

Laboratory astrochemistry: studying molecules under inter- and circumstellar conditions

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Abstract

In this paper, we outline recent developments in and the growing need for laboratory astrochemical measurements. After a short review on experimental methods, we focus primarily upon the utility of multi-electrode ion trapping methods for addressing key problems in reaction dynamics and their applications towards gaining a better understanding of the physicochemical driving forces behind compositional development in interstellar and circumstellar environments. Temperature variable trapping techniques, combined with lasers and molecular beams are unique tools for studying state specific reactions, for ion spectroscopy and for investigating the structure and stability of complex charged objects as a function of their internal energy. Particular emphasis is given to reactions with hydrogen atoms and molecules, H–D exchange leading to isotopic fractionation, problems in hydrocarbon ion chemistry and association chemistry in rarefied environments. In the outlook, we discuss the future needs in astrochemistry in order to pave the way towards understanding the next generation of sophisticated astronomical observations and to prepare for them.

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1. Introduction

About 90% of the known matter of the universe is in the stars; the remaining 10% represent the inter- and circumstellar matter (99% gaseous, 1% grains). Observational astronomy both from the ground and from space has provided a wealth of very detailed information on this matter. In order to exploit these truly unique data and to prepare new observations, it is not sufficient to identify the molecules in various regions via their spectral fingerprints but it is necessary to understand, on a fundamental level, the physical and chemical interaction of electrons, atoms, molecules and nanoparticles among each other and with radiation.

Many of the interstellar molecules, of which more than 100 different ones have been observed today, are anticipated to be synthesized at very low temperatures, often via unusual chemical processes such as radiative association, on icy surfaces of grains or via photochemistry. Molecules are also formed in stellar outflows, where the emitted material starts at temperatures above 5000 K and cools down to 50 K

and where the number density goes from very high values approaching 10^{12} down to 10^6 cm⁻³ and lower. Moreover, a rich chemistry takes place in shocks, during the birth of a star or in formation of planetary systems. To truly understand such environments and what are the most important processes or physical conditions leading to these disparate processes, one must have methods which can properly simulate and prepare a diverse range of physical and chemical conditions for direct studies.

In this paper, we first make a few general remarks concerning the typical characteristics experimental methods should have to be useful in the field of astrochemistry. Then we focus on recent progress made by the use of radio frequency (rf) based trapping devices. The various applications ranging from bimolecular collisions to state specific studies or spectroscopy indicate that a variety of unique experiments can be performed if one combines traps with other innovative modules or tools. In the results section, a few collision systems of astrochemical interest are summarized all of which seldom follow the standard

expectations. In the outlook, we mention a few ongoing and planned activities and speculate on future extensions of trapping techniques.

2. Experimental

2.1. Technical requirements

Since astronomical sources are at very different physical conditions from those in the terrestrial laboratory, it is necessary to develop methodologies the results of which can be directly or indirectly applied to the understanding of the formation or destruction of molecules in space. Progress in techniques and results dealing with neutral reactions have been reported recently [1, 2], whereas here we concentrate on charged objects, mainly for experimental reasons. In the past often standard instruments have been used which have been developed for other purposes, e.g. beam, swarm or ICR techniques. Some related aspects are summarized in a recent review on *mass spectrometric approaches to interstellar chemistry* [3]; however, there are severe limitations of the application of ‘standard’ methods to the field of astrochemistry. Many recent results including bimolecular reactions, photostability of cold molecules or the role of weakly bound or long lived complexes, corroborate that room temperature studies or non-thermal conditions often lead to erroneous conclusions concerning the importance of certain processes in the chemical evolution in space.

One of the experimental challenges was and still is to perform reliable experiments at temperatures prevailing in the inter- or circumstellar regions or other environments. Using cryogenic cooling or supersonic expansions, temperatures down to a few K have been achieved in instruments based on swarm techniques, beam methods, or traps [4–8]. Of importance are also measurements performed at high temperatures or at kinetic energies of a few tens of an eV [9]. For exploring this range, flow tubes are heated or combinations of thermal flow-drift tube techniques are used. A very versatile tool in the transition range from thermal energies to a few eV is the guided ion beam method. Each of these approaches address particular advantages regarding either measurement of systems in thermal equilibrium, state selective measurements of reactivity or reactivity over broader ranges of kinetic energy.

