3.1 Bericht Teilprojekt 7

3.1.1 Titel / Title

Wachstum und Zerstörung von kohlenstoffreichen Molekülen und Clustern unter inter- und zirkumstellaren Bedingungen

Growth and destruction of carbon-rich molecules and clusters under inter- and circumstellar conditions

3.1.2 Berichtszeitraum / reported period

01.07.2003 - 31.12.2006

3.1.3 Projektleiter / principle investigator

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3.2 Zusammenfassung / Abstract

3.2.1 Wortlaut des Antrags / abstract of the proposal

Die Kombination von Speichern und verschiedenen Nachweismethoden mit einem Kohlenstoffstrahl erlaubt es uns, chemische und optische Eigenschaften von Kohlenwasserstoffen $C_nH_m^+$ zu bestimmen ($n < 10000$ and $m \geq 0$). Erste Ergebnisse wurden erhalten für die astrochemisch wichtige Wechselwirkung von H_3^+ mit C_3. Weiterhin wurden Reaktionen von CH_4^+, C_3^+ und C_3H^+ mit H_2 und HD untersucht. Für diese kleinen Systeme werden z. Zt. in Zusammenarbeit mit TP 4 und TP 5 die systematischen Untersuchungen bis zu $n = 4$ ausgedehnt. In der kommenden Bewilligungsperiode wird sich dieses Projekt ganz darauf konzentrieren, einzelne Cluster ($n > 50$) bzw. Nanoteilchen in einem Vierpol (4PT, NPMS Technik) zu speichern, mit *in-situ* Nachweismethoden zu untersuchen und physikalisch oder chemisch zu modifizieren. In einem ersten Experiment wird der Nachweis des gespeicherten Objektes auf der Beobachtung von laserinduzierter Schwarzkörperstrahlung beruhen. Die spektrale Zerlegung des bei verschiedenen Temperaturen emittierten Lichts erlaubt es, optische Konstanten und ihre Abhängigkeit von Größe und Struktur zu bestimmen. Weitere Untersuchungen basieren auf der Veränderung des isolierten, gespeicherten Teilchens durch Anlagerung von weiteren Kohlenstoffatomen, thermischer Relaxation, Heizen bis zum Massenverlust oder chemische Modifikation wie Oxydation, vor allem aber die *in situ* Anlagerung von Wasserstoff. Perspektivisch sollen Methoden entwickelt werden, die die Beobachtung von Photolumineszenz und über Massenverlust die Aufnahme von IR Absorptionsspektren erlauben.

The combination of ion or particle traps and various detection schemes with a carbon beam, allows us to study chemical and optical properties of hydrocarbons $C_nH_m^+$ ($n < 10000$ and $m \geq 0$). Recently, results have been obtained for the astrochemically important interaction of H_3^+ with C_3. In addition various products have been detected from the reactions of CH_4^+, C_3^+ and C_3H^+ with H_2 and HD. For these small systems, the studies are presently extended to $n = 4$ in cooperation with TP 4 and TP 5. In the next funding period the main aim of this project is to concentrate on *in-situ* characterization and modification of clusters or nanoparticles stored in a quadrupole trap (4PT, NPMS technique). In a first approach, detection shall be based on observation of laser induced black body radiation. Spectral analysis of this emission for various temperatures will provide information on the optical constants and their dependence on the particle size and structure. Future experiments shall be based on modifying trapped objects by adding or removing C atoms, thermal annealing, or on other chemical modifications changes such as oxidation or hydrogenation. There are plans, to observe photoluminescence and to develop techniques for recording IR absorption spectra, based on mass loss of physisorbed atoms or molecules.

3.2.2 Zusammenfassung des Berichts / abstract of the report

The aim of TP 7 was to study the formation and destruction of carbonaceous material under inter- and circumstellar conditions, including simple hydrocarbon ions, a neutral carbon beam and carbon nanoparticles. For this purpose, four different rf devices have been used, a ring electrode trap, a 22pole trap, a guided ion beam arrangement, and, in ongoing experiments, a new quadrupole trap. One of the challenges was to provide an

intense carbon beam. For this purpose, a graphite sublimation source has been combined successfully with the other modules. For the first time, it became possible to study collisions between stored ions and small neutral carbon molecules C_n (n = 1-3). Results for $D_3^+ + C_3$ revealed that D^+ transfer dominates over all other exothermic product channels. Formation of C_3D^+ is almost twice as slow as assumed in astrophysical models.

In order to extend our knowledge about ion chemistry involving three carbon atoms, reactions of C_3^+, C_3H^+ and $C_3H_3^+$ with H_2 and HD have been studied between room temperature and 15 K. A large set of data which is important for understanding the hydrocarbon astrochemistry, has been summarized in the PhD thesis of Igor Savić (2004) and in several publications. Many unexpected results have been obtained. For example, the low temperature reactivity of C_3^+ indicates that C_3^+ is floppy. One explanation is a low energy pseudorotation of a cyclic structure. This idea has been corroborated by very recent *ab initio* calculations (Rosmus 2006). For $C_3H^+ + HD$ collisions, a huge isotope effect has been discovered: formation of C_3HD^+ is over one hundred times faster than of $C_3H_2^+$.

