Molecules in Space & Laboratory, Paris, 2007
J.L. Lemaire & F. Combes (eds)

ASTROCHEMISTRY IN ION TRAPS: FROM COLD HYDROGEN TO HOT CARBON

S. Decker[1], I. Savić[2] and D. Gerlich[1]

Abstract. There is a growing need for detailed laboratory data in order to understand and model the formation and destruction of matter in a variety of environments, ranging from very cold dense interstellar clouds via planetary atmospheres to the high temperatures of circumstellar environments. In this report we summarize recent progress made with special instruments the central devices of which are specific ion or nanoparticle traps. Today, temperature variable 22-pole traps are used routinely in several laboratories in the fields of reaction dynamics and spectroscopy. Recent results from such experiments are briefly mentioned including reactions with carbon radicals or slow hydrogen atoms and isotope fractionation. Traps are also well suited for studying matter at temperatures of several thousand K. In the second part of this contribution we report results from rf traps, in which an ensemble of charged particles is exposed to the radiation of a pulsed or continuous laser. First successful tests have been performed with C_{60}^+. Besides thermal stability of hot interstellar grain equivalents the method allows to explore their growth in a suitable gaseous environment.

1 Introduction

The diffuse material between the stars, the circum and interstellar medium (ISM), consists of various phases with huge differences in their thermodynamic properties. There is a complex interaction and exchange between gas phase, grains, ice layers and photons. Modern observations provide a lot of detailed information; however, we are far from understanding the details. For example, one has identified now more than 150 interstellar molecules. How are they created? Because of the low temperatures, prevailing in interstellar space, many of them have been assumed to be direct or indirect products from ion-molecule reactions; however, laboratory work has given hints that also specific neutral-neutral reactions may be of importance in cold environments. In addition, molecules can be produced and destroyed in shocks, during the birth of a star or while a planetary system is formed. In stellar outflows the ejected matter starts at temperatures above 5000 K and can undergo many reactions and modifications before it reaches cool regions. A special field which has attracted

---

[1] Faculty of Natural Science, University of Technology, 09107 Chemnitz, Germany

[2] Department of Physics, Faculty of Science and Mathematics, University of Novi Sad, Trg Dositeja Obradovia 4, 21000 Novi Sad, Serbia

a lot of interest in recent years, is isotope enrichment. The abundance of deuterated molecules reveals many details of astrochemistry, e.g., it provides evidence that cold icy surfaces play an important role in the chemical evolution of interstellar matter. For better understanding the physics and chemistry of such complex systems, dedicated laboratory work with innovative instruments is of crucial importance.

2 Experimental

Experimental developments for addressing key problems in laboratory astrochemistry have been summarized recently [ger06a] with special emphasis on applications of temperature variable trapping methods. There are different techniques to trap ions and charged particles. For low temperature chemistry and spectroscopy the most successful instruments use radio frequency (rf) multielectrode arrangements where confinement is achieved with a so-called effective potential [ger92]. The main advantage of this versatile and sensitive technique is that charged objects (a single one or an ensemble) can be cooled efficiently with buffer gas, the only exception being the Paul trap. After relaxation one can expose them to photons, electrons, atoms or molecules and study a variety of physical and chemical processes. Very long storage times (up to hours) allow one to detect extremely slow processes with high sensitivity. In most trapping instruments, the ions are generated externally and the products are extracted for mass analysis; however, there is also progress with *in situ* synthesis of reactants and non-destructive analysis of products within the trap. For obtaining a cold environment the trapping electrodes are mounted onto a closed cycle helium refrigerator. Surrounded by two radiation shields, temperatures as low as 4 K can be reached with modern cold heads. If one uses an intense pulse of buffer gas, it usually takes only a few ms to cool the translational and internal degrees of freedom of the ions [ger03a].

For astrochemical and other applications, the work horse has become *the* 22-pole ion trap (22PT). First results from such a device have been reported in [ger92c]. A thorough descriptions has been given in [ger95]. Meanwhile some ten 22-poles are in operation. They are used for reaction dynamics [luc05], [ger06a], laser induced reactions [scl06], and as a source for preparing cold ions for storage rings. For example, a 22PT is used to cool H_3^+ for measuring state specific rate coefficients for dissociative recombination [wol06]. In a new 22PT machine, absolute photodetachment cross sections of negative ions have been determined [tri06]. Two 22PT based instruments became operational recently aiming at measuring spectra of large cold ions of relevance to astronomical observations [dzh06] or of very cold protonated biomolecules [boy06].