Another important feature desirable for astrochemical experiments is the flexible variation of the reactants. While there are many ways to prepare specific ions, also in defined states, there are no routine methods to study their interaction with specific targets, e.g. radicals or condensable gases in a cold environment. In addition it has been shown that it is very advantageous to vary the buffer or target gas densities over many orders of magnitude. Detailed information is gained if one can operate an instrument from single-collision conditions all the way to the saturated three body limit or such that the reaction system can be in complete radiative equilibrium with its thermal surroundings or a laser field. In order to follow complex reaction networks pulsed gas inlets allow study of each step directly following internal excitation or as a species collisionally comes to equilibrium with the walls through buffer gas cooling.

2.2. Rf based devices

As already mentioned above, there are a variety of experimental approaches for studying the structure and reactivity of molecules in the laboratory. Interesting results and detailed discussions can be found in the recent literature [1, 3], [6–8]. In this paper, we concentrate on recent developments of innovative instrumentation for astrochemistry which are based on the rf trapping or guiding technology [10].

The use of specific inhomogeneous, time-dependent, electrical fields for guiding and trapping charged objects, has been reviewed already quite often [11, 12], therefore no details are repeated here. The working principle, which is based on an adiabatic approximation can be used for confining electrons, ions, clusters or charged microscopic particles, the only parameter which has to be adapted being the rf or ac frequency. Typical applications include strong focusing lenses in accelerator physics, the Paul trap, the Guided Ion Beam technique or multi-electrode traps. It is important to emphasize that applications are not only restricted to multipoles or ring electrodes but that one has a wide flexibility to construct dedicated electrode geometries, e.g. labyrinths for thermalization. A general feature of traps is the ability to store objects, be it a single one or an ensemble, over very long times and to expose them, perhaps through various sequences, to photons, electrons, atoms or molecules. Due to the high sensitivity and versatility, this opens up many unique measuring procedures: very small rate coefficients such as radiative association become accessible [11]; chemical probing allows one to ask very specific questions [13]; laser initiated changes in the ion cloud provides detailed information on photon-particle interactions. Some examples are given below.

In contrast to general opinion, which is often based on experience from Paul traps, the rf has only a small influence on the kinetic energy of the ions if a multi-electrode arrangement is used [11, 14]. During the developments and explorations of temperature variable ion traps, a variety of strategies and methods have been tested to characterize in detail the temperature of the stored ions [6, 15]. Chemical reactions such as clustering or near thermo-neutral processes such as isotope exchange can be used as a ‘thermometer’, provided that the specific rate coefficients $k_i(T)$ are known. More detailed information can be obtained if one uses laser based methods. If the spectral resolution is sufficient the ion velocity distribution can be determined from the Doppler profile [16]. As discussed in [17], determination of the temperature from the actual population of low-lying states can simultaneously provide information on low-energy collisions on a state specific level.

2.3. Flexibility by combining modules

For studying matter under the extreme conditions prevailing in space, a variety of dedicated rf based instruments have been constructed in the past ranging from the guided ion beam instrument [14] via the liquid nitrogen cooled ring electrode trap [18] and the *standard* 22PT [12] to specific traps for dust equivalents [19]. Meanwhile, low-temperature traps are also used as sources for cold ions at the Heidelberg storage