During this funding period, a significant step forward has been made with the optical detection of stored nanoparticles, one of the main aims of TP 7. Combining an octopole with an efficient optical system, we succeeded to record *in situ* the black body radiation from a cloud of C_{60}^+ molecules which have been heated to temperatures above 3000 K with a pulsed laser. The correlation of the decay via C_2 loss and radiative cooling with the temperature is discussed. These experiments which are continued, open up new methods to study chemistry a very high temperatures. Presently, a quadrupole trap and a CW laser is implemented in order to reach stationary conditions. In parallel to the activities in Chemnitz, cooperations with several groups have been started in order to contribute to the initial goals of TP 7.

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

In the first proposal of TP 7, many different experimental activities have been proposed to study carbonaceous material under inter- and circumstellar conditions. The goals included gas phase collisions with neutral carbon atoms, chemistry of carbon anions, singly and multiply charged C_{60} ions and nanometer-sized carbon particles. The ambitious research plan was based on the combination of the experiences accumulated in the group *Gasentladungs- und Ionenphysik* with those of an assistant, who joined the group in 1999. Several problems (see below) forced us in the second funding period, to reorganize our FGLA projects. As described also in its final report, we decided that TP 5 should concentrate on gas phase reactions, mainly with H atoms, while TP 7 should focus on optical detection of stored nanoparticles.

Despite the large effort undertaken in many laboratories (we just mention here just Joblin *et al.* 2006), investigations of the structure and reactivity of large hydrocarbon molecules at inter- and circumstellar temperatures remain sparse. Concerning gas phase reactions, the current status of the field has been summarized in our recent publications (Savić *et al.* 2005a-c, 2006a,b). The wealth of our new data leads to the conclusions that the description of hydrocarbon reactions under interstellar conditions has to be revised and that more low temperature studies are needed to provide reliable data for astrochemical databases. Stimulated by this and other activities (see TP 5) a new project has been started recently in collaboration with the university of Arizona. In the center is the construction of a new machine similar to ours (see Fig. 10 in the report of TP 5). 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).

Another motivation at the beginning of TP 7 was to learn more about optical properties of carbon molecules and carbon containing compounds. They are certainly responsible for many absorption and emission features of the interstellar medium, e.g. the diffuse interstellar bands (DIBs), the interstellar extinction hump at 217 nm, or emission bands in the infrared. In the past three years a new apparatus has been developed in Basel in the group of John Maier in collaboration of with us (Dzhonson *et al.* 2006). The primary aim of this experiment is to measure electronic spectra of large ions at low vibrational and rotational temperatures, as of relevance to astronomical observations. One special example of mutual interest is to record an optical spectrum of stored C_{60}^+ ions which has been observed so far only in a matrix (Maier 1994).

A third field of interest is to study the interaction of charged hydrocarbons with UV and FUV light. In this context we mention here briefly a proposal by M. Tulej (2006) who intends to create, modify and detect large nanosized singly and doubly charged hydrocarbons by combining synchrotron radiation, ion spectroscopy, and the ion trapping and cooling technology, developed in our laboratory. The main task of this project is the preparation and subsequent analysis of large charged hydrocarbon compounds involving 20 to 200 carbon atoms including hydrocarbon chains and polycyclic aromatic molecules (PAHs) by using of tunable VUV radiation.

In summary one can say that our initial goals have been reached only in part; however, they have stimulated many new initiatives in the field of carbonaceous astrochemistry.

3.4 Angewandte Methoden / Applied methods

3.4.1 RF and AC trapping

TP 7 has utilized a variety of rf and ac traps and ion guides for studying carbonaceous material under inter and circumstellar conditions - ranging from simple hydrocarbon ions to nanostructures (Gerlich 2004). Making use of the modular design, specific ion and particle sources have been combined with neutral beams and rf devices. Fig. 1 shows the arrangement of a carbon sublimation source and a ring electrode trap. Technical details and many fundamental results have been described by Savić *et al.* (2005a). The trap has been operated between 80 K and room temperature; however, it also can be heated to higher temperature (up to 800 K) in order to simulate conditions of circumstellar discs.

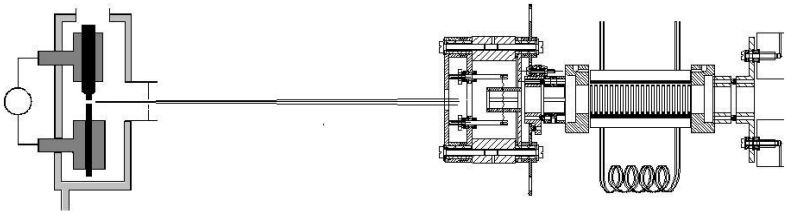

Fig. 1: Schematic diagram of the combination of a carbon evaporator and an ionizer with a ring electrode trap. For analysis, the trapped ions are extracted, mass selected and detected with a Daly type detector (to the right, only the entrance of the QPMS is indicated). The parts are at scale with exception of the distance between the carbon rods and the trap which is 40 cm (the inner diameter of the trap is 1 cm). In the trapping volume C_3 number densities up to 2×10^8 cm^{-3} have been reached.

Another series of experiments (Savić *et al.* 2005b,c and 2006a,b) has been performed in the temperature variable 22PT which has been described thoroughly in the literature (see Gerlich 1995 and related references in TP 4 and TP 5).

