Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 240 (2005) 139–147

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Reactions of C_n ($n = 1–3$) with ions stored in a temperature-variable radio-frequency trap

I. Savić, I. Čermák, D. Gerlich*

Department of Physics, Technische Universität Chemnitz, 09126 Chemnitz, Germany

Received 3 September 2004; accepted 15 October 2004

Abstract

A new experimental set-up has been developed for studying astrochemically relevant collisions between small neutral carbon molecules C_n ($n = 1–3$) and stored ions. The ions are confined for seconds in a ring electrode trap (RET) the temperature of which can be varied over a wide range (presently 80–600 K). There they interact with an effusive carbon beam, which is produced via high-temperature vaporization of a carbon rod. Due to the accessible temperature range and other features of the set-up, rate coefficients can be measured, which are of importance for understanding the chemistry occurring in the outflow of stars, the formation of hydrocarbons in stellar atmospheres, and the interaction of the stored product ions with radiation. Results are reported for the interaction of stored D_3^+ with hot C_n. The D^+ transfer dominates over all other exothermic product channels for $n = 1–3$. The reaction rate coefficients measured for forming C_nD^+ are almost a factor two smaller than values presently used in astrophysical models. Another important class of reactions concerns the growth of pure carbon chains via associative $C_m^+ + C_n$ collisions. First results indicate that the rate coefficients are slower than generally assumed in models. Due to the weak signal, only rough limits can be reported. For future studies, the number density of carbon penetrating the trap must be increased. This and the planned extension of the temperature range is briefly discussed in the outlook.

Keywords: Laboratory astrochemistry; Low and high temperature ion-molecule collisions; Ion trap; Carbon clusters; ISM molecules; Proton transfer; CD^+; C_2D^+; C_3D^+; C_n^+

1. Introduction

Within the last 30 years, a variety of chemical models has been developed for describing the formation and destruction of molecules in different regions of the interstellar medium (ISM) (see for example [1–4]). In early simulations of dense or diffuse molecular clouds, accretion disks, etc., a reaction network using mainly ion-molecule reactions was sufficient for explaining the observed molecular abundances. Ions certainly play an important, if not the dominant role in the formation of molecules at low temperatures since many of their reactions have no barriers [5] and, due to the long range ion-induced dipole attraction, the reactions are often fast. With the growth of observational details, e.g., spatial correlation between specific molecules such as C_4H and C_3H_2 [6], the progress of quantum chemistry and reaction dynamics and the development of new experimental tools dedicated to study the interaction of molecules under conditions in space, more and more information became available. In this way, some specific questions can be answered; however, it also has been realized that the overall understanding of how atoms and molecules are processed in space, is much more complex than described by the early simple models.

Today models for describing the evolution of the ISM are very sophisticated and specialized. In chemical reaction networks neutral–neutral reactions, especially radicals are routinely included. Also the surfaces of grains play an important role in catalysis, in freezing out gas or in providing products synthesized in the ice, e.g., via energetic photons or cosmic rays. Due to this huge complexity, one often has to restrict the number of processes, which one includes in a model

---

* Corresponding author. Tel.: +49 0371 5313135; fax: +49 0371 5313103.
E-mail address: gerlich@physik.tu-chemnitz.de (D. Gerlich).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.10.015

describing a specific object, otherwise one is not able to numerically solve the problem. A typical example is that coupling of a complex chemical network with a dynamic global 2-D model of protoplanetary disk is already beyond present-day computer capabilities [7]. For such attempts one needs, in addition to the help from mathematics and computer science, relevant and selected data from experimental and theoretical astrochemistry. In some cases, simplified rates for the involved physical and chemical processes are sufficient in other situations detailed temperature dependent and state specific rate coefficients are needed. In addition, the evolution of the matter from atoms to molecules and grains is not only determined by the overall elemental abundance or the number densities and chemistry of the formed molecules but, it depends in a complicated way on the environment, e.g., the radiation field, electron density, shocks etc. Therefore, dedicated measurements performed under conditions of astrochemical relevance are needed.

Chemical processes between ions and molecules have been studied originally in plasmas, afterglows and later using beam methods or flow systems and traps defining more or less thermalized conditions, mainly at room temperature. Stimulated by the need to learn more about reactions at the cold conditions prevailing in dense interstellar clouds, the last two decades have seen several successful initiatives to develop special instruments for extending the temperature range down to 10 K and even below [8–10]. Many interesting observations have been made in reactions, which are due to tunnelling, differences in zero point energies in the case of isotope substitution, the energy provided by ortho-hydrogen heating etc. Recent examples from our systematic low temperature studies of the chemistry of hydrocarbons include the formation of CH_5^+ in $CH_4^+ + H_2$ collisions the rate coefficient of which increase by one order of magnitude in going from room temperature down to 15 K [11] or the new efficient routes found for the formation of $C_3H_n^+$ and their deuterated analogues in cold environments [12,13].

Low temperature studies are now becoming routine and it is time to develop innovative instruments, which are able to operate at conditions ranging from the cold interstellar medium to the hot and dense environment prevailing in stellar atmospheres. Many molecules are formed in stellar outflows, where the emitted material cools from 5000 K or higher down to 50 K and where the number density goes from about 10^{12} to 10^6 cm^{-3}. It is concluded [14], that at 1000 K and below, where the expanding gas has a density from 10^{10} to 10^8 cm^{-3}, effective molecule and cluster formation and particle growth occurs; however, there are almost no experimental studies available, especially not of the important processes of radiative association prevailing in the transition region. One central problem is for example the understanding of the chemical pathways, starting from very small molecules C_2, C_3, C_2H or C_3H towards nano-structures and finally to large grains. High temperatures of more then 2000 K are also produced by shocks occurring in supersonic protostellar outflows [15] leading to mostly unknown chemical changes. In addition, the chemistry occurring in the interaction of a stellar jet with a clump in a molecular cloud must also include the intense radiation field generated in the jet-cloud shock [16]. The increasing need for high temperature data has been emphasized in [17] and it has been started, on a rather heuristic way, to extend the range of validity of the rate coefficients contained in the database over a wide temperature range.

