Negative ion relaxation and reactions in a cryogenic storage ring

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Abstract. An overview of recent experimental results of studies of negative atomic and molecular ions in the Double ElectroStatic Ion-Ring ExpEriment, DESIREE is given. Metastable level lifetimes in atomic negative ions have been measured by time-dependent laser photodetachment. Rotational relaxation of diatomic anions is studied by near-threshold photodetachment. Spontaneous decays of small metal cluster anions by electron emission and fragmentation is studied with decay-channel specificity. Finally, mutual neutralisation of pairs of negative and positive ions has been investigated with initial and final state selectivity.

1. Introduction

The storage of fast charged particles have the general advantage that extended observation times and efficient detection of products with different mass-to-charge ratios than those of the stored ion beams are combined. When storage for few seconds is sufficient, this can be reached with room-temperature electrostatic rings and traps for few keV ion beams [1, 2, 3]. For light positive ions a very efficient, albeit costly, method exists to achieve much longer storage times. For these systems the dominating beam-particle loss process is often that of electron transfer to the stored ion from residual-gas collisions and by going to magnetic-confinement rings and much higher energies such losses are effectively eliminated due to the strong projectile velocity dependence of the electron-transfer process ($\sigma \propto v_p^{-11}$) [4] and very long storage lifetimes of many hours may result. For negative ions, the dominating loss mechanism is electron detachment in residual-gas collisions. That process does not have a very strong velocity dependence and thus the only way to eliminate residual-gas collisional losses and to reach very long storage lifetimes is to strongly reduce the residual-gas density. This is realised in the most recent generation of electrostatic ion-storage rings by means of cryogenic operation with several orders of magnitude reduction in
residual-gas density. The cryogenic ion-beam storage rings currently in operation are DESIREE [5, 6], the Cryogenic Storage Ring, CSR [7], at Max-Planck Institut für Kernphysik in Heidelberg and the RIKEN Cryogenic E-ring, RICE [8], at RIKEN, Japan.

2. Brief description of DESIREE
Detailed descriptions of DESIREE are found in refs. [5] and [6], so here only its basic operating features are discussed. DESIREE consists of two electrostatic ion-beam storage rings of 8.7 m circumference, sharing a common straight section of 95 cm length where the two stored ion beams can be merged (see Fig. 1). After each of the three straight sections, position-sensitive micro-channel plate detectors are mounted to detect neutral products of reactions or spontaneous decays and after the common straight section a movable detector is mounted to detect charged fragments. The neutral detector after the merging section has a phosphor screen anode that is being observed in parallel by a CMOS camera and a segmented photomultiplier tube to allow coincident detection of two (or in principle more) neutral products with high time and position resolution. The merging and separation of two stored ion beams require that the two ion species have opposite charge polarity and a maximum ratio of the beam energies of 20. The latter is determined by the maximum voltage on the high-energy ion source platform of 100 kV and the practical lower limit for stable ion-beam storage of about 5 keV. For studies of reactions at close to zero center-of-mass energy this maximum energy ratio immediately translates to a maximum mass ratio of 20. Besides ion-ion reactions, studies are obviously possible of ions decaying spontaneously or after laser irradiation, as will be discussed below. To reach long storage lifetimes and to limit the background signal from ions colliding with residual gas molecules and losing their charge, a very good vacuum is required. In DESIREE this is achieved by applying a nested double vacuum system pumped by serially coupled standard turbomolecular ultrahigh vacuum pumps and cooling the entire inner vacuum volume to cryogenic temperatures (12-14 K) by means of four two-stage closed circuit helium cryogenerators. The vacuum surrounding the cooled inner chamber provides an excellent thermal insulation and in order to limit the effect of thermal radiation from the room-temperature environment, a copper screen covered in insulating material surrounds the inner vacuum chamber and is cooled to about 50 K by the first stages of the cryogenerators. Due to the cryogenic temperature of the inner chamber, residual-gas densities of the order of a few molecules per cubic mm is achieved resulting in storage lifetimes of keV anion beams of about $10^3$ s [5, 9].

