planning. Unfortunately the technical and personal reality forced us to cancel this part of TP 5. Nonetheless it is certain (Schlemmer *et al.* 2004) that this experimental method is well-suited for measuring adsorption and desorption of hydrogen atoms on nano-surfaces or to study catalytic formation of H_2 molecules on interstellar grain analogues. An other innovative application is described in the report of TP 7. Some aspects of the state of the art of the nanoparticle trapping method is described in a few recent publications dealing with (i) the determination of light induced forces on isolated micron-size dust particles confined in an electrodynamic trap (Krauß and Wurm 2004), (ii) photoelectric emission measurements on the analogs of individual cosmic dust grains (Abbas *et al.* 2006), and (iii) the observation of charging mechanisms of trapped nanoparticles which have been exposed to soft X-rays (Grimm *et al.* 2006).

3.4 Angewandte Methoden / Applied methods

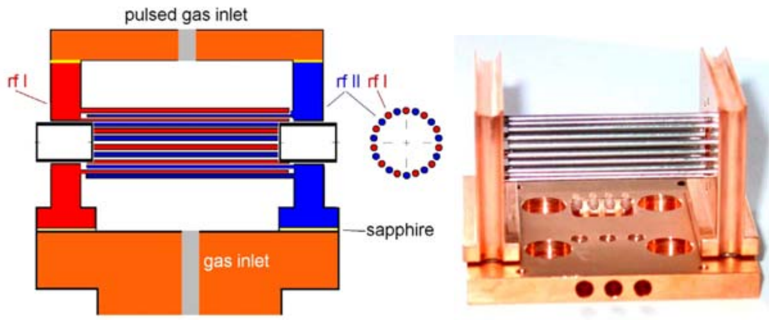

Fig. 1: The 22pole trap shown here has been first described in (Gerlich 1995). Today it is used worldwide in at least eight machines for buffer gas cooling of molecular ions for spectroscopy and reaction dynamics.

Most experiments, performed in TP 4, TP 5 and TP 7 use innovative tools which are based on radio frequency ion guides and traps (Gerlich 1992). The very sensitive instruments allow not only to perform unique fundamental studies of ion-molecule reactions with an unprecedented sensitivity but have also important applications in mass spectroscopy (Gerlich 2003a), chemical analysis (Gerlich 2004), ion spectroscopy (Dzhonson *et al.* 2006, see also TP 4) and nanoparticle research (Grimm *et al.* 2006). One very important module, the 22pole trap, is shown in Fig. 1. Further details of the method, references and its applications in laboratory astrochemistry have been summarized recently (Gerlich and Smith 2006a).

3.4.1 The AB-22PT machine

The Atomic Beam 22-Pole Trap Apparatus (AB-22PT) developed in this project, combines various modules for producing primary ions and neutral reactants with the components from a standard 22pole trapping machine (Gerlich 1995). One version is shown schematically in Fig. 2. A progress report on some technical details and its applications has been presented recently (Luca *et al.* 2005). Since 22PT based machines have been described thoroughly in the literature (see also TP 4) and since many details of the final version will be given in a separate publication (Luca *et al.* 2007) only a few remarks characterizing of the H-atom beam are made here.

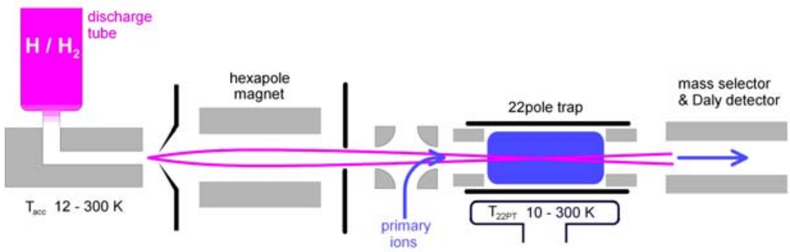

Fig. 2: Schematic view of the combination of a temperature variable (10 - 300 K) 22pole trap with an H-atom beam, focused by an hexapole magnet. Primary ions which are created and mass selected in a part of the machine not shown in the figure, are injected into the trap via an electrostatic quadrupole bender. After a variable storage time in the trap all ions are extracted for mass analysis and detection.

During the thesis work of G. Borodi (2007a) a lot of important additions, modifications and improvements have been made on the AB-22PT machine. More recent progress is due to the graduate student C. Mogo. One of the central technical activities of the last years was the construction of a modular and flexible H atom source and its characterization. The requirements included large flux of atoms, high degree of dissociation, low H_2 background, and slow velocities.