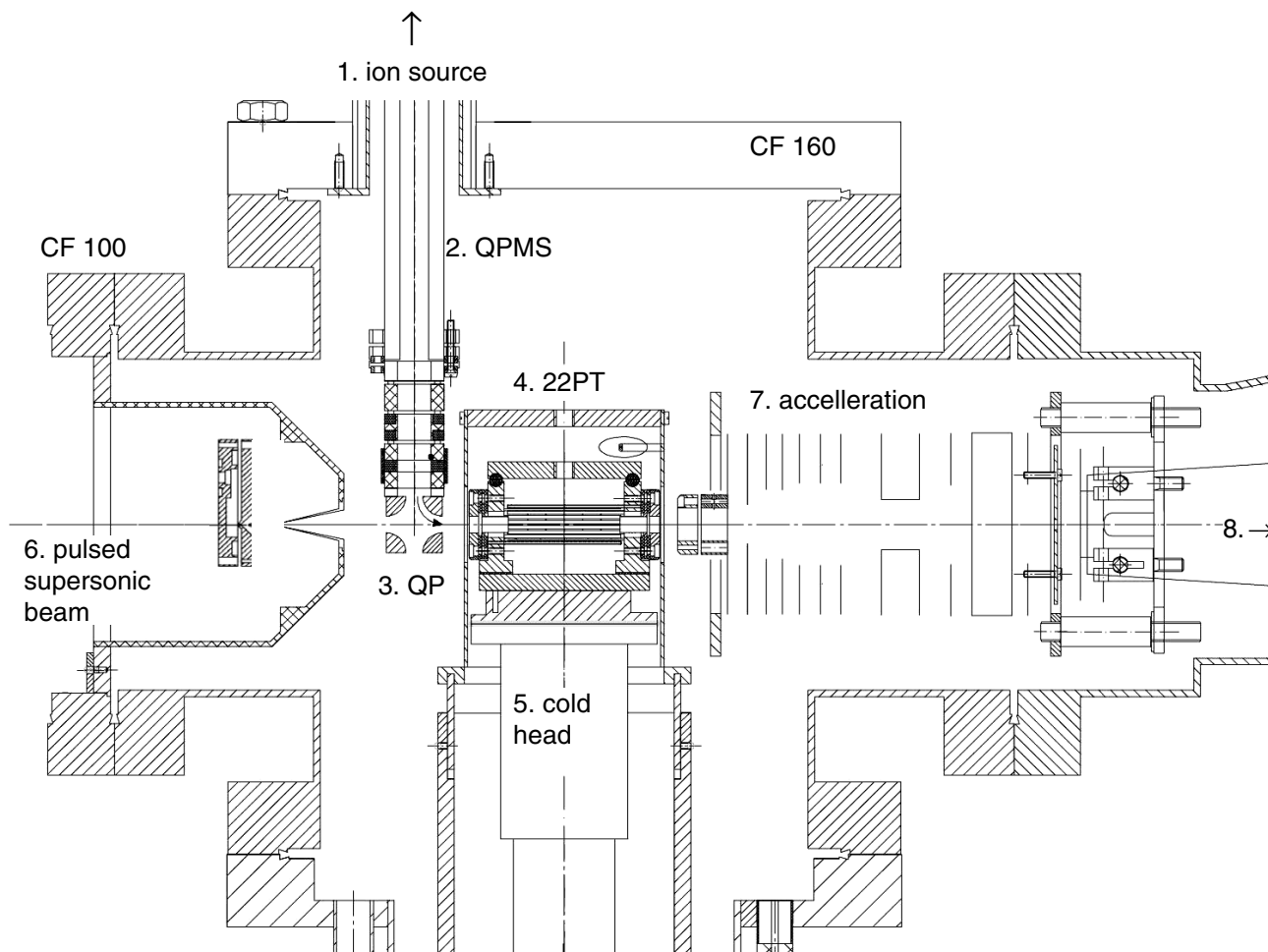


Figure 1. Construction details of the arrangement of a temperature variable 22-pole ion trap and a pulsed supersonic beam in a CF100/CF160 cross. Primary ions are produced in a storage ion source (1, not shown), mass selected in a quadrupole mass analyser (2), deflected in the quadrupole bender (3) and injected into the rf 22-pole trap (4) which is mounted on the two stages of a cold head (5, variable from 4 K to room temperature). There the ions are confined by the rf field and dc voltages applied to the entrance and exit electrodes (~ 100 mV). Buffer gas is used, usually He, for thermalizing the ions. From the left a skimmed molecular beam (6) traverses the trap without colliding with the cold surfaces. For detection, the stored ions are extracted to the right, accelerated to 2 keV (7), mass selected in a magnetic field (8), and counted via a Daly detector. A laser beam can be injected via the detector tract for state selective excitation of the trapped ions.

ring aiming at measuring state selective rate coefficients for dissociative recombination of H_3^+ with e^- [20]. An arrangement, presently used in our group for determining the state populations of cold and ultracold molecular ions such as H_2D^+ via overtone laser induced reactions, is depicted in figure 1 and explained in the figure caption. Several sources can be used for preparing the ions. In specific cases, also the trap itself can be used to synthesize specific reactive precursors, e.g. CD_3H_2^+ via association of CD_3^+ with H_2 [21]. The stored ions are extracted, mass analysed in a quadrupole or magnetic mass spectrometer and detected using single-ion counting. Also the combination of a ring electrode trap with a TOF mass spectrometer has been tested successfully [22].

