Interaction of trapped ions and nanoparticles with atomic and molecular beams

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Introduction

Progress in experimental science is closely related to the development of innovative techniques. This contribution summarizes results which have been obtained in our laboratory by combining atomic or molecular beams with (i) temperature variable ion traps and (ii) storage devices for charged nanoparticles. One of our goals is to study, at temperatures and densities of relevance for astrochemistry, gas phase reactions between cold (or also) hot ions and atoms such as H, C, N. Part of our work is devoted to grow in a trap specific structures of metal clusters or carbonaceous material under well defined conditions. The nanoparticle research aims at getting experimental information on interstellar grain equivalents, e.g., their catalytic activities or the change of optical properties by chemical processes.

Experimental method

The gas phase work is performed in special traps having wide field free regions where the ions are thermalized to the temperature of the cold (or hot) electrodes and surrounding walls via buffer gas collisions (e.g. 22-poles or ring electrode traps). Combining them with atomic or molecular beams significantly extends the flexibility of these devices. First results include the interaction of stored D_2^+ ions with a beam of N atoms.[1] An interesting application of the beam-trap combination is the determination of rates for collisional and radiative relaxation of $Ar^+(^2P_{1/2})$ ions to the $^2P_{3/2}$ ground state.[2] In this experiment a pulsed supersonic beam of hydrogen molecules was used to chemically probe the composition of the stored ion cloud.
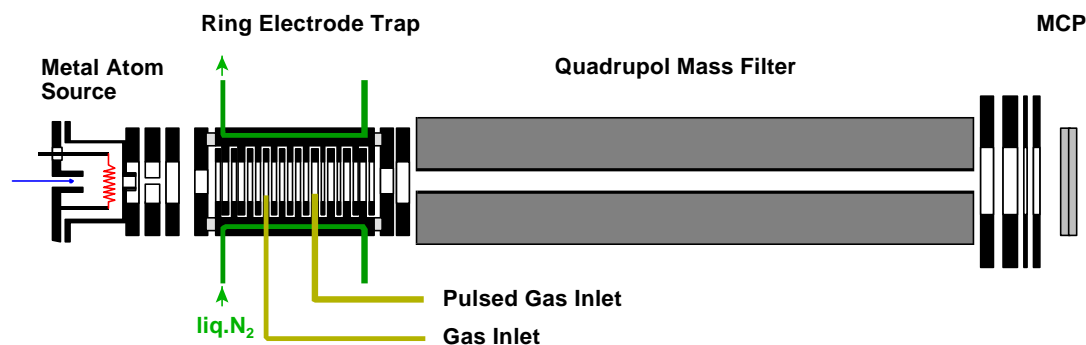

Fig. 1. Trapping apparatus for studying the interaction between stored ions and a beam of metal atoms produced in an electron beam evaporator (left side).

One of the experimental setups presently used is shown schematically in Fig. 1. A thorough description of the technique and measuring procedures can be found in Ref. 3. In the present example primary ions are produced directly in the trap by a beam of elec-

trons or VUV photons emerging from the metal atom source. The ion cloud is stored for a variable time (ms up to minutes) inside the trap. Afterwards the trap contents is extracted by a pulsed gate electrode and injected into a quadrupole for mass analysis. The number of trapped parent and product ions is determined via a conventional ion counting detector employing two micro channel plates in Chevron arrangement.
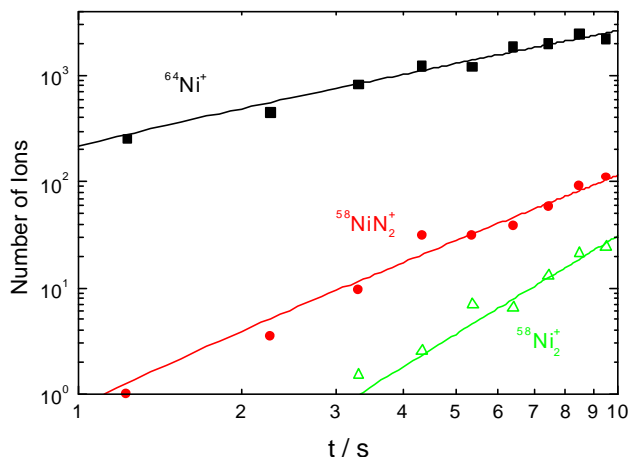

Fig. 2. Time dependence of various trapped ions. Primary ions, produced by VUV from the metal atom source, are N_2^+ (not shown) and Ni^+. Following reactions with ambient Ni atoms lead to other products. A detailed analysis shows that the Ni_2^+ dimers are produced via the intermediate ion $Ni \cdot N_2^+$.