3. Lifetimes of metastable levels in atomic negative ions
Due to the absence of a long-range interaction between a free electron and a neutral atom, most atomic negative ions have only one or a few bound states. Some elements, as for example helium, do not have any stable bound states of the negative ion. However, metastable levels can exist if they are prevented from rapid disintegration by their symmetry. Such metastable negative ions are very efficiently studied with stored beams by just recording the production of neutrals as function of time after ion-injection [10, 11, 12, 13, 14]. For bound excited states of atomic negative ions a slightly more advanced experimental approach is necessary. One such approach is state-selective laser photodetachment which was developed at CRYRING [15]. Here the idea is simply that a laser wavelength is chosen so that the photon energy is less than the electron affinity, but higher than the binding energy of the electron in the excited state. In this way an increase in the rate of neutrals when the laser is applied can be ascribed exclusively to a population of ions in the excited state. Measuring such a signal as function of time after injection gives the decay of ions in the excited state due to the sought spontaneous decay and due to loss of the beam. By a series of careful control measurements the latter can usually be isolated and the real spontaneous lifetime deduced. At DESIREE the excellent vacuum condition has allowed us to use this method to measure longer lifetimes than what has previously been possible, reaching
Figure 1. Drawing of the inner vacuum chamber with all the electrostatic ion-optical elements of DESIREE. Typical ion-beam trajectories are indicated by the light-blue lines.

the $503 \pm 54\ s^{-1}$ lifetime of the upper fine structure level of $S^-$ as the hitherto most longlived state studied [9]. In table 1 we give the results of the atomic negative ion excited state lifetimes measured so far at DESIREE [16, 17]. All the lifetimes listed in table 1 with the exception of

| Ion | Level        | Lifetime | Error  | Reference |
|-----|--------------|----------|--------|-----------|
| $S^-$ | $3p^5\,2P_{1/2}$ | 503 s    | 54 s   | [9]       |
| Se$^-$ | $4p^5\,2P_{1/2}$ | 4.78 s   | 0.18 s | [9]       |
| Te$^-$ | $5p^5\,2P_{1/2}$ | 0.463 s  | 0.008 s| [9]       |
| Ni$^-$ | $3d^4s^2\,2D_{3/2}$ | 15.1 s   | 0.4 s  | [16]      |
| Pt$^-$ | $5d^{10}6s^2S_{1/2}$ | 2.54 s   | 0.10 s | [17]      |
| Pt$^-$ | $5d^{10}6s^2\,2D_{3/2}$ | 0.05-0.2 s | —      | [17]      |

the Pt$^-$-level $5d^{10}6s^2S_{1/2}$ are for upper fine structure levels of the ground state. It was pointed out by Brage and Grumer [18] that for such states a scaling with the measured and calculated fine structure splittings should be fulfilled as the same radial matrix element is the most critical part of both these calculations. By their scaling method, they obtained a better agreement with theory for the case of sulfur. Surprisingly, however, applying the same method for nickel has not been successful and a 25% discrepancy remains for this system [19].

4. Rotationally cold molecular ions
A central motivation for applying cryogenic cooling in DESIREE and the other cryogenic electrostatic storage rings [7, 8] is that one can form and maintain a molecular ion beam with
a dominance of the (few) lowest rotational level(s) only in a cryogenic environment. The OH$^-$ molecular ion is a well-suited system for investigating the rotational cooling and such studies have been performed in CSR [20] and in DESIREE [21]. The experimental method was based on the rotational thermometry by near-threshold photodetachment [22]. Conceptually the idea is similar to the method used in the atomic negative ion lifetime measurements described above. In a narrow range of wavelengths corresponding to photon energies close to the electron affinity, photodetachment will be energetically allowed for all levels, all but $J = 0$, all but $J \leq 1$, all but $J \leq 2$ etcetera, depending on the exact value of the wavelength. In Fig. 2 the effective measured photodetachment cross section in the threshold range is shown for different storage times prior to the laser photodetachment. The staircase-like shape reflects the opening of the photodetachment channel for the three lowest rotational levels and the step heights are directly related to the population in the individual $J$-levels. The relative contributions from $J = 1$ and $J = 2$ decrease with time as the rotational cooling proceeds and thermal equilibrium is approached. Asymptotically, the rotational temperature of the stored ions reach 20.6$\pm$0.5 K. By actively depleting the rotationally excited ions by photodetachment a rotational temperature of 12.3$\pm$0.2 K was demonstrated for OH$^-$ [21]. In a recent unpublished follow-up experiment using OD$^-$ a rotational temperature of 7.4$\pm$0.4 K was reached by the depletion method.

5. Decay of hot small metal cluster anions
In the previous section, the aim was to reach and characterize rotational level distributions of stored very cold molecular ions and cryogenic temperatures of the surroundings were needed. In the experiments described in this section, the focus is on decays of very hot metal cluster anions on the ms and s time scales, and it is not as obvious why these studies require cryogenic temperatures. It turns out, in fact, that the very low residual-gas density provides a tremendous improvement over earlier room-temperature studies. In pioneering work at the ELISA storage ring [1] it was established that ensembles of small, internally hot, cluster anions and many other complex systems decayed in the storage rings not by the well-known exponential law,
Figure 3. Rate of neutral products from the spontaneous decay of hot silver pentamer anions stored in DESIREE as function of time after ion production in a caesium sputter ion source.

but followed a power-law decay. This was ascribed to the large spread of internal energies in the ion ensemble. While all ions populating a particular quantum state would have the same constant decay rate leading to an exponential decay of those particular ions, very many different quantum states were populated in the stored ensemble of ions leading in practice to a continuum of internal energies and decay rates. The summation of all these different contributions leads to the observed power-law decay [23].