For extending studies towards higher *kinetic energies*, ions easily can be accelerated in electrostatic fields, e.g. using the Guided Ion Beam technique (GIB) [ger92]; however, preparing high temperature thermal conditions prevailing in circumstellar environments is a challenge. Our solution is the combination of long time trapping in a well-defined small volume and continuous laser heating. Some aspects of the combination of our high resolution nanoparticle mass spectrometry (NPMS) technique [scl01] with a CO_2 laser have been discussed in [scl04]. Very recently, two successful studies of interstellar grain equivalents at very high temperatures have been made. In the first experiment an octopole ion guide with an integrated efficient optical detection system (see Fig. 46 in [ger92]) has been used in combination with a pulsed Nd-YAG laser (Continuum Powerlite 9030, wavelength λ=1064 nm, pulse width 10 ns, beam diameter of 2 mm). In the second one which is shown in Fig. 1, ions are stored in a stack of specially shaped ring electrodes with integrated high precision parabolic mirrors focusing a continuous CO_2 laser into the center of the electrode arrangement [dec08]. In this rf trap we succeeded, for the first time, to maintain high temperature stationary conditions over many minutes. The temperature of an ensemble of several thousand C_{60}^+ ions has been maintained at fixed values up to 2000 K with less than 10 W of laser power. The hot particles are characterized *in situ* by imaging their thermal emission onto an ICCD camera or by counting the emitted photons in various spectral regions. In this way the total number of stored objects can be monitored, as well as their spatial distribution in the trap and, especially important, their internal temperature. For calibration and consistency checks the ions can be extracted, mass selected and counted using a Daly detector.

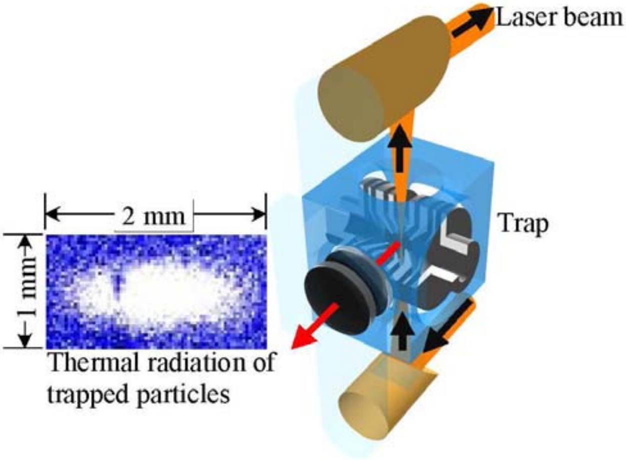

Fig. 1. Perspective view of a set of ring electrodes, creating in the center a 3D quadrupole trap. The trapped particles can be heated with a laser beam which is focused into the trap center via precision parabolic mirrors. They can be observed and characterized via their thermal radiation. Alternatively they can be extracted, mass selected and detected with an ion counting system. The pixel diagram shows the image of an ensemble of stored ions. Note that the shorter extension (FWHW 150 μm) is in the direction of the rotational symmetry axis.

3 Results: gas phase ion chemistry

In recent years many astrochemically important gas phase processes have been studied in rf traps over a wide range of temperatures including radiative association, clustering, isomerization, and isotope fractionation. For cold stored ions, spectral information has been obtained using the method of laser induced reactions [scl06] or other action spectroscopy methods, e.g. photo induced fragmentation [boy06]. A surprising result was that some polyatomic ions become very transparent for VUV if they are cooled below 25 K [dzh07a]. Due to space limitation only a few very recent reactions involving carbon radicals, slow hydrogen atoms, and deuteration are briefly mentioned here. More details can be found in [ger06a], [ger06b] and in references therein.

Possible steps in forming and destroying small hydrocarbons in ISM include collisions of C^+ ions with H and H_2, proton transfer from H_3^+ to C or collisions of CH_n^+ with H. In the last years, many relevant studies have been performed using ion traps. Of fundamental importance is the radiative association reaction $C^+ + H_2 \rightarrow CH_2^+ + h\nu$. For para-hydrogen a rate coefficient of 1.7×10^{-15} cm^3/s has been reported at 10 K, while the value for n-H_2 is 2.5 times smaller [ger94]. First results for $H_3^+ + C \rightarrow CH^+ + H_2$ have been obtained recently by combining an rf trap with a beam of carbon radicals [sav05a]. The measured rate coefficient is almost a factor two smaller than the currently accepted value. This, however, may be in part due to the fact, that the resistively heated carbon source, used in the experiment, creates a rather fast beam of carbon atoms [sav05a]. The dehydrogenation of hydrocarbon ions in collisions with slow H atoms has been studied recently in a new machine, a first description of which has been given in [luc05]. A publication describing this sophisticated instrument is in preparation, discussing thoroughly the combination of atomic or molecular beams and traps with special emphasis on slow H atoms [bor08].