An important modification extending the features of the ‘standard’ 22PT machine [12, 23, 24] is the injection of the ion beam via a dc quadrupole bender. This allows easier integration of atomic and molecular beams or lasers into the machine. Applications include chemical probing of fine-structure transitions in Ar^+ ($^2\text{P}_1$) ion via electron transfer from H_2 [25], reactions between trapped ions and Ni-atoms [26] or low-temperature collisions with CO and H_2O [27]. A

slightly different approach was used to combine a trap and a graphite sublimation source for providing a neutral C_n ($n = 1\text{--}3$) target [28]. For studying reactions with hydrogen atoms, a dedicated trapping machine has been constructed which is shown schematically in figure 2 [29]. Important features of the new setup, the details of which will be published elsewhere, include the possibility to change the velocity distribution of the H atoms and the hexapole magnets for guiding the atoms and for differential pumping. A few additional hints are given in the caption of figure 2. First results are briefly mentioned below.

The acquisition of spectra of molecular ions remains a formidable task since ions are hard to produce in large enough quantities needed for standard spectral methods such as absorption or fluorescence. It can be expected, that laser-trap arrangements together with collisional probing will more and more contribute to ion spectroscopy. So far, successful applications include visible and infrared action spectra of N_2^+ [16], C_2H_2^+ [17], H_3^+ [30] and CH_5^+ [31]. Some more aspects of this innovative tool for ion spectroscopy and additional references can be found in [32]. Most systems studied so far

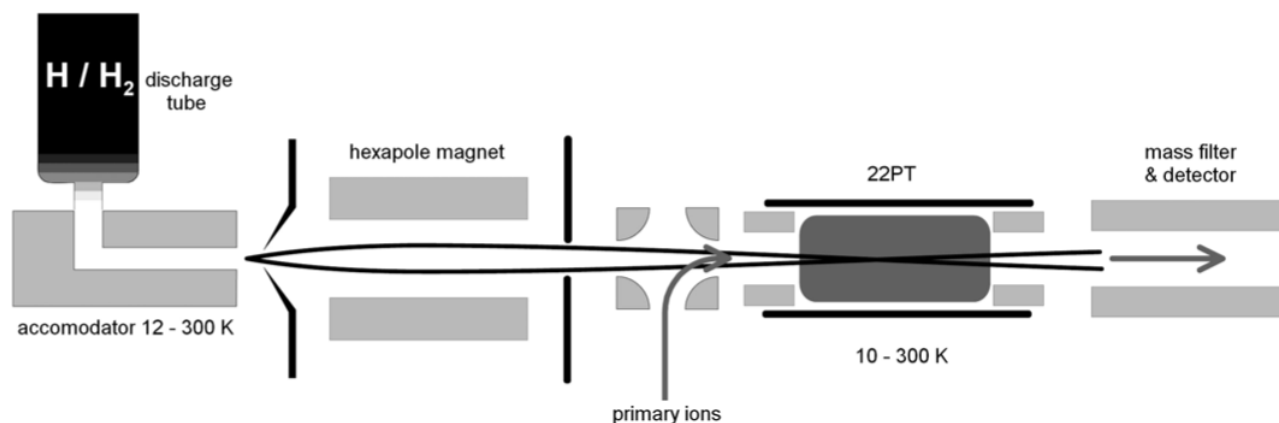


Figure 2. Schematic diagram of the Atomic Beam 22 Pole Trap (AB-22PT) apparatus [29]. This instrument has been developed for studying cold trapped ions (T_{ion}) with H atoms the velocity distribution of which can be selected via the accommodator (T_{H}). Two hexapole magnets focus the beam into the trap. At $T_{\text{H}} = 100$ K the mean density (overlap averaged) of both H and H_2 is 10^9 cm^{-3} . At the lowest temperatures achievable ($T_{\text{H}} = 12$ K, $T_{\text{ion}} = 10$ K) condensation reduces the densities to $[\text{H}] = 2 \times 10^8 \text{ cm}^{-3}$ and $[\text{H}_2] = 5 \times 10^7 \text{ cm}^{-3}$. Due to the high sensitivity of the trapping technique, this is sufficient to measure rate coefficients smaller than $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for reactions between ions and H atoms.