There are many publications describing the creation of H-atoms by dissociation of H_2 molecules using either sufficiently hot filaments or discharges (radio-frequency, microwave). In the present work a standard rf driven plasma source is used. The literature also contains several recipes and tricks for getting dissociation degrees up to 95%. In addition to specific procedures to prepare the surface of the discharge tube and suitable localization of the rf power close to the exit, small amounts of oxygen or water have been added successfully to the purified hydrogen or deuterium. During our tests, G. Borodi has developed a very efficient method to decrease the H-H recombination rate on the walls by coating them with a well-defined amount of water (Borodi 2007a). First results have been presented in 2005 during the Pillnitz meeting, a summary is included in (Luca *et al.* 2007). It is planned to study the specific surface effects which are also of astrophysical interest, in more detail in a specific test arrangement (Borodi, private communication).

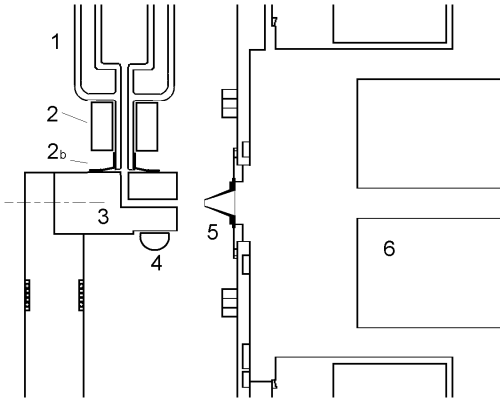

Fig. 3: H-atom source with discharge tube (1), precooling to 100 K (2) and temperature gap (2b). The accommodator (3) cools the atoms to the final temperature determined with a Si temperature sensor (4). A 2 mm∅ skimmer (5) separates first chamber (pumping speed for deuterium 2800 l/s) from the second one containing the first hexapole magnet (6).

For slowing down the H atoms emerging from the hot discharge to velocities which are representative for the low temperatures prevailing in the ISM, cryogenic cooling has been used. As indicated in Fig. 3, the hydrogen atoms pass first through a glass tube surrounded by a precooler (2) followed by a copper piece (3) the temperature of which can be set at values between T_{acc} = 12 K - 300 K. For avoiding recombination it is important that the temperature changes in a very narrow gap (2b) from the 100 K of the preecooler to the final temperature of the cupper piece. The optimum geometry is still searched for.

The effusive beam is skimmed and passes another aperture. All three regions are pumped rather efficiently; nonetheless, the background density of H_2 in the trap is still comparable to that of H. A beam catcher and additional cryo-pumping could reduce this problem. Two hexapole magnets (6) are used for confining those atoms which are in weak field searching states.

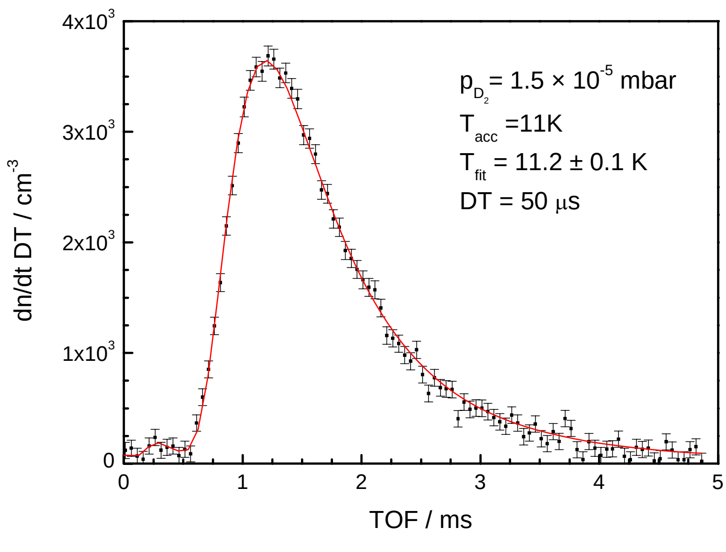

Fig. 4: Measured and simulated TOF distribution of an effusive D_2 beam coming from a T_{acc} = 11 K cold accommodator. P_{D2} is the deuterium pressure in the first chamber, the pressure in the source (3) is several hundred times larger. The red line is a M-B distribution calculated for T_{fit} = 11.2 K.

The number density of H atoms and the H_2 background in the interaction region has been determined by replacing the 22PT with a calibrated universal detector which is based on electron bombardment ionization followed by mass selection and ion counting. At T_{acc} = 100 K, typical H and H_2 densities are some 10^8 cm^{-3} if one operates the discharge at typically 0.03 mbar. Insertion of the hexapole magnets enhances the atomic signal by a factor 25 at 60 K.

At the lowest temperature, T_{acc} = 12 K, the H atom density drops to 2×10^8 cm^{-3}. Due to the sensitivity of the trapping method, this is sufficient to measure rate coefficients down to 10^{-12} $cm^3 s^{-1}$. One advantage to operate the 22PT at 10 K is that condensation of H_2 on the walls reduces the H_2 background to a much lower value, 5×10^7 cm^{-3}.