Another field of importance for astrochemistry and fundamental research is (i) the role of deuterium and (ii) the restrictions imposed by the nuclear spins of H and D. More experimental and theoretical work is needed in order to explain the deuterium enrichment observed in cold interstellar clouds or to understand the role of ortho-hydrogen heating [ger06b]. The simple system $H^+ + H_2$ and isotopic variants is rather well understood [ger02b] while the reaction $H_3^+ + HD \leftrightarrow DH_2^+ + H_2$ is still intriguing. At low temperatures, the measured H_3^+/DH_2^+ ratio depends strongly on very small traces of oH_2 [ger02a]. Currently there are several experimental and theoretical groups working on the H_5^+ collision system. Our group plans to contribute to this field with experimental and theoretical studies on the $H_3^+ + H$ collision system.

4 Trapped nanoparticles at high temperature

Depending on the conditions, carbonaceous material in stellar environments can loose atoms or molecules or grow to larger structures. Trapping technique are well suited to study the related high temperatures processes using radiative heating and/or providing molecules or radicals. In order to establish the technology, tests have been performed with C_{60}^+ ions [dec08].

In a first approach the linear rf octopole trap mentioned above, has been filled with some ten thousand ions and, after a trapping time of a few ms, they have been exposed to an intense infrared pulse (10 ns, up to 10^8 W/cm^2). A few μs later, a multi-channel scaler has been started, accumulating for 5 ms the thermal emission of the heated ions in two wavelength regions (380 nm 460 nm and 455 nm 700 nm). From these results, temperatures have been determined, based on a suitable optical model. For example, a total radiative cooling rate of 600 K/s has been determined. Another experimental result is that, also with increasing laser pulse energies, the detected temperatures never went above 3000 K. This is well understood on the basis of very fast (<ns) evaporative cooling of the ions via sequential ejection of C_2. This explanation has been corroborated experimentally by extracting the ions from the 8P-trap and injecting them into a quadrupole mass analyzer and Daly detector.

The results are shown in Fig. 2. The number of fragment ions, C_{60-2n}^+, is plotted relative to the total number of injected C_{60}^+ ions as a function of the energy per laser pulse. As indicated by the lines, the experimental results can be reasonably well modeled, based on the following assumptions: (i) the internal excitation energy depends linearly on the energy of the laser pulse, (ii) photon emission is described with a simple dielectric model (iii) C_2 loss can be calculated with an Arrhenius like expression $k = A\ \exp(E_b/kT)$. The parameters A and E_b have been taken from [con05]. A critical analysis, however, of the various models which can be found in the literature, reveals that pulsed measurements, like ours, are rather insensitive to the parameters, especially also to the binding energies E_b. In addition to this arbitrariness, systematic experimental errors often may be caused by nonthermal conditions. As a consequence we have changed the strategy and use a continuous laser, stationary conditions and long time observations. First measurements with the trap shown in Fig. 1, have been performed on a well prepared ensemble of ions over storage times extending from minutes to hours. Decay rates of C_{60}^+ as slow as 0.002 s^1 have been determined at a temperature of only 1850 K! It is too early to draw conclusions since some more consistency checks need to be performed; however, there is evidence that our experimental E_b - value, i.e. the energy needed to transfer C_{60}^+ into $C_{58}^+ + C_2$, will be much smaller than the currently accepted binding energy.

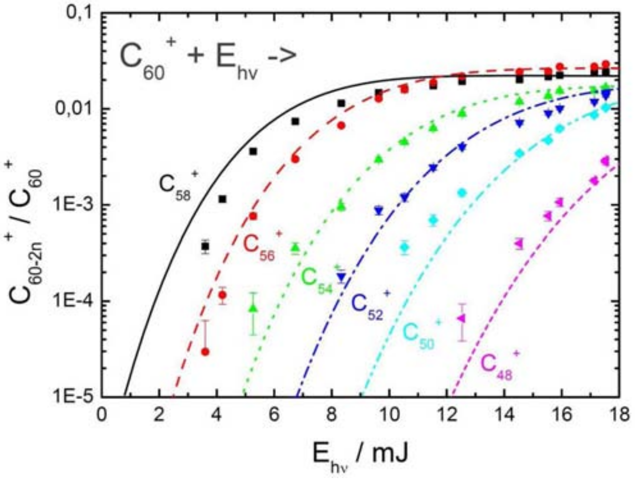

Fig. 2. The measured ratio between the fragments C_{60-2n}^+ (n = 1-6) and primary C_{60}^+ ions rises up to 3 % if the pulse energy of the laser, $E_{h\nu}$, is increased above 10 mJ. At the highest energy almost 10 % of the C_{60}^+ are fragmented. The solid lines are the results of a simple model calculation, using for n= 0 to 5 C_2 binding energies of E_b = 10.7, 8.7, 8.9, 8.55, 8.2 and 8.2 eV.