The Guided Ion Beam arrangement

In order to gain more experience with monitoring hot carbon nanoparticles via photo emission, we have used the well-tested Guided Ion Beam arrangement (GIB) shown in Fig. 2. Via a window and an large optical system (see Fig. 3), light emitted from confined ions can be detected quite efficiently. Originally such an arrangement has been used for monitoring chemiluminescent ion-molecule reactions or photons induced by a laser (Gerlich 1992). In the present experiment we follow the black body radiation emitted from laser heated particles.

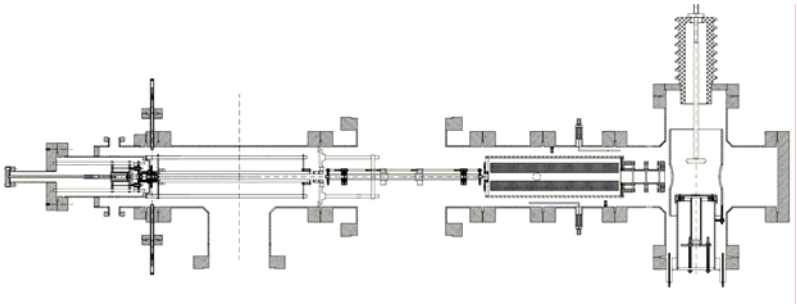

Fig. 2: An octopole ion guide is used in the center of the arrangement for optimizing the optical detection system which has been constructed for monitoring laser heated carbon structures via black body emission.

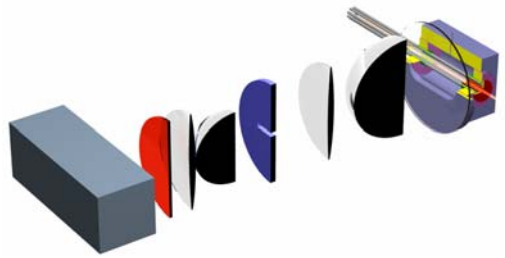

Fig. 3: The optical detection system uses a photomultiplier (R1527P) for single photon detection. The quantum efficiency is 10 %, the visible trapping volume is also about 10% of total storage volume, and the collection efficiency for photons is 2% (through the octopole rods).

The tests which have been performed with C_{60}^+ ions created from gaseous C_{60} in a sublimation oven via electron impact ionization, are described below.

The SRE-4PT

The ultimate goal of this experiment is to monitor, characterize, and modify for long time just one single carbonaceous nanoparticle which is localized in a quadrupolar field. A technical development which is well-suited for this purpose is the high-resolution nanoparticle mass spectrometer (HR-NPMS) developed in our laboratory. It is based on long time trapping of one charged object in a three-dimensional quadrupole field and on non-destructive optical detection (Schlemmer *et al.* 2004, Gerlich 2004, Grimm *et al.* 2006). The charge to mass is derived from observing and evaluating the oscillatory motion in the trap. This allows one to record very precisely changes of the charge and gain or loss of mass.

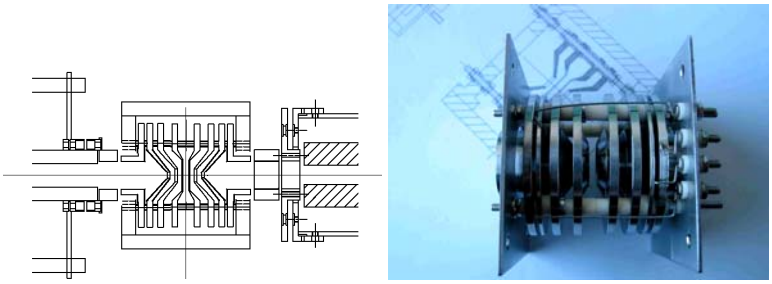

Fig. 4: There are various electrode arrangements to approximate the Paul trap, i.e. the ideal boundary conditions of a quadrupolar field. The depicted design (Decker 2007) which is rotationally symmetric, has many advantages in comparison to electrode arrangement used previously (Illemann 2000).

The innovative technique, however, still needs a lot of investment and effort. Many attempts have been made to improve the geometry (see Fig. 4). Presently we favor arrangement which is rotationally symmetric and where the central electrode (the ring electrode in the quadrupole) is approximated by two rings. So far, the particle has been illuminated by a visible laser and detected via the scattered light. Due to the size dependence of the scattering cross section, this detection scheme is limited to particles larger than 50 nm. In the present project, thermal emission at high temperatures is used for monitoring the trapped object. More details are given below.

The HR-NPMS technique can be used in material science, in aerosol analysis or "just as a scale" in fg-mass spectrometry. In the present project it is used especially for studying astrophysical dust analogous. The special benefit of this techniques lies in the isolation of the particle with respect to disturbing surfaces and gases, i.e., UHV- and low temperature conditions, and in a very good localization of the particle (in principle better than 1 μm). This makes it perfectly suited to sensitive optical detection (scattering, fluorescence, absorption, non linear processes).