For determining the kinetics, the procedure *ion formation / trapping & reaction / analysis* is repeated often for selected storage times and for all product masses of interest. A typical result is shown in Fig. 2. The double logarithmic presentation reveals that the numbers of some ions increase proportional to the time (e.g. Ni^+ and the not shown N_2^+), others are produced in second or third order. The analysis of such measurements is complicated by the fact that the metal atom source produces not only a beam of Ni atoms (number density in the trap up to $10^8\,cm^{-3}$) but also electrons and photons penetrate the trap.

Oxydation of Ni atoms with O_2^+

The reactivity of metal atoms and metal containing molecules plays an important role in chemistry, biology and in technical applications such as catalysis. From several studies[4] involving Ni atoms, Fig 3 shows rate coefficients for the process $O_2^+ + Ni \rightarrow NiO^+ + O$, $\Delta H_0 = -31.6$ kcal/mol. The measurements have been performed at various Ni-densities and using He ions as precursors. The rather high number of $^{16}O_2^+$ ions created by electron transfer to He^+ has been derived indirectly from the measured $^{18}O^{16}O^+$ isotopes (^{18}O abundance: 0.02 %). From the five Ni isotopes, only the products $^{58}Ni^{16}O^+$ and $^{60}Ni^{16}O^+$ for the most abundant atoms ^{58}Ni (68.1 %) and ^{60}Ni (26.2 %) have been measured. Various tests have been made to proof that NiO^+ is really formed via the indicated gas phase reaction and not via parasitic processes in the Ni source. The ion trap was operated at 100 ± 20 K, the temperature of the metal source was estimated to be 1700 ± 100 K. This leads to a reaction temperature of 670 ± 120 K. The resulting rate coefficients are $k_{58Ni} = (8 \pm 2) \times 10^{-10}\,cm^3 s^{-1}$ and $k_{60Ni} = (4 \pm 1) \times 10^{-10}\,cm^3 s^{-1}$.

Concerning the surprisingly large isotope effect many tests and consistency checks have been performed. Obviously it is significant; however, there is not yet any convincing explanation.
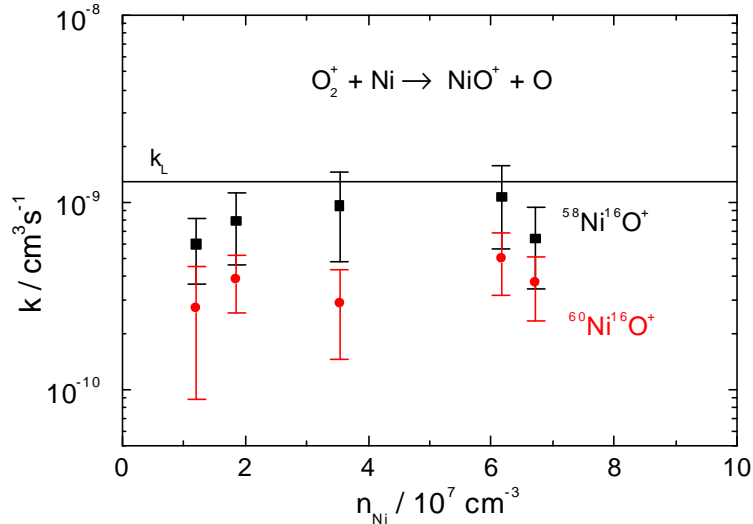

Fig. 3. Rate coefficients for oxidation of Ni atoms, measured at various Ni densities. The values are slightly below the Langevin limit indicated by the solid line. Various tests have been performed in order to find an experimental artifacts explaining the large isotope effect for ^{58}Ni and ^{60}Ni.

