




Ion Mobilities for Heaviest Element Identification

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Abstract

Relativistic effects strongly influence the chemical and physical properties of the heaviest elements, which can significantly differ from the periodicity predicted by the periodic table of elements. Former systematic mobility measurements on monoatomic lanthanide ions revealed the dependence of ion-atom interactions on the underlying electronic configuration and helped in studying the aforementioned effects. Presently, the measurements are being extended to the actinides, where larger deviations from periodicity are expected. Our studies will cover ion mobilities of several actinide elements under different conditions of electric fields, buffer-gas pressures and temperatures, which will constitute benchmark data for state-of-the-art ab initio calculations.

Keywords Ion mobility mass spectrometry · Actinides · Trace analysis

1 Introduction

With the search for the proposed island of stability and thus the discovery of new chemical elements, a new niche for chemical and physical exploration of superheavy elements opened up [1, 2]. Of particular interest in chemistry are relativistic effects, which gain importance with increasing atomic number Z [3]. The high velocities of inner-shell electrons orbiting the heaviest atomic nuclei lead to a contraction of the s - and $p_{1/2}$ -orbitals. The resulting effective shielding of the nuclear potential influences the binding energy of the electrons, the valence electron configuration, interatomic forces, bond lengths, enthalpies, and thus the chemical behavior altogether.

Today, gas phase chemistry with single atoms is the most advanced method to study the chemical properties of the superheavy elements. It has been successfully implemented up to copernicium ($Z=112$) [4] and, most recently, for flerovium ($Z=114$) [5]. The comparison

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with relativistic *ab-initio* calculations [6] is limited to few observables, mainly the adsorption enthalpy. Ion Mobility Spectrometry (IMS) may provide an alternate avenue to study an element's electronic configuration and polarizability [7, 8]. Moreover, studying the transport properties by IMS bears a great potential in developing next-generation techniques of isobaric purification and element identification at minute production quantities. In the following, we present systematic IMS studies in the lanthanides and ongoing work to extend them to the heavier actinides.

2 State of the art

The ion mobility, K , measures how fast ions of choice drift in a uniform electric field, \mathbf{E} , through a given gas environment [9, 10]. The drift velocity \mathbf{v}_d of the ions scales with the mobility according to $\mathbf{v}_d = K(P, T) \cdot \mathbf{E}$, which in turn depends on the mass and the collision cross section of the sample ions with the gas atoms. Ion mobility measurements have been carried out for a variety of systems ranging from single atoms [9] to complex proteins [11]. From the theory point of view, it is possible nowadays to calculate the transport coefficients, mobility and diffusion coefficients, as well as collision integrals and momentum transfer cross sections from the knowledge of the ion-atom interaction potentials with a relatively high accuracy [12]. The interaction potentials can be directly inferred from the mobility data [13], or, alternatively, computed *ab-initio* and then assessed in the transport calculations [14].

IMS on lighter elements revealed deviations in the mobilities as soon as the electron configuration changes drastically. The ion mobility of Cs^+ and Ba^+ in helium, for instance, differs by 9% due to the occupation of the $6s$ orbital in Ba^+ [15], which is not present for Cs^+ [16]. Even the changes for singly occupied to fully occupied s orbitals, e.g. Yb^+ and Lu^+ , lead to a 13.8%-difference in ion mobilities in helium [17]. Moreover, metastable ionic states can be distinguished from their ground states by ion mobility measurements [18]. The mobility of Cu^+ ions in the configurations $[\text{Ar}]d^{10}$ and $[\text{Ar}]3d^94s^1$ drifting in helium gas for example shows a deviation of about 33% [19], caused by the occupation of the s orbital in the metastable state. These findings substantiated the conviction that ion-atom interaction potentials and thus ion mobilities are highly sensitive to the underlying electronic configurations and formed first stepping stones towards electronic-state chromatography and state-selected ion chemistry [20].

As relativistic effects of valence electrons scale roughly with the square of the atomic number Z , we expect an increased diversity in electronic configuration of ions with increasing Z . Figure 1 shows predicted electronic configurations of singly charged ions across the actinide elements [21]. The region between $\text{Pu}^+(Z = 94)$ and $\text{Cf}^+(Z = 98)$ is especially interesting since the electronic configuration differs from one another in neighbouring ions. Nevertheless, systematic ion mobility measurements are lacking across the actinides, so that, to the best of our knowledge, experimental data in the actinide region can be found only for U^+ [22, 23]. For the late actinides ($Z > 99$), atomic physics investigations require extremely sensitive methods, because these elements can only be produced online in small amounts and are often extremely short-lived.