In order to test the efficiency of the accommodator, velocity distributions have been measured using the universal detector in combination with a chopper wheel. The example shown in Fig. 4. has been taken at T_{acc} =11 K for D_2 molecules (discharge switched off). The comparison of the data with a Maxwell–Boltzmann distribution, calculated for an effusive beam with T_{fit} =11.2 K, reveals that there are enough wall collisions in the channel (1.2 mm diameter and 22 mm length) to thermalize the molecules.

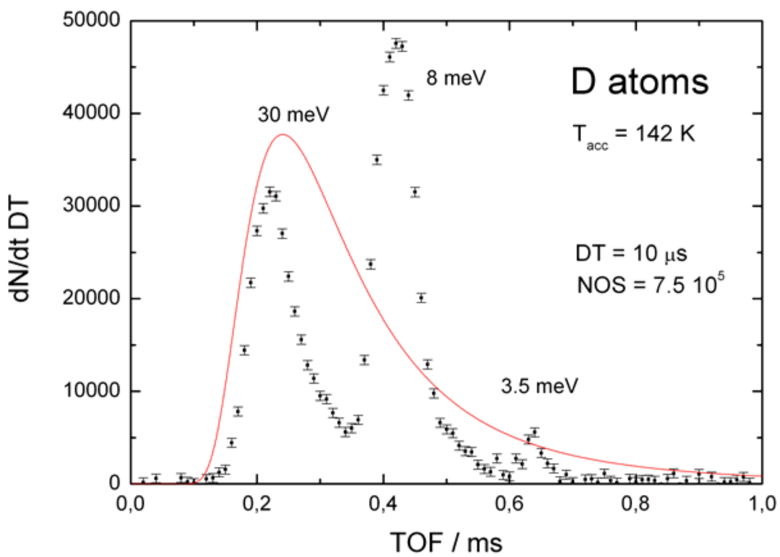

Fig. 5: TOF distributions of D atoms measured for T_{acc} = 142 K. The focusing properties of the two hexapole magnets favor some velocity groups and suppresses other parts. The red curve is a M-B distribution for 142 K.

For the atomic beam, the velocity distribution are structured as can be seen from Fig. 5. This is due to focusing of the effusive neutral beam in the harmonic guiding field of the magnets. For the boundary conditions imposed by the present geometry (see Luca *et al.* (2007) the energies indicated in the figure are transmitted efficiently. The 8 meV peak can be explained by one half wave in the first magnet and a quarter wave in the second one, leading to a parallel beam. Cooling the accommodator to 12 K leads to a beam in which the 3.5 meV part dominates with an half width smaller than 1 meV.

In summary the development of the H-atom beam and its integration into the AB-22PT machine has been very successful (Borodi 2007a). It allows now to study ion-neutral reactions at low ion temperatures and for defined velocity distributions of the H atom beam. Supersonic or effusive beams add to the versatility of the instrument.

3.4.2 Project organization, challenges and problems

During the first funding period it was tried in the group *Gasentladungs- und Ionenphysik* to operate three separate machines devoted to a variety of specific projects both in gas phase and grain chemistry. All projects were based on innovative ion guiding and trapping techniques which, in 1994, have been transferred from Freiburg to Chemnitz. The aim was to improve the machines in a cooperative way, to increase their sensitivity and to utilize or develop together additional tools and new detection schemes. Various ion guides and traps already have been combined in our group successfully with molecular beams, laser based analysis or preparation of selected ions using photons. A number of specific ion sources have been implemented into our machines ranging from standard ionizers via storage sources to a corona discharge source for clusters. Also first steps to integrate a commercial electrospray source have been made. The experimental challenges of our contributions to the FGLA were to measure reactions with H atoms, the integration of a carbon beam, the study of properties of interstellar dust equivalents and the combination with new laser based methods both for spectroscopy and state specific reactivity.

For a variety of reasons the resulting technical demands were to high. One problem was the missing technical support from a technician or a permanent engineer in the laboratory. The mechanical and electrical shops did not have much experience in the sophisticated technical demands of our machines. Moreover the know-how of the group itself decayed after the first generation of graduate students left the TUC. More and more time has been wasted with technical trivialities. As a consequence, it became necessary to reorganize the group in the second funding period. The total number of projects and machines has been reduced in the group. For example the Guided Ion Beam apparatus has been switched off although also this instrument has made significant contributions to astrochemistry as demonstrated with the last publication dealing with ion-molecule reactions of relevance for Titans atmosphere (Nicolas *et al.* 2003).

Other changes were dictated by fluctuations in the personal. The project leader of TP 4 moved with the original 22PT machine to Leiden and later to Köln. There have been significant problems in TP 7 (see report). In 2002, the molecular beam based apparatus and TP 5 was transferred - from a collective of three leaders - to a new assistant (A. Luca). He became responsible, with one graduate student, exclusively for this machine and for its application in the gas phase part of TP 5. These changes finally lead to results which are unique and recognized worldwide.