Due to a variety of reasons carbon atoms and carbon-bearing molecules play a dominant role in all fields of natural science, ranging from physics via chemistry to biology. They are found in all environments, e.g., in the hot outflow of a carbon rich star or in the cold interstellar medium where carbon atoms and ions are important coolers. A challenge for planning dedicated experiments relevant for the early universe is the recent observational hint, that C atoms may have been present already in the early universe [18]. Another unsolved problem are the diffuse interstellar bands (DIB). Many researchers are convinced today that carbon containing molecules are responsible for those spectral features or also for the extended red emission (ERE); however, there are not yet any systematic experimental strategies to get some order into the multifaceted astrochemistry producing and processing the huge variety of carbon containing ions, radicals, and saturated neutrals. A recent simulation of the growth of molecular structures in stellar atmosphere [3] can be used to illustrate the complexity. In this study, the interaction of thousand different species has been modeled at temperatures between 2000 and 7000 K. The sensitivity of the model to the microphysics can be seen from the fact, that already the modification of one single parameter, e.g., the carbon to hydrogen abundance, leads to significant changes. Calculated carbon atoms sputtering yields impacting on amorphous carbon target are dominant at velocities less than ~35 km/s [19] and therefore can be important for sputtering in the outflows of cool stars.

A lot of experimental and theoretical effort has been devoted to investigate pure carbon clusters, ranging from theoretical calculations of stable isomers, to experimental spectroscopy of different size clusters [20–22]. The reason for this is not only the importance of carbon compounds in astrophysics, but also in material science and in combustion processes. From a fundamental point of view carbon is of interest due its fascinating properties and chemical diversity leading not only to the well-known classical structures of aromatic rings, graphite, fullerite, diamond etc. but also to more complicated arrangements if additional elements are included. Already the addition of a proton to hydrocarbons leads to special features as known from the hypercoordinated carbocations characterized by a two electron – three center configuration [23]. The above mentioned protonated methane is the simplest but not yet understood member of this group.

It was only in the last two decades, that experimental efforts have been started to investigate chemical reactions involving pure carbon atoms or molecules. The reason is that it is experimentally difficult to obtain an intense and well defined beam of carbon atoms or molecules needed for studying reaction dynamics. The development of the laser vaporization carbon source lead to the discovery of fullerenes for which the Nobel price has been awarded to R. F. Curl, H. W. Kroto and R. E. Smalley. Significant contributions to the understanding of neutral reactions involving carbon and hydrocarbons have been made in the group of Y. T. Lee using the crossed beam technique [24]. According to the best of our knowledge, there have been no experiments performed so far on reactions between ions and neutral carbon molecules. In the following a new ion trapping – carbon beam instrument is presented. Various details of the machine are explained, which has been developed for studying reactions of astrochemical importance over a wide range of temperatures and densities. Also specific properties of carbon vaporization are discussed since they are not only important for controlling the composition, the velocity etc. of the beam but it also provides some information on carbon chemistry occurring at high temperatures. Results are given for the deuteron transfer from D_3^+ to carbon and for the interaction of stored carbon ions with the neutral carbon beam.

2. Experimental

Many experimental techniques have been developed in the last decades for investigating inelastic and reactive interactions between ions and molecules. The present apparatus is a typical ion trapping machine aiming to study chemical reactions between ions and neutral carbon. As can be seen from a variety of applications [10,25,26] the method to trap ions in inhomogeneous rf field is very versatile. For special purposes, a variety of modules and lasers can be integrated into the systems.

2.1. Apparatus

A dedicated ion-trapping apparatus has been developed for combing a carbon beam with a special ion trap, which can be operated both at low and high temperatures. The most important modules of the experimental set-up, some technical details have been described already in [27], are shown in Fig. 1. They are (from the left) (i) the carbon vaporization source, (ii) an electron bombardment ion source, (iii) the 80–600 K radio-frequency ring electrode trap (C-RET), and (iv) a quadrupole mass spectrometer detector. A few additional hints are given in the following section with emphasis on the carbon evaporator.

A very good vacuum is crucial for this type of experiments in order to suppress parasitic reactions of stored ions with impurities such as CO and CO_2, which, in the present case, mainly emerge from the hot carbon source. From various tests it has been concluded that these molecules are not evaporated directly from the carbon rods after baking them; however they originate from the carbon coated surfaces of the beam chamber, which become oxidized after venting the machine or also by background gas. Therefore, effective differential pumping was needed. A total of four turbo pumps have been integrated into the system two of which (pumping speeds 2 l/s × 230 l/s) evacuate the trapping and the detector chamber and two of which are used for differentially pumping the main and the second chamber of the carbon source (pumping speeds 170 and 56 l/s, respectively). The two source chambers and the main chamber are separated from each other by two apertures (diameters 3 mm and 6 mm, respectively). The source can be closed using a UHV gate valve. In the trapping chamber the pumping system sustains a background pressure