suffered from the fact that the gas used for chemical probing (Ar, CO_2) restricts the temperature range due to condensation. A skimmed molecular beam as shown in figure 1 will eliminate this problem. Moreover detection of laser induced products may be simplified due to the specific reaction geometry, a well-defined neutral beam passing through a near stationary ion cloud, in combination with specific reaction dynamics. In most collision systems, laser excitation starts a complex reaction network and it is an experimental challenge to make use of all experimental possibilities the trap-laser-beam combination offers (storage time, laser duration and power, buffer and target gas density, pulsed gas inlets) for getting quantitative information on all elementary reaction steps involved, including also astrochemically important relaxation and excitation rate coefficients. An important advantageous fact is that one operates with a small, fixed number of confined ions (typically 1000 per filling) which allows one to depopulate specific states.

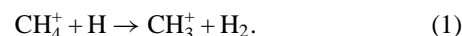
Chemical reactions occurring on interstellar dust are a real experimental challenge since these nanoparticles behave quite differently from laboratory surfaces. This is caused by the small heat capacity (temperature spiking), the composition (substrate and ice layer), the radius of curvature, the charge state, magnetic properties, or quantum size effects for particles of a few nm. Specific experiments which are based on storing single-charged objects in time-dependent fields, have made the very first contributions to this field. Of importance for understanding basic processes such as sticking or desorption of gas or catalytic activities is the nanoparticle mass spectrometry (NPMS) method [19]. Note that only *one single* object is used in this approach and that changes in particle mass or other properties are continuously monitored with high resolution. The exact localization of the particle in a suitable ac trap (in principle sub- μm) makes it perfectly suited to sensitive optical detection (scattering, fluorescence, absorption, etc). Presently the method is used for *in situ* characterization and modification of hot trapped carbon particles via their blackbody emission.

3. Summary of typical results

Within the last 15 years many astrochemically important gas phase processes have been studied in traps; however, it must be stated that many more rate coefficients etc. could have been measured if one compares the potential of the technique with other methods used in ion chemistry and mass spectrometry. Nonetheless, there is not the space here to summarize all results obtained for elementary reactions, radiative association, isomerization, isotope fractionation, etc. In the following, a few very recent results are mentioned, especially reactions with H atoms, the growth and deuteration of small hydrocarbons and reactions with polar molecules.

3.1. Collisions involving H atoms

Despite the fact that H is the simplest atom, experiments with a well prepared ensemble of this radical are still a challenge. As a consequence, many interactions of H with ions, radicals and surfaces are unknown or in some cases in error. The most obvious example is the interstellar formation of the H_2 molecule itself from two atoms. Other examples include specific state-to-state cross-sections, ortho-para transitions of H_2 in collisions with H, and H-D isotopic scrambling. The new instrument shown schematically in figure 2, allows us to study a variety of important and interesting gas phase processes under controlled conditions. Figure 3 shows a typical set of data obtained for the reaction



Plotted is the number of primary and product ions per filling as a function of storage time. Obvious is the exponential decay of the CH_4^+ ions with a time constant of ~ 1.4 s. This reactive loss is mainly due to CH_3^+ formation via reaction (1) while the reaction of CH_4^+ with the ambient H_2 , leading to CH_5^+ , is much slower [23]. The sum of all ions is independent of storage time, indicating that all charges are safely confined in the trap. More details concerning the experimental parameters and the

