Astrochemistry in Ion Traps: From Cold Hydrogen to Hot Carbon

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Astrochemistry deals with the formation and destruction of matter in various environments including the early universe, cold dense interstellar clouds, hot circumstellar regions, planetary atmospheres etc. In this contribution I try to summarize previous, present and planned experimental activities in this field using radio frequency (rf) traps for ions and nanoparticles. After a more technological retrospect with selected applications, new results for reactions of slow H atoms with stored CH⁺ and H⁻ ions are presented as well as decay rates for C₆₀⁺ ions, heated with a CW CO₂ laser to temperatures up to 2200 K.

Experimental

The eighties have seen several innovative experiments developed for exploring gas phase chemistry at low temperatures. An early summary can be found in Ref. [1] which also refers to the pioneering work of G. Dunn. His group used a l-He cooled Penning ion trap for studying collision between ions and neutrals. Alternative approaches started with rf ion traps where confinement is achieved with the so-called effective potential. Fig. 1 shows the first trap which could be operated down to 80 K but also up to 500 K. It was presented at the SASP 1988 [2]. Meanwhile, using closed cycle refrigerators, the temperature range down to 4 K has been opened up. From the various multi-electrode arrangements, the 22-pole is probably the most common ion trap used to cool ions for reaction dynamics and spectroscopy.

Figure 1: Left: first rf trap which can be cooled with l-N₂. Right: CH₃⁺ ions reacting to CH₅⁺ with H₂ at a number density of 10¹³ cm⁻³. For details see SASP 1988 (La Plagne) [2].
However, already in 1993, during the Faraday Symposium 28 on *Chemistry in the Interstellar Medium*, Alec Dalgarno emphasized, that also detailed experiments at high temperatures are needed for understanding the complex interaction between gas phase, grains, ice layers and photons in the universe. For ions, translational energies of several eV are easy to obtain; however, e.g. for understanding the chemistry in the outflow of stars, all degrees of freedom have to be heated. Also for this purpose traps are well suited. One technical realization is the Split Ring Electrode Trap (SRET), a stack of specially shaped electrodes with integrated high precision parabolic mirrors for focusing a continuous CO$_2$ laser into its center [3].

![Figure 2](image)

**Figure 2**: Left: 22-pole ion trap combined with an H-atom beam. Right: Split Ring Electrode Trap for heating and monitoring high temperature particles confined in the center.

The stored particles are characterized *in situ* by imaging their thermal emission (BBR) 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. Besides thermal decay of hot interstellar grain equivalents, the method allows one to explore their growth in specific gaseous environments. Successful tests with C$_{60}^+$ are mentioned below.

**Results**

Many gas phase processes involving ions have been studied in rf traps, including bi- and termolecular reactions, radiative association, clustering, isomerization, and isotope fractionation. For applications in spectroscopy and anion chemistry see the contributions from J. Maier, S. Schlemmer and R. Wester to this SASP conference. One of our recent activities has concentrated on the formation and destruction of small hydrocarbons in collisions with H$_2$ and H atoms. Of fundamental importance are the results for CH$^+(v=0,J) + H \rightarrow C^+ + H_2(J')$. As shown in Fig. 3 and discussed in [4], CH$^+$ in the rotational ground state does not react! So far there is no convincing explanations.
The primordial chemistry and the formation of the first stars is determined by atomic and molecular processes involving mainly hydrogen (H, D), helium (^3He, ^4He), electrons, and radiation. One of the key questions until recently was, how efficient is formation of H\textsubscript{2} molecules from H-atoms [5]. There are no grains, but also under early universe conditions this process requires a catalyst, the dominant one being the electron. The first step is the formation of H\textsuperscript{+}, followed by associative detachment with a second H atom. In our ion trap experiment (see Fig. 3 and Ref. [6]), the temperature of both reactants could be varied independently and a range between 10 and 135 K has been accessed experimentally, for the first time. The results are in good accordance with a simple capture model, using the long range potential.

Figure 3: Low temperature collisions. Left: H-atom abstraction reaction, right: associative detachment. For more details see the references [4] and [6].

Figure 4: Decay rates of some thousand C\textsubscript{60}\textsuperscript{+} at temperatures above 1900 K [3].

So far, all experiments which monitored the decay of highly excited C\textsubscript{60}\textsuperscript{+} started with ions with rather undefined internal energies. In the SRET trap we succeeded, for the first time, to maintain stationary equilibria over long periods, meaning that, in time average, the same energy is emitted as absorbed. With less than 10 W of CO\textsubscript{2} laser power, conditions have been reached which may be described by "temperatures" ranging from 1900 to 2300 K. Trapping
times up to 15 min without any loss of ions allow us to follow very slow decay of C_{60}^+ via C_2 ejection. In Fig. 4, rates between $10^{-1}$ and $10^{-3}$ s^{-1} are plotted. At 1850 K, $k$ is as low as 1 h^{-1}. Evaluation of the results using an Arrhenius type function leads to "activation energies" $E_A$ between 2 and 5 eV [3]. Although our experiment really monitors the thermal decay of C_{60}^+ in a high temperature radiation field, it is not yet clear how to correlate $E_A$ with the binding energy of C_2.

Conclusions, Outlook, Acknowledgement

Instruments, using inhomogeneous rf fields are very versatile. It started with W. Paul in the fifties and more than 40 years ago, the first guided ion beam apparatus has been developed. 25 years ago, the first cooled rf ion trap became operational. In combination with optical methods, beams of molecules and radicals, and using the variety of features the rf technique offers, many unique experiments have been performed. The long storage times allow one to detect extremely slow processes with high sensitivity. Activities in the near future (in Prague) will improve and extend our H^+ + H results by using D^+ + H → H^+ + D for calibrating the H-atom beam and by measuring the competition between electron transfer and associative detachment in D^+ + H collision. More state specific rate coefficients for primordial chemistry are on the list, e.g. the reaction HeH'(J)+ H → H_2'(v,J') + He. By closing the trap with meV barriers, it will become possible to observe the exothermic reaction H^+ + H_2(J=1) → H^+ + H_2(J'=0). A real innovative experimental challenge is to superimpose a linear rf multipole with a suitable magnetic field guiding electrons in and out the trap. Trapping nanoparticles opens up a wide, still unexplored field including the very precise mass determination.

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References