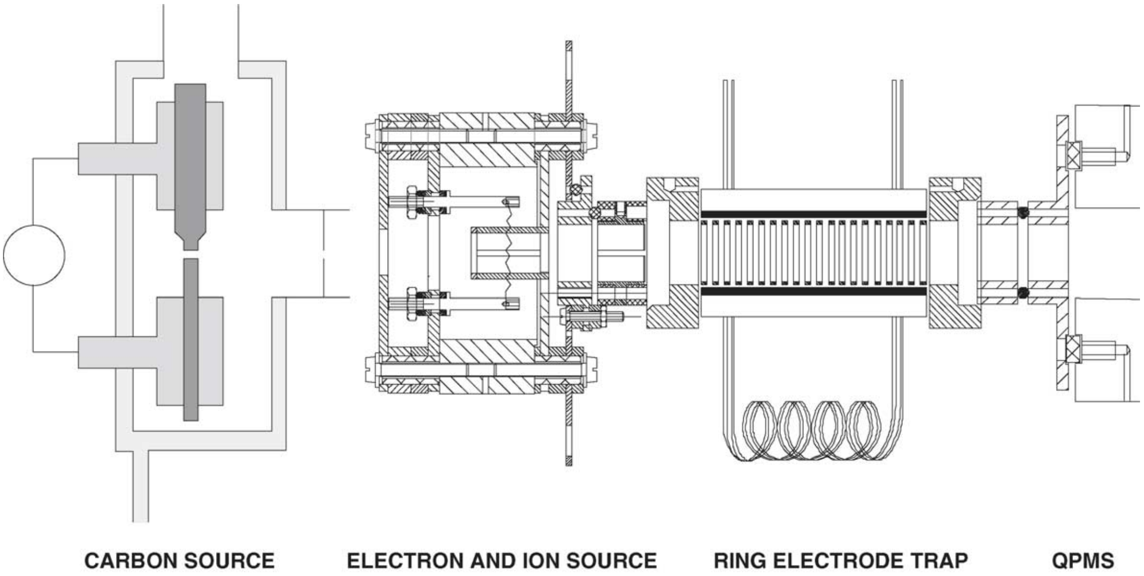

Fig. 1. Schematic diagram of the experimental assembly consisting of the carbon evaporator, the ionizer, the ring electrode trap. For analysis, the trapped ions are extracted, mass selected and detected with a Daly type detector (only the entrance is indicated). The parts are at scale with exception of the distance between the carbon rods and the trap which is 40 cm. In the trapping volume C_3 number densities up to 2×10^8 cm^{-3} have been reached. The electron bombardment ion source is used for creating reactant ions and for analyzing the composition and density of the effusive carbon beam.

below 3×10^{-10} mbar. Additional cooling of the RET with liquid nitrogen leads to additional reduction of background gas. At such conditions, less than 1% of primary ions are converted through reactions with the residual gas at a storage time of 1 s. The versatile gas inlet system allows for introducing pure or mixed gases into the trap or the ion source, either continuously via a leak valve or pulsed using a fast piezo driven valve. A spinning rotor gauge (MKS SRG2) is connected via a stainless steel tube to the main chamber for monitoring the pressure and calibrating the ion gauge.

As can be seen from Fig. 1 and explained in more detail in [28] the ionizer which is based on a commercial construction originally developed for quadrupole mass spectrometers (Extranuclear), is located between the carbon source and the ion trap. It has several functions such as (i) preparation of primary ions and loading them into the trap (ii) monitoring the carbon flux or (iii) injecting electrons directly into the trap. It consists of cylindrical electrodes with axial apertures. The open construction allows the neutral carbon beam to pass through the source into the RET. Below 10^{-8} mbar, this source operates in a space charge trapping mode leading to very high collection efficiencies. All ions produced are mass selected in a quadrupole (rod diameter $d = 18$ mm, 260 mm long, r.f. frequency 1.6 MHz) and detected using an ion detector of the Daly type [29].

2.2. Ring electrode trap

The central part of this machine is the ring electrode trap (RET) shown in the center of Fig. 1. It is mounted onto a flange via a light stainless steel structure, which has such a good heat insulation that the trap can be easily cooled with liquid nitrogen or heated to high temperatures. Already without a heat shield, a temperature of 600 K has been reached just from the rf power dissipated in the coil. Besides the wide temperature range, an important advantage of the RET design is, in contrast to the 22-pole trap, that it is rather insensitive to coating with carbon since most insulators are protected by shields. In addition the complete set-up is easy to clean.

The geometry of the electrode arrangement was first described in [30] and in more detail later [31–33]. The trapping region is defined by 20 electrodes alternatively connected to two metal bars. The gap between successive electrodes is 1 mm, the electrodes themselves are 1 mm thick and have a circular hole with a radius of $r_0 = 5$ mm. The metal bars are welded to metal tubes. These tubes are used both for electrical connections and for flowing liquid N_2 through the whole system including the metal bars. In addition they are wound to form a coil which is the inductance of the resonant circuit supplying the trap with rf. For more details see the figure in [30].

For excitation, this circuit is connected to an rf generator. Using two external capacitors the operating frequency has been lowered to $f = 7.8$ MHz. Typically, the trap was operated with amplitudes up to $V_0 = 250$ V. The dc potential of the trapping region has been defined by applying a voltage to the center of the coil via a low frequency band pass circuit. In the radial direction, ions are confined by the effective rf potential. Adequate conditions for ion trapping can be estimated by using simple calculations [31]. Usually one chooses the effective potential high enough for safely storing all ions in a volume of radius $r = 0.8\ r_0$, Combining the equations for the effective potential and the adiabaticity parameter and using $\eta < 0.3$ and $r = 0.8\ r_0$ leads to the minimal values for the frequency and the voltage. Since in the present case the parameters have been set for carbon clusters, the light ion H_3^+ was already at the limit. Therefore, deuterium has been used since storing simultaneously D_3^+ and C_3D^+ posed no problem.

In the axial direction, the trap is closed and opened by applying suitable voltages to the trap entrance and trap exit electrode. For safe trapping, voltages of a few 100 mV are sufficient. After thermalization of the injected ion cloud much lower values are sufficient. For extracting the ions, a small negative pulse, typically −1 V, is used. The trap is equipped with two steering electrodes, the electric field of which penetrates into the interior. For fast ejection, e.g., for TOF-MS [33] suitable axial potential gradients have been applied just before or during ion extraction. The electrodes are also used routinely for testing inhomogeneities of the trap potential caused by surface effects and for reducing their influence.

2.3. The carbon source

The astrochemical importance of reactions involving carbon atoms, molecules, and clusters has been emphasized in the introduction. As a consequence, several attempts have been made in recent years to construct suitable carbon sources, e.g., based on laser ablation of carbon rods, sublimation of graphite, or evaporation of suitable carbon containing compounds. The source used in this work is based on vaporizing graphite rods in high vacuum by resistive heating with an electric current of several hundred Amperes. The construction used was developed in Krätschmer's group in Heidelberg for spectroscopic studies on matrix-isolated carbon molecules [34]. Only minor changes have been made on the basic design while the control of the source parameters has been improved leading to a better longtime stability [27,28].