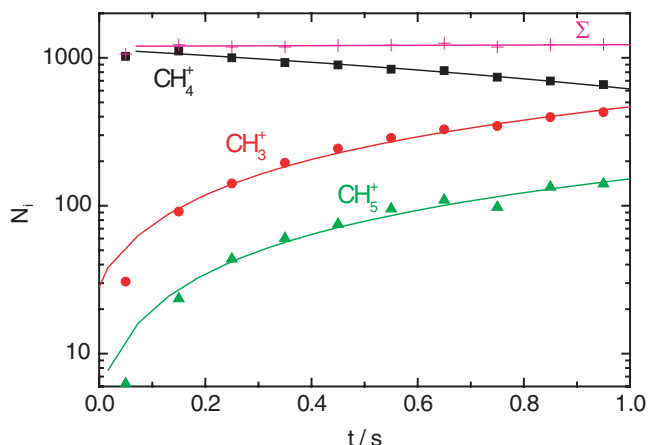


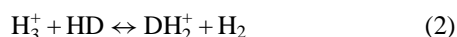
Figure 3. Reactions of initially injected CH_4^+ ions ($T_{\text{ion}} = 80$ K) with hydrogen atoms ($[\text{H}] = 9 \times 10^8 \text{ cm}^{-3}$, $T_{\text{H}} = 100$ K) and molecules ($[\text{H}_2] = 1.4 \times 10^9 \text{ cm}^{-3}$) studied in the AB-22PT shown in figure 2. Plotted is the number of ions per filling, N_i , as a function of the storage time t . The rate coefficient for reaction (1) is $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 80 K and increases slightly towards lower temperatures.

resulting rate coefficient are given in the figure caption. In an early ICR experiment [33] reaction (1), although 2.7 eV exothermic, has not been observed. This may be due to an experimental error or indicate a very steep temperature dependence. Related measurements are in progress. More ions the reactions of which have been studied recently with H, include NH^+ , CO_2^+ , CH^+ , CH_3^+ , C_2H_3^+ and C_3H_2^+ [29]. A comparison of the experimental findings with theoretical results or expectations indicates that our understanding of these systems is still quite limited.

3.2. Deuteration

In order to correlate quantitatively the enrichment of deuterated molecules, observed in astrophysical environments, with the ambient D/H isotope ratio, one has to know in detail the kinetics and dynamics of many physical and chemical processes including radiative transitions, inelastic collisions and chemical reactions. In addition one has to account for the fact that astrophysical environments are generally not in thermal equilibrium, especially concerning the ortho- to para-hydrogen ratio. As a consequence it is rather certain that interstellar-isotopic fractionation cannot be predicted using simple thermodynamics or the statistics of equilibrium systems. The situation has been illustrated with the astrophysically important H^+H_2 collision system in several isotopic variants [34]. This fundamental system is well understood, and most experimental results are in good accordance with predictions from a dynamically-biased statistical model.

Less well understood are the different isotopic combinations of H_3^+ . The exchange process



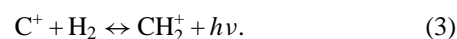
has been and still is the matter of an ongoing debate [34, 35]. It has been seen in beam experiments that simple statistical models fail and that the outcome of the reaction strongly depends on the total energy of the collision complex, i.e., on its lifetime. Low temperature experiments have shown that

the $\text{H}_3^+/\text{DH}_2^+$ ratio is a sensitive function of the o- H_2 /p- H_2 ratio. For measuring separately the influence of the rotational excitation of DH_2^+ , laser induced experiments are in progress, using the 4 K-trap shown in figure 1 and using for the first time a supersonic beam for chemical probing. The results are also of importance for the state selective measurements of the H_3^+ dissociative recombination rate coefficient [20].

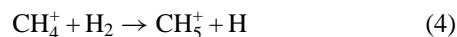
Other recent results obtained for deuteration of ions can be found in [21, 24, 36, 37]. They demonstrate that isotope enrichment at low temperatures is not only a unique astrochemical probe but it provides deep insight into molecular structures, reaction dynamics and especially the consequences of nuclear spin conservation and its chemical consequences.