Condensation on nanoparticles

Gas-grain interactions are one of the key frontiers in Astrophysical Chemistry. Traditionally these interactions are investigated by probing the surface with analytical tools during or before and after the process. A non-interfering method for monitoring ad- or desorption of gas to a substrate is the microbalance where the increase in mass leads to a shift of the resonance frequency of the probe. In our laboratory we use three-dimensional local confinement of a particle in a quadrupole like trap which enables the study of the kinetics on micro- or nanosized surfaces. A non-destructive and high-resolution mass determination is achieved by detecting scattered light. The information on the eigenfrequencies of the motion is extracted from the intensity modulation. Controlled charging/discharging of the particle in steps of single elementary charges leads to the determination of the absolute charge and thus also of the absolute mass. Integration over long periods of time can lead to resolution in the ppm regime. The apparatus has been described in detail in a recent publication.[5]

First studies of adsorption and desorption of molecules on nanoparticles have been performed using an effusive beam of C_{60} interacting with a trapped nanoparticle. The observed mass changes were corresponding to a few monolayers and there were some experimental indications that the adsorption rate was a function of coverage. In order to perform such experiments with well prepared, clean surfaces the stored nanoparticle is heated with a CO_2 laser with a few Watts/cm^2. Accounting for the small surface this corresponds to an irradiated power of 10^{-8} Watts. A typical result is shown in Fig 4. The mass of the 500nm SiO_2 particle (about 1.12×10^{-16} kg) changes as a function of time. The slow increase is due to condensation of rest gas molecules (most probably H_2O).

Analyzing the initial slope leads to a condensation rate of about 500 molecules/s. This corresponds to a sticking probability of 5%, assuming a partial pressure of 5 10^{-9} mbar. The curvature of the increase indicates that saturation starts to play a role after deposition of several layers.[6] In the near future the nanoparticle experiments will be used to determine ad- and desorption rates for molecules of interstellar relevance (especially CO). More quantitative details will be presented at the conference.
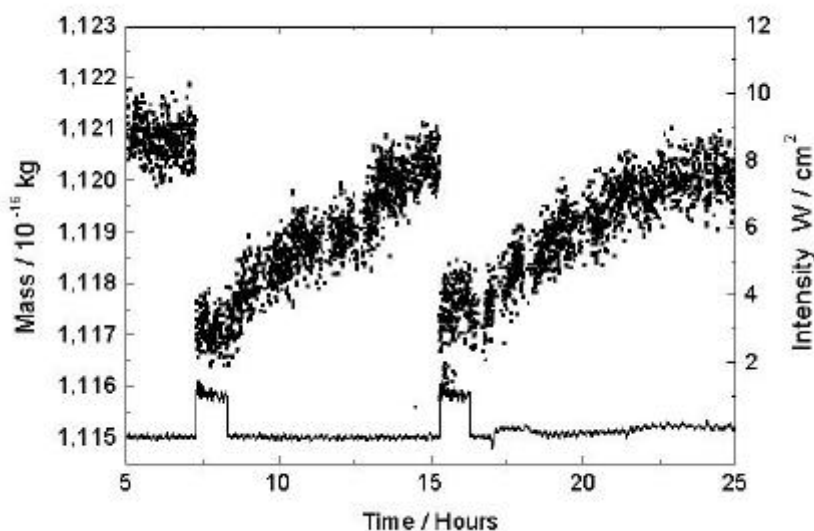

Fig. 4. Increase of the mass of a single SiO_2 nanoparticle (diameter ~500nm) due to adsorption of residual gas. Each point represents the result of a 10 s measurement. At t=7 h and 15 h, the particle is exposed to a CO_2 laser (lower trace, scale at right). The heating process leads to a temperature increase to about 500 K and to an abrupt (< 10 s) loss of $4{\times}10^{-19}$ kg corresponding to ~10^7 H_2O molecules.

Acknowledgement

References

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