Two graphite electrodes (cathode 4.6 mm and anode 6.15 mm diameters, RW4 type, impurities < 2 ppm, SGL Carbon) are pressed together and resistively heated using in a serial-parallel arrangement four switching power supplies (Philips PE 1980, 5 V, 200 A each). Note, that the polarity does not play a remarkable role. For cleaning the carbon, a new rod must be baked first for 5–7 h with 600–700 W. Vaporization of carbon starts at about 1 kW. The power can be increased up to a maximum of 1.3 kW: above this limit, the system becomes unstable. In order to reduce excessive heating of the vacuum chamber, a copper radiation shield and water cooling is used.

A sensitive characteristic of the operating conditions of the source is the rod resistance, which is monitored continuously via a four-point scheme. The resistance drops with increasing temperature and it reaches finally, for the electrodes used, a mean value of about 20 mΩ. A control program stabilizes the heating power independent on changes of the rods resistance. Via a stepping motor the carbon rods are pushed against each other for maintaining a constant pressure, which is estimated to be in the order of 10 N/cm^2. It was an erroneous hypothesis that the temperature of the emitting area would be an even better control parameter. A pyrometer has been used for localizing and monitoring this region. However, the maximum average surface temperature, which could be found was at most 2300 K indicating that the emitted carbon flow does not sublimate from an outside surface area of the rods. For future improvements of the source the discovery was very important that the carbon material is ejected in a pulsed mode from the interior of the contact area, i.e., vaporization occurs between the two rods pushed against each other [28]. Whether the eruptions, which occur a few times per second, are due to hot carbon gas or liquid bubbles enclosed in the interface is still uncertain. Therefore, the temperature of the emitted carbon is uncertain but it is estimated to be 3000 K or above. Another problem, which is correlated with this observation, is the condensation of carbonaceous material in the vicinity of the contact area, reducing the efficiency of the source by 75%.

A simple way to determine the total amount of evaporated material is to measure the mass loss, which occurs exclusively at the expense of the 4.6 mm rod. Typically, 7.5 cm of the rod are vaporized in 8 h, corresponding to 2.6 μm/s. Only 25% of this vaporized material, corresponding to 1.9×10^{-5} g/s, actually goes into the gas phase, the rest condenses in macroscopic structures and finally falls down. Assuming for simplicity that C_3 is isotropically emitted with a temperature of 3000 K, one obtains in the trap which is 40 cm away from the rod a number density of 1×10^{8} cm^{-3}. This is in excellent agreement with the number density measured at the location of the trap with a calibrated electron bombardment ionizer. This universal detector has also been used to find out the carbon cluster distribution. The result 80 ± 8% C_3, 8 ± 2% C_2, and 12 ± 6% C is in full accordance with the distribution determined by chemical probing. For monitoring the absolute carbon flux during regular operation, the ionizer (see Section 2.1) has been calibrated in situ using nitrogen and the spinning rotor gauge.

2.4. Measuring procedure

The primary ions are produced by electron impact (see Section 2.1) directly in the trap and stored for a given time. They are continuously exposed to the carbon beam. After a period, which is varied between ms and min, the content of the trap is analyzed by extraction, mass selection and counting. Directly after this, the flux of the carbon beam is monitored to correct for drifts of the carbon source. In the present experiment measurements have been performed in two different ways.

For better understanding the operation of the carbon source, the trapping time was held fixed and the number density of the neutrals was changed by varying the heating power. The relative change in the carbon temperature (3000 K, see above) was only a few hundred Kelvin and is negligible in comparison with the uncertainty in the actual temperature of the carbon gas. Note that the temperature of the trapped ions is defined separately. In most experiments liquid nitrogen cooling of the trap was used. As can be seen from Fig. 2, measurements have been performed at carbon number densities starting at values as low as 10^6 cm^{-3} and going up to a maximal value of 2×10^8 cm^{-3}.

In the second group of experiments, the trapping time was changed while the number density of the carbon target was stabilized at a constant value. For determining the changes of the ion composition due to reactions, the sequence (i) ion formation, (ii) injection, (iii) relaxation and reaction, (iv) analysis and (v) carbon flux determination is repeated many times for each product mass and typically for 5–10 different storage times. More details of typical trapping measuring procedures and applications can be found in recent publications [26,35,36].

3. Results and discussion

3.1. Reactions of D_3^+ with C_n

Selected experimental results for forming $C_nD_m^+$ in collisions between D_3^+ and C_n are presented in Figs. 2 and 3. The D_3^+ primary ions have been prepared by introducing a short intense gas pulse of D_2 into the RET. With a certain delay a pulse of electrons with an energy of 70 eV was injected into the trap using the filament of the ionizer. The primary D^+ and D_2^+ ions produced by electron bombardment collide with the ambient D_2 gas. D_2^+ ions are almost completely converted to D_3^+. By changing the delay between the gas and the electron pulse, the composition of the ions in the trap can be controlled. Some isotopic variants of D_2^+ and D_3^+ are present in small amounts due to the isotopic composition of the introduced gas. In the present experiment, HD_2^+ and D_2^+/H_2D^+ could be suppressed to 2 and 0.1% of D_3^+, respectively.