3.5 Ergebnisse und ihre Bedeutung / Results and their importance

The AB-22PT machine has been used in several developments stages for measuring reactions between a variety of stored ions and the H- or D-atom beam (Borodi *et al.* 2007a) First results have been reported in Luca *et al.* (2005). Since there are no other experiment at all that allow to study the interactions between cold ions and a slow H-atom beam, it was necessary to perform a lot of consistency checks. There are standard reactions, e.g. with CH_4^+ or CO_2^+, which have been used at room temperature for tests and calibration purposes. Other measurements gave new insight into the new field of ultracold chemistry. Many unexpected results have been obtained. For example hydrogen abstraction in $CH_5^+ + H$ collisions occurs at low temperatures, in contradiction to predictions using the proton affinity of methane. In order to query such an "established" value, it became necessary to better characterize the energy distribution of the H atom beam.

<u>$CH_4^+ + H$</u>

Typical features of the AB-22PT apparatus are demonstrated with results measured for the 2.7 eV exothermic reaction (Luca *et al.* 2007).

$$CH_4^+ + H \rightarrow CH_3^+ + H_2 . \qquad (1)$$

Fig. 6 shows the exponential decay of the injected CH_4^+ ions. They have been thermalized to the trap temperature of 80 K via collisions with ambient He buffer gas. The temperature of the H atom source has been set to T_{acc} = 100 K. Although the H-atom density is lower than the H_2 background (see figure caption), formation of CH_3^+ via reaction (1) prevails. In addition a few CH_5^+ are formed via the hydrogen abstraction reaction

$$CH_4^+ + H_2 \rightarrow CH_5^+ + H . \qquad (2)$$

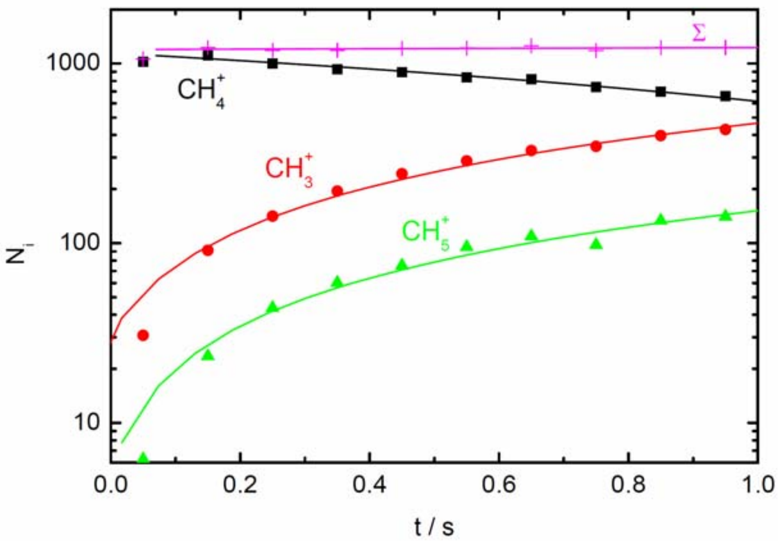

Fig. 6: Reactions of CH_4^+ with hydrogen atoms (0.9×10^9 cm^{-3}, T_{acc} = 100 K) and hydrogen molecules (1.4×10^9 cm^{-3}) at T_{22PT} = 80 K. Plotted is the averaged number of ions per filling, N_i, as a function of the storage time t. The ions are thermalized via collisions with He (3.7×10^{12} cm^{-3}).

This reaction is rather slow at 80 K, $k = (1.1 \pm 0.2) \times 10^{-10}$ cm^{3}s^{-1}, in accordance with recently publisher 22PT results (Asvany *et al.* 2004a). The rate coefficient for reaction (1) has been determined to be $k(80\text{ K}) = (5 \pm 1) \times 10^{-10}$ cm^{3}s^{-1}.

<u>$CO_2^+ + H / H_2$</u>

Another reaction which is of importance for characterizing the machine, has been studied some time ago by Tosi *et al.* (1984) in a drift tube at energies between 60 and 140 meV. These measurements have shown that CO_2^+ ions react both with atomic and molecular hydrogen with a rather large rate coefficients. Fortunately, the reactions lead to different products,

$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H\,, \qquad (3)$$
$$CO_2^+ + H \rightarrow HCO^+ + O\,. \qquad (4)$$

Therefore this reaction can be used as an *in situ* calibration standard for the effective H and H_2 number density prevailing in the ion trap (Luca *et al.* 2007).