Carbon source

An important experimental progress made in this TP was the integration of a graphite sublimation source (see Fig. 1) into a trapping machine. The early version of the arrangement has been described by Čermák *et al.* (2002). There are various standard methods to form a carbon beam, based on laser ablation of carbon rods, sublimation of graphite, or evaporation of suitable carbon containing compounds. The carbon source used in this project has been described in detail by Decker (2003), Savić (2004), and Savić (2005a). It was developed originally in Krätschmer´s group in Heidelberg for spectroscopic studies on matrix-isolated carbon molecules (Čermák *et al.* 1998). 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.

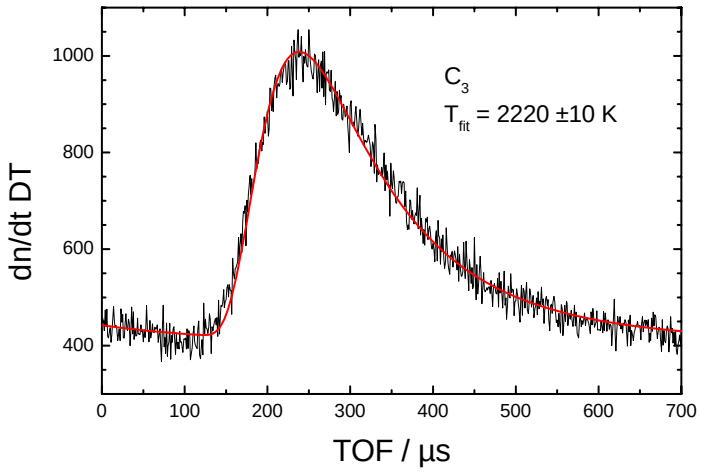

Fig. 5: Measured TOF distribution of C_3 emerging from the resistively heated carbon rod. The red line is a fit with $T = 2220$ K. This value is in accordance with the surface temperature measured with a calibrated pyrometer.

Recently an universal detector has been used to determine the composition and velocity distribution of the carbon cluster beam. The results, 80 ± 8 % C_3, 8 ± 2 % C_2, and 12 ± 6 % C, are in good accordance with the distribution determined in the trap using proton transfer from H_3^+ (chemical probing). In the ion trap (= interaction region, see Fig. 1) which is 40 cm away from the carbon rods, one obtains a number density of some 10^8 cm^{-3}.

There are various physical properties which have been used for characterizing the operating conditions of this carbon source. One of them is the rod resistance which is measured via a four-point scheme. There are other parameters such as surface temperature, total flux, cluster composition or velocity distribution. A not expected observation was that the material is ejected in intense quasiperiodic pulses with a few Hz (Decker 2003).

The TOF distributions measured recently (see Fig. 5) have revealed that the translational temperature of the beam is 2220 K. This is in accordance with the surface temperature measured with a pyrometer. This and the pulsed nature is a hint that the emitted carbon flow does not sublimate directly from the surface area of the rods. Whether the quasi-periodic eruptions are due to high pressure carbon gas in small cavities or liquid bubbles produced inside of the rods, is still uncertain. More studies are in progress in collaboration with I. Savić and W. Krätschmer.

3.4.2 Project organization, challenges and problems

As discussed in more detail in the report of TP 5 (Section 3.4) we have tried during the first funding period to operate, in a cooperative way, three separate machines devoted to a variety of specific research projects. For several reasons, ranging from lack of technical support to loss of know-how in the group, the resulting expectations were too high, especially since TP 7 intended to cover a wide field reaching from molecular to solid state physics, and including anorganic and organic chemistry.

Looking back it seems to be obvious that our group of researchers was too small for making the progress which has been promised seven years ago. A key problem in TP 7, however, was caused by the fact that Dr. I. Čermák, who has joint the TUC in 1999 and who has stimulated the ambitious carbon proposal, became sick in summer 2002. Unfortunately, he could not come back to work until his contract as assistant ended in February 2005. He did not contribute at all to put together the report in 2003 and to the proposal for the second funding period. Nonetheless the graduate student, I. Savić, finished his PhD successfully, in part with work performed on a different apparatus (Savić 2004). The remarkable progress made on the carbon trapping machine in the last years is mainly due to the graduate student S. Decker who started with his PhD work in 2004.

3.5 Ergebnisse und ihre Bedeutung / Results and their importance

The astrophysical motivation for the experiments of this project is to contribute to our understanding of growth and destruction or chemical modification of carbonaceous structures. The experiments we have performed are relevant as well for the chemistry of cold interstellar molecular clouds as well for processes occurring in hot and dense circumstellar environments (see Fig. 6 for illustration).

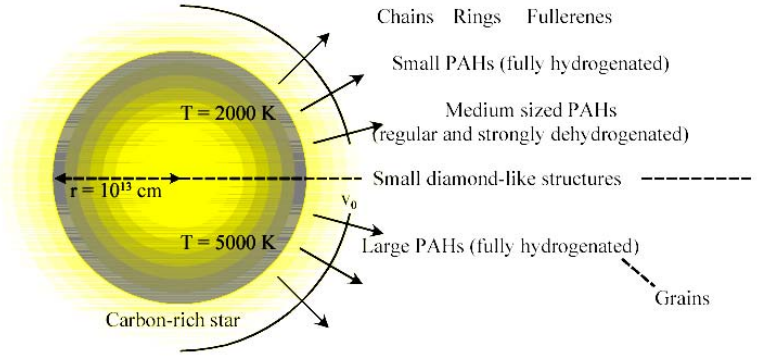

Fig. 6: Summary of typical carbon molecules and clusters formed in the outer atmosphere of a carbon-rich star (Pascoli and Polleux 2000). Many molecules are formed in stellar outflows, where the emitted material cools from 5000 K or higher down to 50 K and where the number density goes from about 10^{12} cm^{-3} to 10^{6} cm^{-3}. Some more details are discussed in the thesis from Savić (2004).