Fig. 2 shows the dependence of D_3^+, C_3D^+ and $C_3D_2^+$ ions as a function of the number density of C_3 after 1 s storage time. The most abundant product is C_3D^+ formed in the reaction

$$D_3^+ + C_3 \rightarrow C_3D^+ + D_2. \quad (1)$$

It can be seen from the figure that more C_3D^+ and $C_3D_2^+$ products are formed at higher number densities; however, there are some nonlinearities in the dependence. Especially the loss of D_3^+ at high number densities is larger than the gain in C_3D^+ and $C_3D_2^+$. This is only to a minor fraction

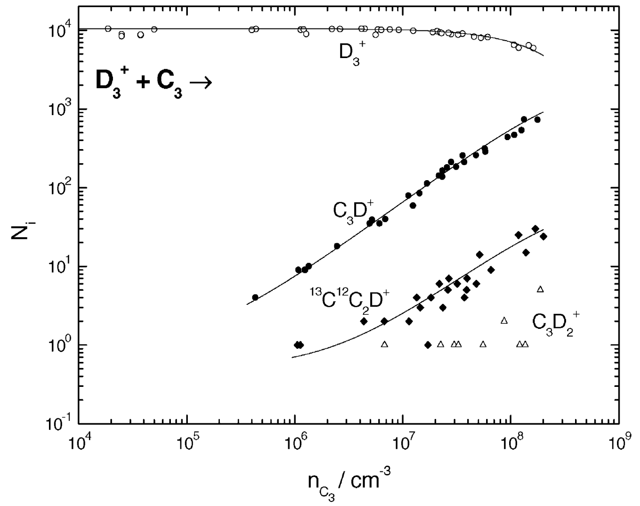

Fig. 2. Number of ions per filling, N_i, as a function of the number density of C_3. The primarily injected D_3^+ ions have been exposed to the carbon flux during a storage time of 1 s. The data obtained for D_3^+, C_3D^+ and $C_3D_2^+$, are fitted (solid lines) using a model described in the text. For the C_3D^+ products shown in this plot a rate coefficient $k_1 = 6.3 \times 10^{-10}$ cm^3 s^{-1} has been obtained. Using the same value for reactions with $^{13}C^{12}C_2$ and accounting for the natural abundance of ^{13}C, a perfect fit of the measured $^{13}C^{12}C_2D^+$ ions has been obtained. As can be seen from the open triangles, only traces of $C_3D_2^+$ are produced.

due to the fact that not all product ions are presented in this figure. The main reason is that at large fluxes, the trap or ion optics become coated non-uniformly with a carbon layer influencing the work functions, and in this way, the trapping and transmission properties. A clear indication is that this process is not directly reversible but has a rather long time constant. In order to reduce this problem additional water cooled baffles and apertures limiting the beam have to be included into the set-up.

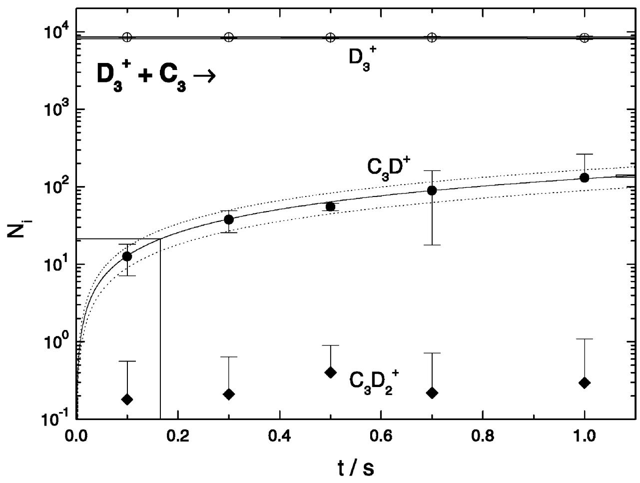

Fig. 3. Number of ions per filling, N_i, as a function of storage time t. The C_3 number density has been stabilized at 2×10^7 cm^{-3}. The data obtained for D_3^+, C_3D^+ and $C_3D_2^+$ ions are normalized for monitored fluctuations of the number density and the total sum of ions. For details see the text.

Table 1
Measured reaction rate coefficients for various $D_3^+ + C_n$ reactions

Reaction	k/10^{-10} cm^3 s^{-1}	
	This work	UMIST[a]
$D_3^+ + C_3 \rightarrow C_3D^+ + D_2$	7.3[b]	14.7
$D_3^+ + C_2 \rightarrow C_2D^+ + D_2$	5.7[b]	13.4
$D_3^+ + C_2 \rightarrow C_2D_2^+ + D$	1.0[c]	
$D_3^+ + C \rightarrow CD^+ + D_2$	4.7[b]	15.5
$D_3^+ + C \rightarrow CD_2^+ + D$	2.2[c]	
$D_3^+ + C \rightarrow CD_3^+$	0.4[c]	

[a] The UMIST values [17] which are included into the database only for H_3^+, have been converted by accounting for the reduced mass.

[b] The error for deuteron transfer is 50%.

[c] Due to uncertainties with secondary reactions the errors can be larger than 50% (see text).

In the present evaluation of the data an empirical density-dependent term for ion loss has been introduced into the standard kinetic model. Inspection of Fig. 2 reveals that the resulting fit (solid line) follows nicely the experimental data points. The main result from this evaluation procedure is the rate coefficient for reaction (1) which is given in Table 1. It is gratifying that the line following the $^{13}C^{12}C_2D^+$ data has been obtained without any additional assumption, just by using this rate coefficient and taking in account the natural abundance of $^{13}C^{12}C_2$ of 3.3%. Formation of traces of $C_3D_2^+$ have also been detected; however, the data have not been fitted because the signal is too low.

A typical result from an experiment where the trapping time was changed is presented in Fig. 3. The number density of C_3 was fixed at a mean value of 2×10^7 cm^{-3}, fluctuations have been monitored and accounted for. The sum of all experimental data measured at different storage times has been used for normalization. Also here the data have been fitted (solid lines) using the solutions of a simple rate equation approach. The resulting reaction rate coefficient, $k_1 = 7.5 \times 10^{-10}$ cm^3 s^{-1} is in accordance with the final value given in Table 1. The dotted lines in Fig. 3 which have been calculated with two extreme values of k_1, illustrate the accuracy of the fitting procedure (±20%).