In addition, the two reactions (3) and (4) and the deuterated variants have been studied at temperatures between 20 K and 300 K. Although exothermic, reaction (3) increases significantly with decreasing temperature,

$$k_{H2} = 1.0 \times 10^{-9}\ \text{cm}^3\text{s}^{-1}\ (T / 300\ \text{K})^{-0.23}\,,$$
$$k_{D2} = 0.5 \times 10^{-9}\ \text{cm}^3\text{s}^{-1}\ (T / 300\ \text{K})^{-0.38}\,,$$

while reaction (4) is independent both on the ion temperature and the H atom energy,

$$k_H = 4.4 \times 10^{-10}\ \text{cm}^3\text{s}^{-1}\,,$$
$$k_D = 2.3 \times 10^{-10}\ \text{cm}^3\text{s}^{-1}\,.$$

A publication of these interesting results is in preparation (Borodi *et al.* 2007b).

<u>$CH^+ + H$</u>

CH^+, the simplest hydrocarbon ion, was the first charged molecule discovered in the interstellar medium. Whereas early simple gas-phase models predicted the observed neutral CH abundances quite well, this was not the case for ionic CH^+. The pathways of its synthesis are still subject of discussions. Given the ubiquity of H atoms, the reaction

$$CH^+ + H \rightarrow C^+ + H_2 \qquad (5)$$

represents an important destruction mechanism of CH^+. Until recently the rate coefficient for reaction (5) has been predicted just by using phase space theory (Gerlich *et al.* 1987). Our first measurements which have been reported by Luca *et al.* (2005), are depicted in Fig. 6. The temperature dependence is in accord with the trend predicted by the high temperature SIFDT data.

While phase space theory is in reasonable agreement with the measured data, the RIOSA-NIP calculations underestimate the measured values significantly. It is obvious that more theoretical developments are needed in order to understand this fundamental triatomic hydrocarbon collision system from first principles. For stimulating theoreticians, additional experimental results at different trap temperatures (i.e. for different rotational populations of CH^+), for various energies of the H-atom beam, and for deuterated variants (see below) will be reported soon (Borodi *et al.* 2007c).

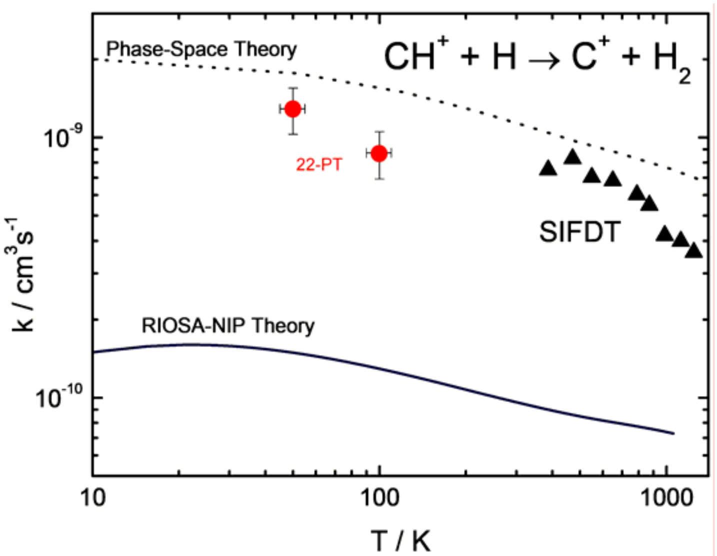

Fig. 6: Temperature dependence of the rate coefficient for hydrogen abstraction in CH^+ + H collisions (Luca *et al.* 2005). The results of phase space theory are slightly larger while calculations using the RIOSA-NIP method (Stoecklin and Halvick 2005) are one order of magnitude to small.

$CH_5^+ + H$

The CH_5^+ ion has attracted a lot of interest in recent years (see TP 4 and Gerlich 2005). As discussed briefly by Luca *et al.* (2005) a rather surprising result has been obtained for the reaction

$$CH_5^+ + H \rightarrow CH_4^+ + H_2\,. \qquad (6)$$

Based on accepted thermodynamical data the thermal rate coefficient for this reaction should become negligible at temperatures below 80 K (see dotted line in Fig. 7). Nonetheless a significant CH_4^+ production rate has been observed at the coldest conditions T_{22PT} =10 K and T_{acc} =12 K. Our standard analysis results in a rate coefficient of 10^{-11} cm^3s^{-1}. However, as discussed above, the hydrogen beam has a mean kinetic energy of 3.5 meV under these conditions. In order to predict the effective rate coefficient as a function of the kinetic energy of the H atoms, a more detailed analysis is necessary. Corresponding work including the separate determination of the proton affinity of methane, is in progress and will be published soon (Borodi *et al.* 2007c).