Reactions with C_n

Exchange or association reactions with neutral carbon atoms and molecules play an essential role in the chemistry of interstellar clouds and of circumstellar discs; however, performing related laboratory work is an experimental challenge. During the FGLA, an experimental set-up has been developed for the first time which allows us to study collisions between trapped ions and carbon molecules C_n (n = 1-3) and . The machine which uses a ring-electrode trap (RET) is shown schematically in Fig. 1. Concerning description of experimental details we refer to Savić (2004) and Savić *et al.* (2005a). Specific test measurements have been summarized recently by Savić *et al.* (2006a).

Results for two classes of reaction systems have been included in Savić *et al.* (2005a): reactions with D_3^+ and with carbon ions. An important observation is that, in collisions of D_3^+ with C_n, deuteron transfer dominates over all other exothermic product channels, i.e.,

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

Despite this preference, the absolute rate coefficients for forming C_nD^+ are a factor two smaller than the values used in astrophysical models. The collision systems $C_m^+ + C_n$ are important for the growth of pure carbon chains or rings, also via radiative association. First results indicate that, also in this case, the rate coefficients are much slower than generally assumed. Due to the weak signal, only upper limits could be determined. Accounting for the sensitivity of the apparatus we concluded that the association rate coefficient for

$$C_3^+ + C_3 \rightarrow C_6^+ + h\nu \qquad (2)$$

is smaller than 1×10^{-11} cm^{3}s^{-1}.

Reactions of $C_mH_n^{\pm}$

One of the motivations to study in more detail reactions involving three carbon atoms, was the large abundance of the C_3H_2 molecule and its deuterated variants observed in dark interstellar clouds. In order to improve the input data of astrochemical models, a large table with results for reactions of $C_3H_n^+$ with H_2 and HD has been published by Savić and Gerlich (2005b). Many results have been unexpected, e.g. the reaction

$$C_3^+ + HD \rightarrow C_3D^+ + H \qquad (3)$$

is 6 times faster ($k = 9.3 \times 10^{-10}$ cm^{3}s^{-1}) than previously assumed. For the first time a radiative association process,

$$C_3^+ + HD \rightarrow C_3DH^+ + h\nu\,, \qquad (4)$$

has been observed in a small reaction system with a competing exothermeric channel ($k_r = 6 \times 10^{-11}$ cm^{3}s^{-1}). The reaction system $C_3H^+ + H_2$ shows a strong temperature dependence. In $C_3H^+ + HD$ collisions an incredible isotope effect has been discovered favoring deuteration. Some additional aspects on the various routes in forming hydrocarbon ions with three carbon atoms and deuterated variants under interstellar conditions have been summarized recently (Savić and Gerlich 2006b). One of the general conclusions from all the new results is

that, in contrast to the general opinion that such systems have been well studied, more systematic studies of carbon clusters are needed, especially over a wide range of temperatures.

Although it is very important to go to larger systems (m > 3) there are still open questions for m = 1 and m = 2. Some of them have been mentioned in the reports of TP 4 and TP 5. Reactions of $C_2H_3^+$ or $C_3H_2^+$ with H are still pending. A special role plays protonated methane, CH_5^+. Of astrochemical importance is its formation via radiative association of CH_3^+ with H_2 (Gerlich and Horning 1992) and its destruction via

$$CH_5^+ + H \rightarrow CH_4^+ + H_2 \qquad (5)$$

which is discussed in TP 5 (Borodi *et al.* 2007). Very interesting, from a fundamental point of view, is also the reactivity and the structure of this hypercoordinated carbocation, characterized by a two electron – three center configuration. A summary of collision experiments which provide information on the structure of CH_5^+ ions and deuterated variants has been published recently (Gerlich 2005a). A big step forward was the first global IR spectrum mentioned in TP 4. Also these results can be found in the literature together with new calculations (Asvany *et al.* 2005).

Carbon at high temperatures

As illustrated in Fig. 6 carbonaceous material can grow in stellar environments to large structures including fullerenes, PAHs, HACs, or graphite like particles. In addition to the gas phase work described above, it was the aim of TP 7 to study growth, destruction and chemical modification of large carbonaceous structures (1 nm < d < 100 nm) at high temperatures. For this purpose two experimental arrangements described above (Section 3.4) have been constructed. The experimental strategy is based on the combination of destructive (QPMS) or non-destructive (NPMS) mass spectrometry with optical detection, i.e. monitoring and characterizing the hot trapped particles via blackbody radiation. The spectral distribution of the light allows directly to get a measure for the mean excitation energy (~ temperature) of the trapped ions or nanoparticles.