3.3. Hydrocarbons

Formation of hydrocarbons in interstellar space usually starts with the radiative association process [6]



Measured rate coefficients for both para- and normal-hydrogen have been summarized in [12]. As emphasized in [14], the reliable determination of such small but very important rates is one of the achievements made possible with low-temperature traps. Further addition of hydrogen to CH_2^+ leads via CH_3^+ to CH_5^+ and, at low temperatures also to $\text{CH}_5^+(\text{H}_2)_n$. Protonated methane is of central importance in interstellar chemistry of hydrocarbons. There are many reactions leading to or starting with CH_5^+ . While radiative association of $\text{CH}_3^+ + \text{H}_2$ is well documented in the literature, the reaction



has been studied only recently at low temperatures [23]. As emphasized in [29], predictions for this reaction system are handicapped by the fact that even the asymptotic energies are uncertain.

Since the structure and reactivity of CH_5^+ is also of fundamental interest, it has been the subject of many experimental and theoretical investigations (see [21] and references therein). Nonetheless our knowledge is still quite limited. Very recently, the first IR overview spectrum for free CH_5^+ has been recorded using proton transfer to CO_2 in a 22-pole arrangement at 110 K [31]. Although this experiment is a big step forward, comparison of the low resolution results with state-of-the-art calculations still does not answer the question regarding the structure of this fluxional ion. Here, a real step forward may be made by cooling the ions to a few K and by recording a pure rotational spectrum of CH_5^+ starting with a high-resolution spectrum of the $J = 1 \leftarrow 0$ transition at ~ 200 GHz. As mentioned in [21], a promising method for state specific chemical probing is the resonant proton transfer to a supersonic beam (figure 1) of cold CH_4 molecules.

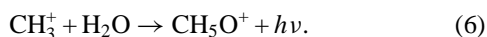
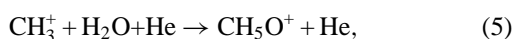
In order to study in more detail the formation of small hydrocarbons at low temperatures, a dedicated research program has been started in our laboratory based on combining atomic and molecular beam methods with ion trapping. So far results have been published for the interaction of D_3^+ with a neutral beam containing C, C_2 , and C_3

[28] and for the interaction of $C_3H_n^+$ ions with hydrogen molecules [38]. Most of these data clearly show that it is dangerous to extrapolate room temperature results towards lower temperatures. For example, hydrogenation of C_3^+ is rather slow at room temperature but becomes much faster at low temperatures [38]. Most probably this is caused by the structure of C_3^+ and the freezing of soft modes below 50 K (bending or pseudo-rotation). For $C_3H^+ + H_2$ our ion trap results prove that formation of $C_3H_2^+ + H$ is not endothermic but rather fast, in contradiction to erroneous conclusions from flow tube experiments and *ab initio* calculations. An interesting isotope effect has been obtained for $C_3H^+ + HD$: formation of C_3HD^+ is over one hundred times faster than the production of $C_3H_2^+$. It is an open question whether this can be explained by a specific H–HD exchange reaction taking place via an open-chain propargyl cation intermediate.

A conclusion from these results is that more systematic studies of carbon clusters C_m^+ and hydrocarbons $C_mH_n^+$ are needed at low temperatures. ICR experiments at 300 K have shown that the reactivity of pure carbon ion clusters with H_2 decreases as m increases up to 9 where it becomes non-measurable using this technique. Is this also true at 10 K? There are other general conclusions made for $C_mH_n^+ + H_2$ or H as a function of n and m which may not hold at low temperatures. For example the statement that C_mH^+ adds only one more H atom in collisions with H_2 and only for even values of m must be corrected for $m = 3$. It can also be expected that C_5H^+ which did not react with H_2 at a measurable rate in the SIFT, will add more hydrogen at the temperatures of dense interstellar clouds. Open also is the question of how reactive cyclic carbon cluster ions are at low temperature. Similarly, for those ions which reach terminal structures in the reaction pathways with H_2 , one can ask what will be their fate in regions where H atoms are present.