In the same way reactions of primary ions with C_2 and C have been followed as a function of the total carbon density and the interaction time. Note that in the present experiment, the number density of C_2 and C cannot be controlled separately but it is determined by vaporization. It is derived from the measured C_3 number density and the rather temperature-independent C_2/C_3 and C/C_3 ratios determined in independent experiments (see Section 2.3). Due to this complication and since, in addition, traces of D_2 are still present in the trap, it was necessary to make several simplifying assumption for evaluating the data. For example C_2D^+ ions are most probably formed in the reaction

$$D_3^+ + C_2 \rightarrow C_2D^+ + D_2. \qquad (2)$$

Also a minor part (<20%) of $C_2D_2^+$ has been detected. In the evaluation it has been assumed to be formed directly via

$$D_3^+ + C_2 \rightarrow C_2D_2^+ + D; \tag{3}$$

however, some of these products may have been formed in the secondary reaction $C_2D^+ + D_2 \rightarrow C_2D_2^+ + D$ with the traces of D_2 remaining in trap. In the analysis, $C_2D_3^+$ ions could not be accounted for because they have the same mass as the COD^+ ions (see below). However it is rather save to assume that radiative association reactions of D_3^+ with C_2 (and also C_3) are negligible at the high internal temperatures of the neutral target.

Products containing only one carbon atom, i.e., CD^+, $^{13}CD^+$, CD_2^+ and CD_3^+ are most likely formed via

$$D_3^+ + C \rightarrow CD^+ + D_2, \tag{4}$$

$$D_3^+ + C \rightarrow CD_2^+ + D, \tag{5}$$

$$D_3^+ + C \rightarrow CD_3^+. \tag{6}$$

Also in these cases it cannot be excluded, that CD_n^+ ($n = 2$ and 3) ions are produced in the subsequent reactions $CD_{n-1}^+ + D_2 \rightarrow CD_n^+ + D$.

The rate coefficients reported in Table 1 for reactions (1)–(6) have been derived from the measurements by neglecting secondary reactions or any other complications such as formation of C_2 containing ions in collisions with C_3. In general the overall accuracy of the rate coefficients is determined by statistical errors and the fitting procedure (here 20%), by uncertainties in the number density of the carbon beam, and its overlap with the ions cloud. In the present experiment additional problems arise from the fact that with increasing temperature of the carbon rods and the source chamber the CO and CO_2 background gas increases leading to formation of COD^+ and CO_2D^+ ions in collisions with stored D_3^+ ions. Also VUV radiation emitted from the hot surfaces can lead to ionization. Weighting the various influences it is estimated that the resulting rate coefficients for deuteron transfer, reactions (1), (2) and (4), have an overall uncertainty of 50%. The rate coefficients for reaction (3) and (5) can be regarded as upper limits. The same holds for reaction (6); however it must be mentioned, that it is also possible that a fraction of CD_3^+ has been formed via radiative association since in the case of the atomic target the collision temperature is mainly given by the ion temperature. Note that the trap is cooled with liquid nitrogen and it can be assumed that the ions undergo enough collisions with the deuterium gas pulse used for ion preparation.

The measured data are compared in Table 1 with values derived from the UMIST data for $C_n + H_3^+ \rightarrow C_nH^+ + H_2$ [17]. The values of $2 \times 10^{-9}\,cm^3\,s^{-1}$, $1.8 \times 10^{-9}\,cm^3\,s^{-1}$ and $2 \times 10^{-9}\,cm^3\,s^{-1}$ for $n = 1$, 2 and 3, respectively have been converted just by accounting for the reduced mass. It is noted that these values may have an error of up to factor 2. It is assumed that the values are independent from temperature, and therefore, they are used at 10 K in dense interstellar clouds as well as in stellar atmospheres. The Langevin model predicts larger rate coefficients, especially if one takes the larger polarizability reported in C_3 [37].

Stimulated by the experiments, also theoretical work has been started [38] including the calculation of the potential energy surface and molecular dynamics simulations of the $H_3^+ + C_3$ collision [39]. Formation of the most stable collision complex, c-$C_3H_3^+$ has been determined to be $907\,kJ^{-1}$ below the energy of the reactants. Both the proton transfer $C_3 + H_3^+ \rightarrow$ l-$C_3H^+ + H_2$ as well as the reaction $C_3 + H_3^+ \rightarrow C_3H_2^+ + H$ is exothermic by the same value of about $330\,kJ^{-1}$. More details on the energetics and the accuracy of the calculations can be found in [39]. In accordance with our experimental results the trajectory calculations show that proton transfer is by far the dominant reaction channel in $H_3^+ + C_n$ collisions. The thermal reaction coefficients derived from the calculations are given in Table 2. The results are well below the Langevin value indicating that the outcome of the reaction is not determined by the long-range capture, but rather by structural changes required in the collision complex. Protonation occurs via two mechanisms, direct transfer of H^+, $C_n + H_3^+ \rightarrow C_nH^+ + H_2$ or passage through an excited intermediate but leading to the same product, $C_n + H_3^+ \rightarrow (C_nH_3^+)^* \rightarrow C_nH^+ + H_2$. More complicated reactions are infrequent. These findings are in accordance with earlier ab initio quantum mechanical calculations performed for the collision system $C + H_3^+$ [40] showing that proton transfer prevails while there is no pathway without a significant activation energy to lead to the $CH_2^+ + H$ product channel. Also for the $C_2 + H_3^+$ it has been found that the main reaction channel is formation of C_2H^+ instead of $C_2H_2^+$ [38].