Feasibility studies for the pairs (Fm^+ , Cf^+) and (Am^+ , Pu^+) drifting in argon were reported in Ref. [24, 25]. Since these studies were prone to large systematic uncertainties, we anticipate systematic IMS measurements across the heaviest actinide elements to deepen the understanding of mobility changes in the actinide region.

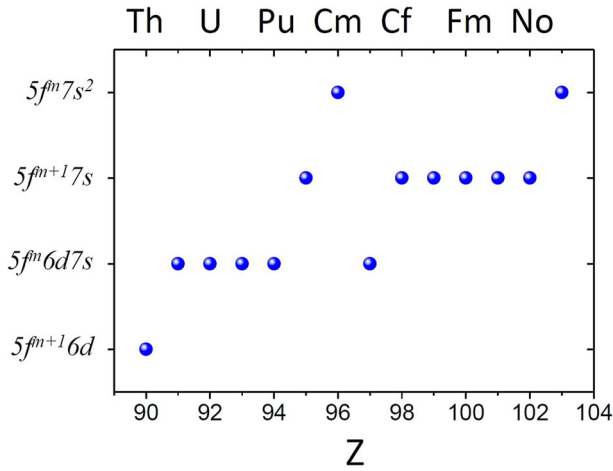


Fig. 1 Electronic configuration of singly ionized actinide atoms. The configurations are taken from Ref. [21] with $m = Z - 89$

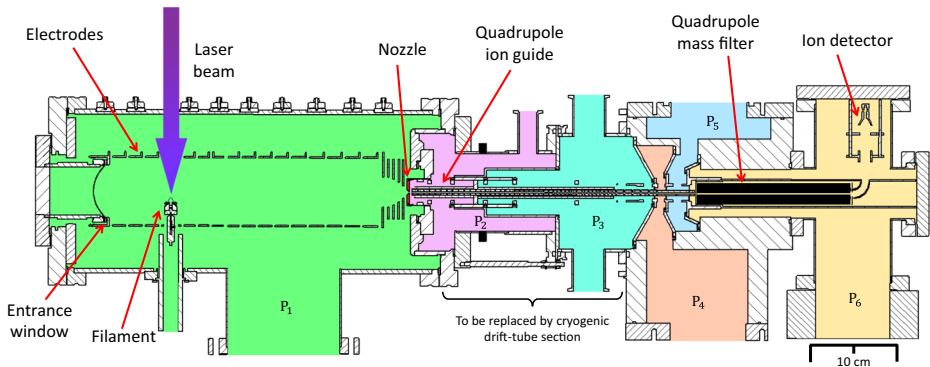


Fig. 2 Experimental setup. The ions are produced from the filament by resonance laser ionization, drift through argon, are extracted through the nozzle and are transported to the quadrupole mass filter by a quadrupole RF-structure. After mass selection, they are deflected to a channeltron detector. The pressures amount to $P_1 = 40$ mbar, $P_2 = 10^{-2}$ mbar, $P_3 = 10^{-3}$ mbar, $P_4 = 1$ mbar, $P_5 = 10^{-4}$ mbar, $P_6 = 10^{-6}$ mbar and $P_7 = 10^{-7}$ mbar

3 Experimental

To study the transport properties of the heaviest elements in order to reveal electronic configurations and examine the underlying interaction potentials, the drift time spectrometer developed in Ref. [26] will be used.

For mobility measurements, the atoms of interest are evaporated from a sample filament and resonantly laser ionized in an element-selective two-step two-color photoionization scheme [27–29] by a laser pulse, that starts the measurement. The created ions drift under the influence of low electric fields inside the spectrometer buffer-gas cell and are extracted through a nozzle before mass selection in a quadrupole mass filter and final detection by a channeltron detector, see Fig. 2. The arrival time of the ions at the detector reflects mainly