5 Conclusions and outlook

Trapping machines for applications in astrochemistry are sophisticated and complicated experimental tools; however, they can provide a lot of important information which is required for understanding astronomical data and for preparing observations or the next generation of astronomical instruments. New laboratory instruments for studying more complex gas phase reactions are under development, e.g. *The next* *generation 22PT for astrochemistry* at the University of Arizona. For getting spectral information, for obtaining state specific rate coefficients, etc., more optical and laser based methods need to be combined with storage devices. A nice example is the following procedure for getting spectral information and optical constants of hot nanoparticles: in addition to the heating CO_2 laser, a tunable laser irradiates the trapped nanoparticle. At wavelength where selective absorption occurs, the power of the basic heating laser is reduced such that the temperature of the particle remains constant.

6 Acknowledgement

Financial support by the EC and the DFG is acknowledged, especially via the Forschergruppe *Laboratory Astrophysics* (FGLA).

References

[bor08] Borodi, G., Luca, A., Mogo, C., Smith, M., & Gerlich, D. *Rev. Sci. Instr. in preparation*

[boy06] Boyarkin, O. V., Mercier, S. R., Kamariotis, A., & Rizzo, T. R. 2006, JACS 128, 2816

[dec08] Decker, S. 2008, PhD thesis TU Chemnitz, in preparation

[dzh06] Dzhonson, A., Gerlich, D., Bieske, E.J., & Maier, J.P. 2006, J. Mol. Struc. 795, 93

[dzh07a] Dzhonson, A., Jochnowitz, E.B. & Maier, J.P. 2007, J. Phys. Chem. 111, 1887

[ger02a] Gerlich, D., Herbst, E. & Roueff, E. 2002, Planetary and Space Science, 50, 1275

[ger02b] Gerlich, D. & Schlemmer, S. 2002, Planetary and Space Science 50, 1287

[ger03a] Gerlich, D. 2003, Hyperfine Interactions , 146/147, 293

[ger06a] Gerlich, D. & Smith, M. 2006, Phys. Scr., 73, 25

[ger06b] Gerlich, D., Windisch, F., Hlavenka, P., Plašil, R. & Glosik, J. 2006, Phil. Trans. R. Soc. Lond. A 364, 3007

[ger92] Gerlich, D. 1992, Adv. in Chem. Phys. LXXXII, 1

[ger92c] Gerlich, D. & Horning, S. 1992, Chem. Rev., 92, 1509

[ger94] Gerlich, D. 1994, in: "Molecules and Grains in Space", I. Nenner (ed.), AIP Press, New York, 489

[ger95] Gerlich, D. 1995, Phys. Scr., 59, 256

[luc05] Luca, A., Borodi, G. & Gerlich, D. 2005, in XXIV ICPEAC 2005, ed. F. D. Colavecchia, P. D. Fainstein, J. Fiol, M. A. P. Lima, J. E. Miraglia, E. C. Montenegro & R. D. Rivarola, (Singapore, World Scientific), 494

[sav05a] Savic, I., ermák, I. & Gerlich, D. 2005, Int. J. Mass Spectrom., 240,139

[scl01] Schlemmer, S., Illemann, J., Wellert, S. & Gerlich, D. 2001, J. Appl. Phys. 90, 5410

[scl04] Schlemmer, S., Wellert, S., Windisch, F., Grimm, M., Barth, S. & Gerlich, D. 2004, Appl. Phys. A, 78, 629

[scl06] Schlemmer, S., Asvany, O., Hugo, E. & Gerlich, D. 2006, Proceedings of the 231st IAU Symposium, Lis, D., Blake, G.A. & Herbst, E. (eds.), Cambridge University Press

[tri06] Trippel, S., Mikosch, J., Berhane, R., Otto, R., Weidemüller, M. & Wester, R. 2006, Phys. Rev. Lett. 97, 193003

[wol06] Wolf, A., Kreckel, H., Lammich, L., Strasser, D., Mikosch, J., Glosík, J., Plašil, R., Altevogt, S., Andrianarijaona, V., Buhr, H., Hoffmann, J., Lestinsky, M., Nevo, I., Novotny, S., Orlov, D. A., Pedersen, H. B., Terekhov, A. S., Toker, J., Wester, R., Gerlich, D., Schwalm, D. & Zajfman, D. 2006, Phil. Trans. R. Soc. Lond. A 364, 2981