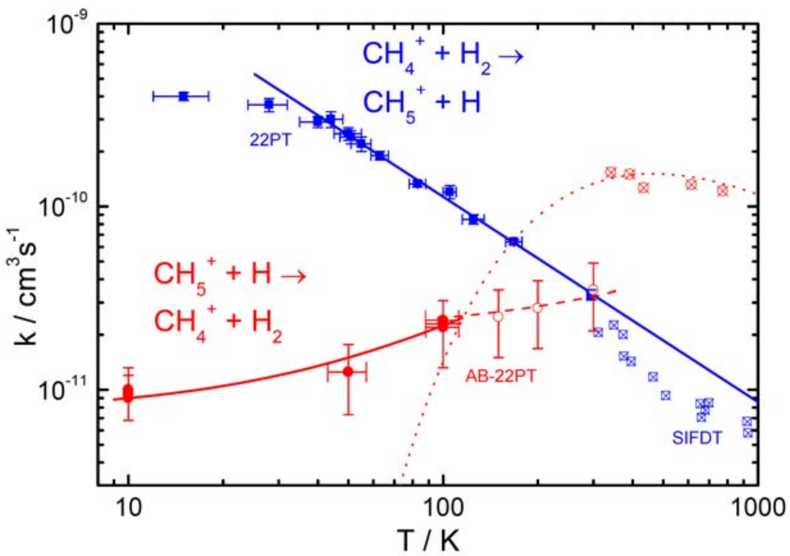

Fig. 7: Temperature dependent rate coefficients for the reaction $CH_4^+ + H_2 \rightarrow CH_5^+ + H$ (Asvany *et al.* 2004a) and its backward reactions (Luca *et al.* 2005). The high temperature data have been obtained with a SIFDT apparatus while low temperature data have been measured in two different 22pole traps. The solid red circles have been measured for $T = T_{acc} = T_{22PT}$, the open ones for T_{acc} = 100 K and $T = T_{22PT}$.

Low temperature deuterium fractionation

During the 6 years of our FGLA activities, observation of singly and multiply deuterated molecules became quite popular, requiring new reaction rates for understanding the astrophysical process of deuterium fractionation. Some aspects have been discussed for example by Roberts *et al.* 2004. Closely correlated to these activities, we have started dedicated laboratory studies (Gerlich *et al.* 2002a, Gerlich and Schlemmer 2002b, Asvany *et al.* 2004b, Schlemmer *et al.* 2006). The work has concentrated first on reactions with HD. Later D_2 has been used, too (Gerlich *et al.* 2006b) since this molecule may be quite abundant in cold interstellar clouds. In addition we have started in TP 5, to put some emphasis on H-D exchange reactions in collisions of hydrogenated ions with D atoms.

One important result was the experimental verification, that CH_5^+ ions cannot be deuterated in collisions with HD. The rate coefficient is smaller than 4×10^{-17} cm^3 s^{-1} (Asvany *et al.* 2004a). Since it was speculated that deuteration of protonated methane could be achieved by the simple exchange

$$CH_5^+ + D \rightarrow CH_4D^+ + H\,, \qquad (7a)$$

we have studied this reaction; however, also in this case the rate coefficient is too small, $k = 1.3 \times 10^{-12}$ cm^{3}s^{-1}, that reaction (7a) could play a role in astrochemistry. In addition it competes with HD formation via

$$CH_5^+ + D \rightarrow CH_4^+ + HD\,. \qquad (7b)$$

The rate coefficient for reaction (7b) has been determined to be $k = 5.5 \times 10^{-13}$ cm^{3}s^{-1}. No formation of CH_3D^+ could be detected above the background. Comparison with the results shown in Fig. 7 reveals that there is a strong isotope effect: hydrogen abstraction in reaction (7b) is 40 times slower than in reaction (6).

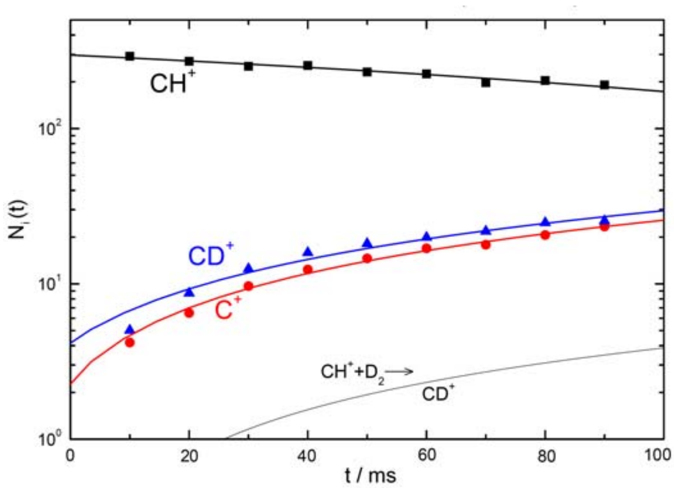

Fig. 8: Reaction of CH^+ with D (8×10^8 cm^{-3}) and D_2 (3×10^9 cm^{-3}) at T_{22PT} = 80 K and for T_{acc} = 36 K. As indicated by the simulation in the lower part, contributions to CD^+ via reactions with D_2 are negligible.

A similar competition between H-D exchange and hydrogen abstraction occurs in

$$CH^+ + D \rightarrow CD^+ + H \qquad (8a)$$

$$\rightarrow C^+ + HD\,. \qquad (8b)$$

As can be seen from Fig. 8, both channels react very fast ($k = 1.2 \times 10^{-9}$ cm^{3}s^{-1}) while reactions with the 3 times more abundant D_2 is negligible.