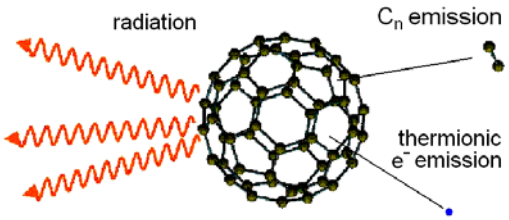

Fig. 7: Laser heated carbonaceous structures are studied in an octopole trap by measuring a correlation between the black body radiation and mass or charge loss. Under the conditions of our experiments, thermionic emission is negligible.

For testing the experimental setup, C_{60}^+ ions have been produced by electron bombardment of C_{60} in the sublimation source shown in Fig. 2. After mass selection, the ions are trapped in the linear rf octopole using suitable potentials on two ring electrodes. For heating the stored ensemble a pulsed Nd:YAG laser has been used (Continuum Powerlite 9030, wavelength λ=1064 nm, pulse width 10 ns, repetition rate 30 Hz, beam diameter of 2 mm). The laser beam passes nearly parallel through the machine in axial direction. Intensities up to 10^8 W/cm² have been used.

The octopole trap has been filled 30 times a second with some thousand ions per cm^3 each time. After a trapping time of 5 ms , the laser has been fired; however, only every second time for background subtraction. Following the excitation with an IR pulse (energy 10 - 30 mJ), the hot ions are stored for another 5 ms. During this time the emitted photons are detected with a multi-channel scaler in the two wavelength regions, 380 nm - 460 nm and 455 nm - 700 nm,. Based on a dielectric model and accounting for the geometry, detection efficiencies etc., temperatures have been determined by simulating the emission in the two different spectral ranges. A typical result is shown in Fig. 8.

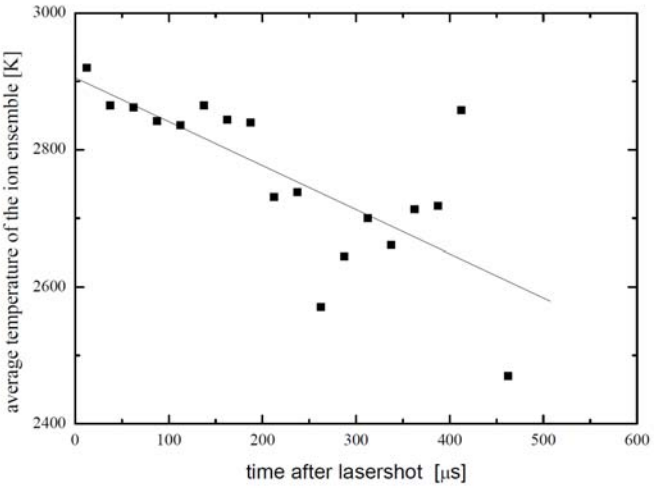

Fig. 8: Temperature drop of C_{60}^+ ions heated with a 10 ns IR laser pulse. The temperature has been derived from thermal emission recorded in two wavelength ranges. The straight line is the result from a model calculation explained in the text.

The highest temperatures observed with the time resolution used (>10 µs) was always below 3000 K although the energy content of the ions certainly gets higher during the laser pulse. The reason is efficient cooling of the hot ions via sequential emission of C_2 molecules,

$$C_n^+ + n\,h\nu \;\rightarrow\; C_{n-2}^+ + C_2\,. \qquad (6)$$

Mass analysis of the stored ions corroborates this. As an example, Fig. 9 shows the number of various C_n^+ fragments after heating the stored ensemble with single laser pulses with energies between 10 mJ and 30 mJ.

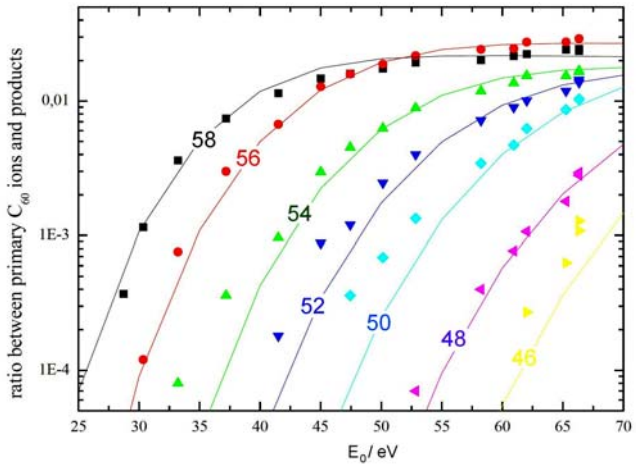

Fig. 9: Number of C_n^+ fragments (n = 58, 56 ...) measured relative to the injected number of C_{60}^+ as a function of the internal energy E_0, calculated from the mean laser energy per pulse (see Eq. 7). The solid lines indicate that the experimental data can be nicely simulated with a kinetic model which is based on sequential C_2 emission.

From an experimental point of view it is important that there is quantitative agreement between the loss of C_{60}^+ and the sum of fragments. This indicates that the trapping potential was high enough to confine also the fragments accelerated by the laser induced fragmentation process. In some measurements Helium buffer gas up to 10^{-5} mbar has been used; however, no significant additional cooling or relaxation has been observed. Emission of a second electron from C_{60}^+ can be neglected at the conditions of our experiment.