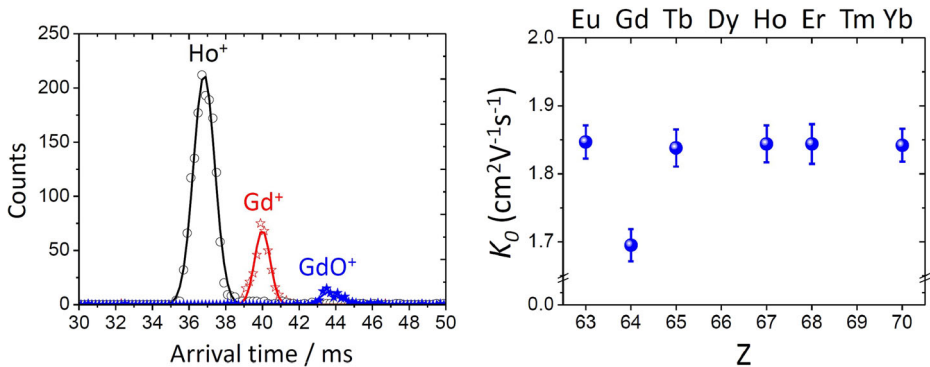


Fig. 3 **Left:** Arrival time distributions for Gd^+ ($4f^7 5d6s$), Ho^+ ($4f^{11}6s$) and GdO^+ drifting in 42.4 mbar argon at room temperature and a ratio of electric field strength to gas number density $E/N = 1.8$ Td. The solid lines are Gaussian fits to the obtained distributions. Data taken from Ref. [26]. **Right:** Measured reduced mobility (K_0) of some lanthanide cations at an argon gas temperature of 300 K. Error bars indicate systematic errors. Statistical errors are much smaller than the data marker size and cannot be seen in the figure. Adopted from [26]

the drift time t_d that the ions need to reach the nozzle, since the transportation time from the nozzle to the detector is about two orders of magnitude smaller than t_d .

With this spectrometer, low-field mobilities were measured in the past across the lanthanides. Thereby it was demonstrated that K is sensitive to the occupation of the $5d$ orbital [8]. Figure 3 (left) shows superimposed arrival time distributions that were registered for Gd^+ and Ho^+ drifting in argon gas under the same conditions. Noticeably, Gd ions need about 3 ms longer for the drift in 42.4 mbar argon at 1.8 Td compared with Ho ions. The gadolinium peak could be clearly resolved from other peaks in the arrival time distributions. As shown in Fig. 3 (right) the reduced mobility K_0 of Gd^+ , a mobility normalized to the standard pressure and temperature, was found to be about 8% lower than for all other investigated lanthanide cations. While normally the $4f$ shell is gradually filled across the lanthanide cations, Gd^+ exhibits an occupied $5d$ shell. This irregularity has a significant impact via the Coulomb repulsion term and the attractive dispersion term on the ion-atom interaction potential. The latter term can be understood as a backlash of the charge-induced dipole field of the argon atom on the ion itself [26], which is expected to be different for ionic species of different electron configurations and distinct polarizabilities.

For systematic IMS measurements in the actinides only trace amounts will be used. Elements featuring long-lived radioisotopes such as ^{242}Pu , ^{243}Am , ^{245}Cm , ^{249}Bk and ^{249}Cf are of particular interest in our investigations, as drastic changes in the electron configuration are expected along these element series, cf. Fig. 1. Suitable sample preparation techniques have already been developed in Ref. [30]. Here, the atoms of interest are electrodeposited on a tantalum filament, which is then passivated by a sputtered titanium layer. Such created filaments are placed inside the gas cell and heated up to provide the sample atoms for subsequent laser resonance ionization. First tests are planned to be performed with filaments containing about 10^{14} electrodeposited lanthanide atoms. These experiments using moderate quantities of sample atoms will allow developing skills and techniques to handle radioactive actinide species at a later stage. Proper laser excitation schemes for the actinide elements are already developed [31]. Although ion mobilities can be measured only at room temperatures with the present apparatus, we expect mobility differences to be large enough, enabling a disentanglement between the different electronic configurations.