3.2. Reactions of C_m^+ with C_n

One of the major aims of the constructed machine was and is to study the growth of pure carbon clusters in the trap over a wide range of temperatures. One of the basic questions is to find out the conditions under which a strongly bound collision complex just “sticks” together. Another interesting problem is the formation of isomers or transitions between them, e.g., from linear to ring structures. Unfortunately the number density of the carbon target is not yet high enough or the sensitivity of the apparatus is not yet sufficient

Table 2
Thermal reaction rate coefficients calculated by G. Seifert and coworkers [39,38] for the indicated reactions

T/K	$k/10^{-10}\,cm^3\,s^{-1}$	
	$C_3 + H_3^+ \rightarrow C_3H^+ + H_2$	$C_3 + D_3^+ \rightarrow C_nD^+ + D_2$
100	5.1	4.1
200	6.7	
300	7.7	5.9
400	8.5	
500	9.1	7.1
1000	11.0	8.6

Table 3
Measured upper limits of rate coefficients for $C_n^+ + C_3$ ($n = 1$–3) association reactions

Reaction	k
$C^+ + C_3 \rightarrow C_4^+$	$<4 \times 10^{-11}$ cm^3 s^{-1}
$C_2^+ + C_3 \rightarrow C_5^+$	$<4 \times 10^{-10}$ cm^3 s^{-1}
$C_3^+ + C_3 \rightarrow C_6^+$	$<1 \times 10^{-11}$ cm^3 s^{-1}

to answer such questions in detail. Nonetheless, first results for the formation of C_4^+ and C_5^+ have been obtained.

In this experiment the neutral carbon beam was first used as the precursor for the ions. Ionized with 70 eV electrons, the ions are accumulated for typically 200 ms in the trap. In addition the stored ion cloud consisting of the C^+, C_2^+ and C_3^+ is exposed continuously to the flux of carbon. Storage times have been varied between 0.5 and 5 s. Since there are several loss mechanisms competing with the formation of reactive products, the largest number of products has been observed at a storage time of 3 s. Typically only a very few counts per filling are obtained and it takes averaging over many iterations until useful information on the rate coefficients can be extracted. In addition the carbon beam flux is measured periodically in order to account for fluctuations. Systematic studies of the loss of primary or product ions are impossible under these conditions. Nonetheless it is a rather good approximation to assume that parasitic reactions or loss from the trap affects all C_n^+ ions from $n = 2$–6 in the same way at the conditions the trap is operated.

In order to evaluate data from this experiment certain simplifications have been made, since three different ionic reactants are allowed to react with three different neutral partners. Since C_3 is by far the dominant constituent of carbon vapor, it has been assumed that the three following reactions dominate: $C^+ + C_3 \rightarrow C_4^+$, $C_2^+ + C_3 \rightarrow C_5^+$ and $C_3^+ + C_3 \rightarrow C_6^+$. In the evaluation the simple linear approximation can be used, $K = N_2/(N_1[C_n]t)$. N_1 is the number of primary ions, N_2 the number of products, $[C_n]$ the number density, and t is the trapping time. It is obvious that other reactions also can contribute to the formation of C_4^+, C_5^+ and C_6^+ and therefore, the rate coefficients presented in Table 3 are only estimated upper limits. Nonetheless important conclusions can be made from these studies the most important being that the association reaction $C_3^+ + C_3 \rightarrow C_6^+$ is not fast. The reaction rate coefficient is certainly smaller than 1×10^{-11} cm^3 s^{-1}!

The results can be compared only with a rather crude theory [41]. In this simple model the rate coefficients for $C^+ + C_n \rightarrow C_{n+1}^+ + h\nu$ have been parameterized simply by $K = f \times k_L$ where k_L is the Langevin rate. The fraction $f = 0$ for $n = 1$ is in accordance with the fact, that collision complexes are very short-living in atom–atom collisions and, therefore, radiative association is very unlikely. The values for $n = 2$ and 3 are $f = 10^{-7}$ and $f = 10^{-3}$, respectively. For $n > 3$ arguments have been given, that the collision complex, formed with the Langevin rate, is stabilized with unit efficiency. This is based on the assumptions that in the C_4^+ collision complex, the total number of degrees of freedom is already so large, that it lives longer than the time needed for radiative stabilization. The present $C_3^+ + C_3$ result is in contradiction to this. May be this discrepancy can be explained with a steep dependence of the radiative rate coefficient and the fact that in the present experiment the C_3 molecules are still too hot.

4. Conclusions and outlook

First reactions between neutral carbon atoms and clusters and stored D_3^+ and C_n^+ ions have been studied at a rather undefined effective temperature which is determined by the ions stored at 80 or 300 K and by the fast and hot beam of C_n molecules, with an estimated translational and internal temperature of 3000 K or higher. The new experimental set-up which is still under development aims at studying not only reactions relevant for interstellar clouds but to simulate also conditions which are important for understanding the chemistry in stellar atmospheres, stellar outflows, shocks etc. The instrument is equipped with a trap the temperature of which can be varied over a wide range. With minor changes such as adding a heat shield, trapping temperatures of 1000 K can be easily reached. In addition, higher ion velocities are accessible by confining in the trap an ion beam with the desired kinetic energy [10]. The method of CO_2 laser heating is already being tested for obtaining hot stored ions or nanoparticles.

More work is needed to prepare a better beam of carbon atoms or clusters, to achieve higher number densities in the trap, and to avoid partial coating of the trap and the electrodes. On one side it is planned to use a laser ablation source similar to the one described in [42] in which the $C/C_2/C_3$ ratio and the temperature can be modified by changing the laser parameters and the expansion conditions. On the other side, it is also intended to continue to utilize the present source, although carbon emission from the heated graphite rods is not yet fully understood. It is sure that carbon is not vaporized by sublimation from the surface but ejected from inner regions of the contact area where much higher temperatures prevail. As soon as this process is understood in more detail, the source can be used more efficiently, especially for measuring high temperature rate coefficients with a very hot target. In the process of further testing the source, it is also planned to use the carbon evaporator as a flow system and to use lasers for probing (LIF, REMPI) or modifying (heating with Nd-YAG or CO_2 laser pulses) the concentrations very close to the rods. It can be foreseen that such tests will provide additional information on high temperature carbon chemistry.

Acknowledgments

The authors thank Stephan Schlemmer for many stimulating discussions and comments as well as Silvio Decker for help in characterization of the carbon source. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged, especially via the Forschergruppe FOR 388 “Laboratory Astrophysics”.