Hot fullerene neutrals, cations and also anions have been investigated rather often in the last decade using sophisticated experimental methods (Mitzner and Campbell 1995, Wörgötter *et al.* 1996, Concina *et al.* (2005), Hertel *et al.* (2005), Bekkerman *et al.* (2006)). From the point of view of the technology the Aarhus storage ring experiment is somewhat related to our approach (Tomita *et al.* 2001, Andersen *et al.* 2001). The observations are usually analyzed using more or less complex simulations. They account, often in a simplified way, for the heating processes, the evolution of the internal energy, cooling via blackbody radiation, and ejection of particles. A critical inspection of the publications and the reported parameters reveals that the model calculations always have enough free parameters to obtain satisfying agreement between observations and simulation. Also our data

can be nicely approximated as can be seen from Fig. 8 and Fig. 9. In our simulations, the simple linear relationship between the mean energy of the laser pulse, E_{hv}, and the obtained internal excitation E_0 is used,

$$E_0 / \text{eV} = 2.7 \times E_{hv} / \text{mJ} + 18 \, . \qquad (7)$$

As common in the literature, photon emission is described with a simple dielectric model while C_2 loss is calculated with the Arrhenius like expression

$$k = A \exp(-E_b/kT) \, . \qquad (8)$$

For A and E_b we have used the parameters published by Concina *et al.* (2005), e.g. $A = 1.2 \times 10^{21}$ s^{-1} and $E_b = 10.7$ eV for C_{60}^+. Earlier experiments have used $A = 2 \times 10^{19}$ s^{-1}, lowering the dissociation energy by 0.8 eV. The rather large uncertainties in the pre-exponential factors and the binding energies may be caused by non-equilibrium conditions in various experiments. As illustrated by the model calculation shown in Fig. 10, a special problem is the very fast sequential decay of highly excited ions.

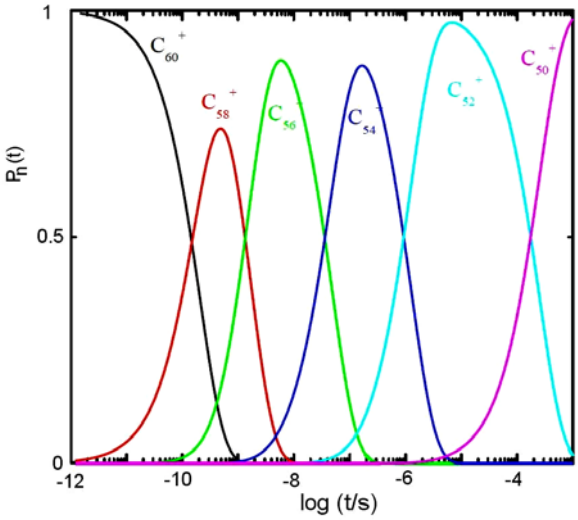

Fig. 10: Simulation of the sequential decay of a C_{60}^+ ion starting at t = 0 s with an internal energy of $E_0 = 65$ eV. The calculation is based on reaction (6), Eq. 8, and the assumption, that emission of a C_2 reduces the total energy just by its binding energy.

The main conclusion from our experiment (and also from others) is that better strategies are needed in order to understand the high temperature chemistry of carbonaceous material. Heating an ensemble of molecules by a pulsed laser or by particle bombardment often leads to uncertain or even ill-defined initial conditions. A better approach is to confine the particles in a trap for long times and to heat them using a continuous laser beam.

Recently the 8PT in the machine shown in Fig. 2 has been replaced by the quadrupole trap described above. This allows for very good localization of the C_{60}^+ ensemble. Estimates indicate that a continuous CO_2 laser beam with up to 20 W, focused to 100 µm, is sufficient to maintain a stationary equilibrium at temperatures up to of 3000 K. The wide range of storage times and the sensitivity of the trapping technique will allow us to record decay rates between 0.001 s^{-1} and 1000 s^{-1}. Presupposing that Eq. 8 and the parameters reported by Concina *et al.* (2005) are correct, this corresponds to temperatures between 2237 K and 3061 K, respectively. Such experiments are well suited to determine reliable thermochemical values. A fundamental question is whether the concept of a temperature is adequate at all for describing an ensemble of non-interacting C_{60}^+ ions or a single isolated carbon nano-particle stored in a laser beam.

There are many other interesting applications of the new instrument. Maintaining a stationary state at low decay rates will allow for recording precisely the emission spectrum of nanoparticles and provide optical constants for astrophysical models of hot regions. Inert buffer gas will introduce another week cooling mechanism which can be studied in detail. The use of molecular gases such as methane or acetylene leads not only to collisional cooling but also to dissociation and chemical reactions. It is planned to determine the deposition rate of carbon at high temperatures. Finally, the combination of the carbon source with the trap will allow us to investigate in temperature depended growing rates, a process of huge importance for the chemistry of carbon rich stars.