3.4. Beyond hydrogen as target: $CH_3^+ + H_2O$

So far most of the low temperature studies with ion traps have worked with a hydrogen target; however, other atoms such as N and O or metals also play an important role in interstellar chemistry. In addition there are many interesting reactions occurring with molecular radicals or polar molecules. The example presented in figure 4, for ternary and radiative association of CH_3^+ and H_2O has been selected to demonstrate that such studies are possible today with ion traps. The results have been measured with an experimental setup similar to figure 1 [27]. Formation of protonated methanol occurs via the two reactions



Such experiments have to be performed over a wide range of number densities of buffer gas (here He). In the presented case the ion trap was fixed at 20 K. Accounting for the conditions of the supersonic beam, the ‘temperature’ of the collision complex has been estimated to be (50 ± 30) K. From the slope of the data shown in figure 4, ternary and radiative association rate coefficients have been obtained (see figure caption). Reaction (6) has been considered to be one of the

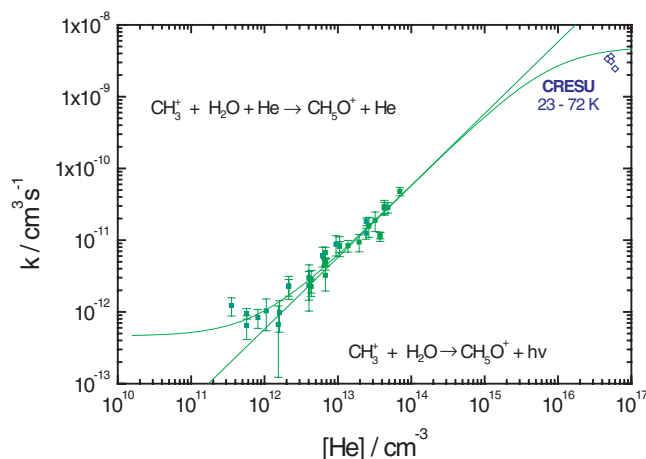


Figure 4. Dependence of the effective rate coefficient for the indicated association reactions as a function of the He number density, measured with a pulsed beam of H_2O molecules [27]. The ion trap was operated at 20 K. The time and space averaged H_2O number density was $8 \times 10^7 \text{ cm}^{-3}$. The data have been fitted with $k^* = k_3 [He] + k_r$ (thin line) leading to $k_3 = 5.8 \times 10^{-25} \text{ cm}^6 \text{ s}^{-1}$ and $k_r = 5.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. The data obtained in the CRESU experiment at He densities of $5 \times 10^{16} \text{ cm}^{-3}$ and at temperatures between 23 and 72 K are in the saturation regime as indicated by deviations from the straight line (ternary regime).

reactions for producing methanol in space via dissociative recombination with electrons; however, our measured value of k_r is much smaller than needed in astrochemical models, leading to the assumption that methanol must be formed on grain surfaces.

4. Conclusions and outlook

It is often stated that our understanding of the formation of molecules via gas phase processes is in a mature state. This may be true in comparison to the chemistry occurring on the surfaces of interstellar grains; however, there are still many simple molecules such as H_2 , C_3H_2 , methanol, or ammonia the formation of which is not yet fully understood. There are also many open questions concerning basic problems such as isotope enrichment, ortho-hydrogen heating, reactions with N and O atoms, or the role of isomers in small molecule chemistry. It is obvious that the situation does not get better if one asks how complex molecules (including bio-relevant ones) are formed or destroyed.

In the last decade, significant progress has been made by using more and more complicated ultrahigh vacuum machines, integrating beams of atoms, molecules and radicals and by using a variety of sophisticated analytical tools. Nonetheless it is our belief that laboratory work related to astrophysics or -chemistry is still focusing too much on standard methods used in established fields such as mass spectroscopy, material science etc. In order to address more directly the questions raised by astronomers, dedicated new generation instruments will need to be developed for laboratory astrochemistry.

This review has shown that rf based ion traps already have made significant contributions to this field; however, more activities and developments are needed. Since molecules in space are detected and studied by their spectra, it is obvious

that more optical methods should be utilized to get both spectra and state specific rate coefficients. In many regions of space there is a complex balance of photo- and collision-induced chemistry. The ability to synthesize cold, complex molecular ions and store them for long exposure times under collisional or collisionless conditions makes rf traps ideally suited for such investigations. Of specific importance is the VUV photostability or -lability of internally cold polyatomic ions and their dissociation pathways. There are new initiatives to develop a new trap which can cover the temperature range from the cold interstellar medium to hot stellar atmospheres.

Finally, one should not forget that many more activities are needed to understand the role of interstellar dust and nanoparticles in chemistry. Also in this field rf and ac traps could contribute much more provided that the details of the technique described in [19] become more popular.

Acknowledgments

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