References

[1] E. Herbst, C.M. Leung, Asrophys. J. Suppl. Series 69 (1989) 271.

[2] B.E. Turner, E. Herbst, R. Terzieva, Asrophys. J. Suppl. Series 126 (2000) 427.

[3] G. Pascoli, A. Polleux, Astronom. Astrophys. 359 (2000) 799.

[4] H. Nomura, T.J. Millar, Astronom. Astrophys. 414 (2004) 409.

[5] M.A. Smith, in: C.Y. Ng, T. Baer, I. Powis (Eds.), Current Topics in Ion Chemistry and Physics, vol. 2, Wiley, New York, 1993, p. 183.

[6] M. Gerin, D. Fosse, and E. Roueff, in: C. L. Curry and M. Fich (Eds.), Proceedings of the Conference Chemistry as a Diagnostic of Star Formation, University of Waterloo, August 2002. NRC Research Press (2003); http://arxiv.org/PS_cache/astro-ph/pdf/0212/0212058.pdf.

[7] T. Henning, in: D. Gerlich, T. Henning (Eds.): Structure, Dynamics and Properties of Molecules and Grains in Space, FOR 388, Report 2000–2003 (2003) 79.

[8] I.W.M. Smith, B.R. Rowe, Acc. Chem. Res. 33 (2000) 261.

[9] M.A. Smith, Intl. Rev. Phys. Chem. 17 (1998) 35.

[10] D. Gerlich, Hyperfine Interact. 146/147 (2003) 293.

[11] O. Asvany, I. Savić, S. Schlemmer, D. Gerlich, Chem. Phys. 298 (2004) 97.

[12] I. Savić, D. Gerlich, Phys. Chem. Chem. Phys., submitted for publication.

[13] I. Savić, S. Schlemmer, D. Gerlich, Astrophys. J. 617 (2004).

[14] A.B.C. Patzer, T.M. Köhler, E. Sedlmayr, Planet. Space Sci. 43 (1995) 1233.

[15] C. Codella, R. Bachiller, M. Benedettini, P. Caselli, T. Giannini, B. Nisini, P. Saraceno, L. Spinoglio, C.M. Walmsley, in: G.L. Pilbratt, J. Cernicharo, A.M. Heras, T. Prusti, R. Harris (Eds.), Proceedings of the Symposium on *The Promise of the Herschel Space Observatory*, ESA SP-460, 2001, p. 381.

[16] D.A. Williams, A.J. Lim, S. Viti, RevMexAA (Serie de Conferencias) 13 (2002) 114.

[17] Y.H. Le Teuff, T.J. Millar, A.J. Markwick, Astronom. Astrophys. 146 (2000) 157.

[18] M. Harwit, M. Spaans, Asrophys. J. Suppl. Series 589 (2003) 53.

[19] C. Covatto, P.A. Aannestad, Mon. Not. R. Astron. Soc. 318 (2000) 67.

[20] J.P. Maier, J. Phys. Chem. A 102 (1998) 3462.

[21] M.S. Deleuze, M.G. Giuffreda, J.-P. François, L.S. Cederbaum, J. Chem. Phys. 111 (1999) 5851.

[22] M.S. Deleuze, M.G. Giuffreda, J.-P. François, L.S. Cederbaum, J. Chem. Phys. 112 (2000) 5325.

[23] G.A. Olah, Angew. Chem. Int. Ed. Engl. 34 (1995) 1393.

[24] R.I. Kaiser, Habilitationsschrift Chemnitz (2002);
R.I. Kaiser, Chem. Rev. 102 (2002) 1309.

[25] D. Gerlich, J. Anal. At. Spectrom. 19 (2004) 581.

[26] S. Schlemmer, T. Kuhn, E. Lescop, D. Gerlich, Int. J. Mass Spectrom. 185 (1999) 589.

[27] I. Čermák, I. Savić, D. Gerlich, in: Safránková, (Ed.), Proceedings of Contributed Papers, Part II, WDS'02, Matfyzpress (2002) 281.

[28] I. Savić, Ph.D. Thesis, TU Chemnitz (2004) http://archiv.tu-chemnitz.de/pub/2004/0132.

[29] N.R. Daly, Rev. Sci. Instrum. 31 (1960) 264.

[30] D. Gerlich, G. Kaefer, Asrophys. J. Suppl. Series 347 (1989) 849.

[31] D. Gerlich, Adv. Chem. Phys. LXXXII (1992) 1.

[32] D. Gerlich, S. Horning, Chem. Rev. 92 (1992) 1509.

[33] A. Luca, S. Schlemmer, I. Čermák, D. Gerlich, Rev. Sci. Instrum. 72 (2001) 2900.

[34] I. Čermák, M. Förderer, I. Čermákova, S. Kalhofer, H. Stopka-Ebeler, G. Monninger, W. Krätschmer, J. Chem. Phys. 108 (1998) 10129.

[35] D. Gerlich, S. Schlemmer, Planet. Space Sci. 50 (2002) 1287.

[36] M.A. Smith, S. Schlemmer, J. von Richthofen, D. Gerlich, Asrophys. J. Suppl. Series 578 (2002) 87.

[37] A. Abdurahman, A. Shukla, G. Seifert, Phys. Rev. B 66 (2002) 155423.

[38] R. Scholz, M. Schreiber, G. Seifert, in: D. Gerlich, T. Henning, (Eds.), Structure, Dynamics and Properties of Molecules and Grains in Space, FOR 388, Report 2000–2003 (2003) 53.

[39] G. Fischer, R. Barthel, G. Seifert, submitted for publication.

[40] D. Talbi, D.J. DeFrees, D.A. Egolf, E. Herbst, Asrophys. J. Suppl. Series 374 (1991) 390.

[41] K.F. Freed, T. Oka, H. Suzuki, Asrophys. J. Suppl. Series 263 (1982) 718.

[42] R.I. Kaiser, A.G. Suits, Rev. Sci. Instrum. 66 (1995) 5405.