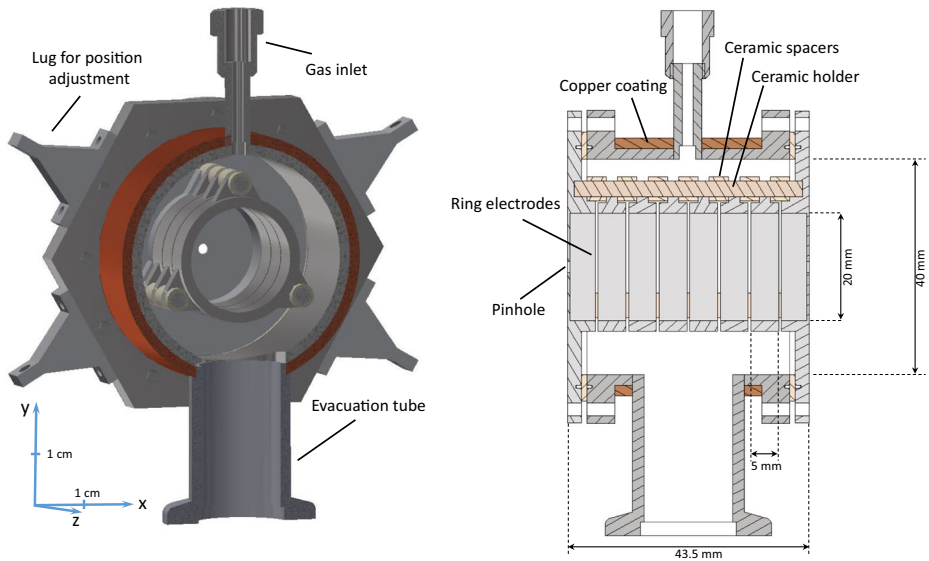


Fig. 4 Schematic view of the cryogenic drift tube. The former drift cell will serve as an ion source, while the ions drift in the cryogenic drift tube. The temperature of the cryocell can vary between 100 and 300 K. The total drift length is 43.5 mm. **Left:** Front view. **Right:** Side view

4 Cryogenic Drift Cell

Systematic ion mobility measurements utilizing various buffer gases at different gas temperatures will be performed as well. These will enable to assess theoretical “standard” *ab-initio* methods describing the interaction of heavy ions with noble gases. A new vacuum section connecting the mass filter with the gas cell is being developed, which allows better evacuation of the gas emerging from the nozzle while simultaneously providing the opportunity to install a cryogenic drift tube, see Fig. 2. The design of the cryogenic drift tube will enable to reach gas temperatures as low as 100 K, following similar concepts devoted to ion mobility measurements on lighter transition metals [32, 33].

A schematic view of the drift tube is shown in Fig. 4. The tube consists of six drift electrodes enclosed by two electrically isolated endcaps. The ring electrodes have an inner diameter of 20 mm and a width of 5 mm while the distance between the electrodes is fixed by ceramic spacers to 0.5 mm. The two endcaps have a ring electrode geometry, but in contrast are closed from one side by a plate of 0.5 mm thickness that exhibits a pinhole of 2 mm diameter in its center. Three ceramic holder rods for the ring electrodes are fixed at these endcaps. The triangular holding structure ensures an efficient evacuation of the drift volume as well as a homogenous distribution of the injected and cooled buffer gas. The drift voltage is applied to the entrance endcap and successively scaled down by a resistor chain to all electrodes of the drift tube. The pressure is adjusted by using a needle valve, that controls the gas flow entering the tube via a VCR inlet connector. Copper connections to the cryocooler (type: CryoTel-CT) allow an efficient and fast cooling of the drift cell to temperatures as low as 100 K with a precision of ± 0.1 K. Moreover, the cryocell housing exhibits a copper coating to ensure a uniform cooling. For evacuation, a tube with 16 mm diameter will be used. The ions extracted from the nozzle will be transported by a radiofrequency ion guide

to the cryogenic drift tube, before being guided by a second RF structure to the quadrupole mass filter. Since the resolution of the arrival time spectra scales with $\frac{1}{\sqrt{T}}$, reducing the gas temperature leads to better separation of drifting ions. This is particularly necessary in order to distinguish ions generated by laser ionization from those resulting from chemical reactions and subsequent photoionization but undergo molecular cracking within the gas jet behind the nozzle.

5 Summary and Outlook

Ion mobility spectrometry is a powerful tool to investigate ion-atom interaction potentials. The sensitivity of ion mobilities to the electronic configuration has been proven for various elements across the periodic table. Systematic mobility measurements across the lanthanides [8] are presently being extended to the actinides. Since drastic changes in the electronic configurations are predicted to exist for elements from Pu ($Z = 94$) to Cf ($Z = 98$) [21] offline experiments with primed filament samples are in preparation. As a test bench for state-of-the-art *ab-initio* calculations the measurements will be carried out at different gas temperatures and E/N ratios. For this purpose, a cryogenic drift cell is currently under development. We hope by our studies to open up a new niche for isobaric purification and element identification in the research of actinides and transactinides.

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