There are some speculations that pre-protostellar cores can become so cold that all heavy elements vanish from the gas phase and become integrated into ice layers coating dust grains. In such a situation the hydrogen chemistry gets an enormous weight as illustrated by the simulations carried out by Walmsley *et al.* (2004). Inspection of the table of reactions they use in their model reveals that many of the rate coefficients are based on pure speculations. This statement also holds for the important class of low temperature collisions with H or D atoms.

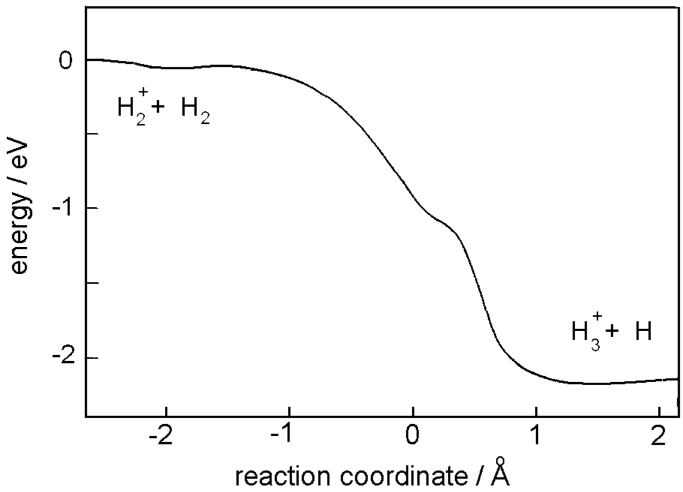

Fig. 9: Schematic illustration of the H_4^+ interaction potential along the reaction coordinate. Low temperature collisions are significantly influenced by the long range attractive van der Waals interaction (not to scale).

The overall status of our present knowledge about $H_mD_n^+$ collision systems has been reviewed recently for m+n ≤ 5 (Gerlich *et al.* 2006b) ranging from the simple 3 protons 2 electrons system $H^+ + H_2$ to the complex five center reaction system H_5^+. An intermediate case is the four center system H_4^+. Relevant for the work of this project and important for astrochemical applications is the scrambling reaction

$$H_3^+ + D \rightarrow H_2D^+ + H \qquad (9)$$

which is exothermic by 860.1 cm^{-1} (598 K). So far there are no measurements available with cold ions; however, it is planned that they will be a part of C. Mogo's thesis. As can be seen from Fig. 9, this process occurs on a very weakly interacting potential energy surface which is presently calculated with modern methods (J. Bowman, private communication 2006). A special interesting aspect of H - D interaction is the role of nuclear spin or, with other words, the fact that there are mainly fermions in reaction (9) while bosons dominate in the D_3^+ + H collision system.

Reactions with other radicals and condensable gases

It was planned to use the AB-22PT arrangement in addition for studying collisions between cold ions and condensable gases using molecular beams. With a pulsed beam first results have been obtained for association of CH_3^+ with H_2O at low temperatures (Luca *et al.* 2002). In principle it is no problem to replace the complicated atomic beam with a beam of a molecule of astrochemical importance such as CO, H_2O, HCN, NH_3, C_2H_2, CH_4, CH_3OH, or CH_3CN. Because of condensation reactions with these targets cannot be studied in the standard 22PT. As explained in Section 3.4 this goal could not be reached, exclusively because of lack on suitable men power.

3.6 Zusammenfassung und Ausblick / Summary and future

Zusammenfassung / Summary

In the center of the activities of TP 5 was hydrogen, especially in its atomic form. Although this atom is the simplest one - just one electron and one proton - and although it is several orders of magnitude more abundant in the universe than any other element, there have been almost no studies of specific reactions which may be, for example, of basic importance for star formation in very cold gas clouds.

The central engineering challenge was the development of the *Atomic Beam 22-Pole Trap Apparatus* (AB-22PT), a complex ultrahigh vacuum machine in which several innovative modules had to be combined and tested. The central element is our 22pole ion trap, a very sensitive instrument which not only allows to perform unique fundamental studies of ion-molecule reactions with unprecedented sensitivity but also has important applications in mass spectroscopy, chemical analysis, and ion spectroscopy. In this device the temperature and pressure can be lowered so far that one can simulate conditions prevailing in "dense" pre-protostellar discs. Another technical problem was the construction of a modular and flexible H- or D-atom source and its characterization. Most requirements such as sufficiently large flux, high degree of dissociation, low H_2 background, and slow velocities have been fulfilled. The new machine - it is still a prototype - allows now to study collisions between cold ions confined in the trap and a neutral beam of atoms, molecules or radicals traversing the trapped ion cloud with a controllable velocity distribution.