3.6 Zusammenfassung und Ausblick / Summary and future

Durch seine chemische Vielfalt ist Kohlenstoff ein faszinierendes Atom. Da es außerdem das häufigste nichtflüchtige Element im Universum ist, spielt es eine wichtige Rolle in der Astrochemie. Das Hauptziel des TP 7 war es, die Bildung und Zerstörung von einfachen Kohlenstoffketten, Kohlenwasserstoffen und Nanoteil-

chen im Labor unter inter- und zirkumstellaren Bedingungen zu verfolgen. Dies wurde durch den Einsatz von verschiedenen innovativen Speichertechniken ermöglicht, einem Ringelektrodenspeicher, einem 8-Pol und einem 22-Pol, und einer neuen Vierpolfalle. Eine besondere Herausforderung war der Aufbau eines Kohlenstoffstrahls und seine Integration in eine Ionenspeicher-Apparatur. Damit konnten erstmals Ratenkoeffizienten für Reaktionen zwischen Ionen und neutralem Kohlenstoff C_n (n = 1-3) unter zirkumstellaren Bedingungen gemessen werden, z.B. für den Protonentransfer in $H_3^+ + C_3$ Stößen. Um unser Verständnis der Bildung von einfachen Kohlenwasserstoffen mit drei C-Atomen zu vertiefen, wurden umfangreiche Untersuchungen zu Reaktionen von C_3^+, C_3H^+ und $C_3H_3^+$ mit H_2 and HD durchgeführt. Viele der gemessenen Ergebnisse waren überraschend. Es zeigte sich z. B., dass selbst einfache Fragen noch nicht geklärt sind, wie z.B. die Struktur von C_3^+, ganz zu schweigen von einem Spektrum unter interstellaren Bedingungen. Ein anderes Beispiel betrifft einen extremen Isotopeneffekt: Die Bildung von C_3HD^+ in $C_3H^+ + HD$ Stößen ist über 100 mal wahrscheinlicher als die von $C_3H_2^+$. In der Astrochemie sind H und D auf keinen Fall chemisch äquivalent!

Neben einfachen Gasphasenexperimenten wurde damit begonnen, nanometergroße Kohlenstoffteilchen in einer Falle zu speichern Der Nachweis basiert auf dem Heizen mit einen infraroten Laser und der Beobachtung der resultierenden Schwarzkörperstrahlung. Die spektrale Zerlegung des bei verschiedenen Anregungsenergien emittierten Lichts erlaubt es, die Temperatur, optische Konstanten und ihre Abhängigkeit von Größe und Struktur zu bestimmen. Erste erfolgreiche Testmessungen wurden an einem Ensemble von C_{60}^+ Ionen durchgeführt, die in einem Achtpolspeicher mit einem gepulsten Laser auf bis zu 5000 K geheizt wurden. Eine detaillierte Analyse des emittierten Lichtes und des Abdampfens von C_2 zeigte, dass derartige Experimente im stationären Strahlungsgleichgewicht durchgeführt werden müssen. Daran wird gegenwärtig gearbeitet. Neben der Bestimmung von astrochemisch wichtigen Daten soll dabei auch in Zukunft der grundsätzlichen Frage nachgegangen werden, ob die Temperatur eines einzelnen gespeicherten Nanoteilchens überhaupt sinnvoll definierbar ist.

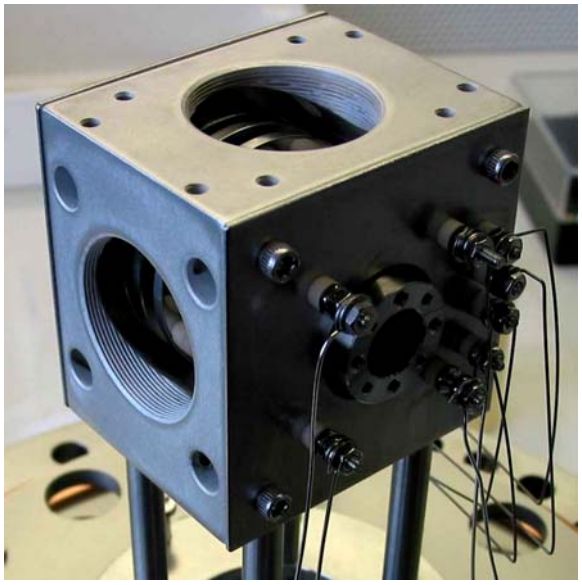

Fig. 11: The new quadrupole trap which is described in Section 3.4 and shown in Fig. 4 is nearly ready. It is especially designed for optical applications.

Future

There are many other questions which can be answered using the experiences gained in TP 7. With the high sensitivity of the trapping technique one can proof whether cyclic carbon cluster ions are really non-reactive in dense clouds. Important for astrochemical applications is a systematic study of adding low velocity H atoms to cold $C_mH_n^+$ ions via radiative association (see TP 5). An even more complex project is the in-situ synthesis of branched carbon structures by adding carbon atoms to cold trapped ions. First tests performed into this direction indicate the feasibility of such experiments. Very interesting from a dynamical point of view is C_3 elimination, observed for C_6^+ and $C_8^+ + D_2$. Such and many more interesting projects are in the focus of the new instrument which is, with our contribution, under construction in Tucson (see Fig. 10 of TP 7)

One of the most innovative technique which has been developed in our group is the combination of quadrupole trapping and optical detection. In TP 7 a significant step forward has been made by replacing the optical detection scheme, which was based exclusively on light scattering by *in situ* observation of the dust analogue via laser heating and black body radiation. A new trap which is especially suited for optical

experiments has been finished (Fig. 11). It can be foreseen that this instrument will provide new insight into the role of hot carbon particles.

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