During the various stages of development, the instrument has been used for studying reactions between ions of astrochemical importance and cold hydrogen atoms. Since there exist worldwide no other experiment at all that allows to study these class of processes, it was necessary to perform specific consistency checks. Standard reactions, e.g. with CH_4^+ or CO_2^+, have been used at room temperature for tests and calibration. Several unexpected results have been obtained with the innovative instrument. For example hydrogen abstraction in $CH_5^+ + H$ collisions is not in accord with the proton affinity of methane. In order to query such an "established" value, it became necessary to characterize the energy distribution of the H atom beam. Another important class of reactions, we have started to explore is **isotope enrichment** in collisions of ions with D-atoms. In cold H and D containing chemical reactions, the nuclear spin plays a central role, or with other words, H and D are not really chemically equivalent at very low temperatures. In addition to differences in zero point energies, caused by the different masses of the isotopes, exchange processes are influenced by the fermionic and bosonic properties of H and D, respectively.

Ausblick / future

This project has made unique contributions to low temperature astrochemistry and opened up new fields of research. Unfortunately A. Luca has decided - very recently - to leave the university this year; however, there are various plans how the new instrument itself could be used in the future after C. Mogo has finished the experimental work for his thesis.

Our FGLA activities have stimulated several other groups to use low temperature multipole traps or nanoparticle traps for new applications. In order to continue some of the initiatives started in the FGLA, we have contributed to the planning and development of several new projects in Heidelberg, Basel, Prag and especially Tucson. In the Max-Planck-Institute für Kernphysik in Heidelberg, a 22PT ion source has been developed with our help for determining state selective rate coefficient for dissociative recombination in low-energy $H_3^+ + e^-$ collisions (Krekel *et al.* 2005a, 2005b). First evidence for nuclear spin effects has been obtained recently (Wolf *et al.* 2006). Our method of laser induced reactions has been used successfully for characterizing the stored H_3^+ ion cloud (Mikosch *et al.* 2004). It is planned to continue - together with S. Schlemmer (TP 4) and J. Glosik (Prague) - the fruitful cooperation in order to gain more information on the $H_mD_n^+$ collision system (Gerlich *et al.* 2006b). In Basel a new apparatus has been developed in collaboration of John Maier with us with the aim of measuring the electronic spectra of large ions at low vibrational and rotational temperatures, as of relevance to astronomical observations (Dzhonson *et al.* 2006).

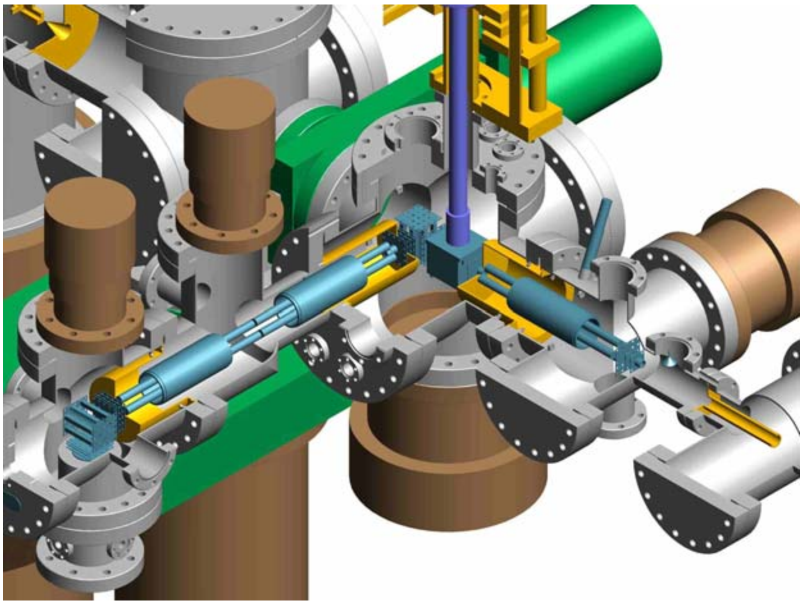

Fig. 10: Next generation trapping machine for astrochemical applications (PI: M. Smith, University of Arizona). Ions which are prepared in the lower left part interact in a multipole trap (in the center) with a beam of radicals coming from the upper left part. The detector is on the right side. The temperature can be varied over a wide range (4-700 K) using liquid He cooling or heating.

A new large project which is very closely related to the activities of TP 5, has been started recently in Tucson. In the center is the construction of a machine similar to ours (see Fig. 10). It is supported by an NSF grant (PI: Mark A. Smith, University of Arizona) and an NSF CRIF-Instrument Development grant (Co-Investigator D. Gerlich). It can be foreseen that several of the ambitions experiments of astrochemical importance which could not be performed in the last 6 years in Chemnitz may be performed in this new machine. The scientific environment in Tucson ranging from world class astrophysics to laboratory astrochemistry certainly will stimulate a lot of new ideas and projects.

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