A limitation in studies of hot metal cluster decays is that ions with insufficient excitation energy to decay spontaneously may still contribute to the background neutral-particle count rate due to collisions with molecules of the residual gas. For this reason, room-temperature studies of such decays are typically only possible up to about 100 ms when the signal can no longer be separated from the background. So even if the storage lifetimes are often of the order of 1-10 s, the background collisions prohibit measurements beyond 100 ms. However, with the dramatically improved vacuum of DESIREE and other cryogenic systems [24], the background is dramatically decreased and decays in the second range may be studied. In Fig. 3 we show the measured decay when Ag\(^5\)\(^-\) is stored in DESIREE [25]. That same system was studied in the original ELISA work [23] but only until 50 ms, showing only the power-law decay and not the strong deviation from it, which only becomes visible after several hundred ms of storage and is ascribed to radiative cooling by infrared emission.

These much improved experimental conditions were used in measurements of decays for small clusters of copper [26] and silver [25]. In a recent study, metal dimer anions of silver and copper have been investigated with a slight addition to the detection scheme. Now not only the neutral products but also fragment ions can be detected. The new results confirm the conclusion of previous work from ELISA [27] that the dominating decay process for the tens of ms time range accessible in the ELISA experiment was fragmentation of highly rotationally excited dimer anions by tunneling through the centrifugal barrier. However, the new measurements also show that for times after injection in excess of 100 ms, the dominating decay is vibrational autodetachment of vibrationally highly excited dimers in lower angular-momentum states [28]. This is a surprising observation as no crossings are available between the initial and final states as function of the internuclear distance, which is the only parameter describing the dynamics on the Born-Oppenheimer surfaces of the dimer systems. Hence, the observation of vibrational autodetachment for this system constitutes a dramatic demonstration of the break-down of the Born-Oppenheimer approximation.
Figure 4. The straight section of DESIREE where the two stored beams can be merged is surrounded by sets of drift tubes. The split cylinders (yellow) marked PU1 and PU2 are position-sensitive electrostatic pickup electrodes applied to optimize the beam overlap. The seven green cylindrical electrodes can be put on bias voltages to adjust the center-of-mass energy. The ion beams are indicated in magenta and the two dashed lines are illustrating the trajectories of a pair of neutrals formed in an MN process inside one of the drift tubes.

6. Mutual neutralisation in DESIREE

As we have seen in examples above, the ability to store a beam of molecular ions for a long time in one of the storage rings inside the cryogenic environment of DESIREE yields excellent conditions for a range of different experiments. The construction of DESIREE as a double ring was, however, chosen in order to be able to investigate the interactions taking place between pairs of ions, one from each ring. In the mutual neutralisation (MN) process a pair of a positive and a negative ion react to form two neutral particles: \( X^+ + Y^- \rightarrow X + Y \). The construction of DESIREE is optimized for this particular process. In Fig. 4, the merged-beams section and the path for a pair of neutrals towards the position and time-sensitive detector is shown. The distance in all three dimensions between the two neutrals is deduced from the measured detector impact positions and the time difference of the two neutrals. As this distance is given by the available kinetic energy in the relative motion of the two neutral products, its determination reveals the quantum states formed in the process. In a recent, as yet unpublished, study it was demonstrated that final states in neutral lithium of the configuration \( 1s^23s \) could be fully separated from states of the configurations \( 1s^23p \) and \( 1s^23d \) formed in the MN process: \( \text{Li}^+ + \text{D}^- \rightarrow \text{Li} + \text{D} \) [29]. Evidently the distance between the two neutrals as they arrive at the detector will depend not only of their relative velocity but also on the distance from the detector at which the reaction took place.

The two beams are merged over a distance of 95 cm and the distance to the detector from the center of the interaction region is 160 cm. In order to reach sufficient resolution, it is therefore necessary to run the experiment in such a way that the MN reactions taking place in only a small portion of the merged-beams section can be separated from other MN events. In the case of the \( \text{Li}^+/\text{D}^- \) experiment mentioned above, this was achieved by storing the two beams at different energy/mass ratios and then tune in the ions to reach close to zero center-of-mass energy by applying a bias voltage on the three central drift tubes with a combined length of 25 cm. The \( \text{Li}^+ \) beam was stored at 17.0 keV, the \( \text{D}^- \) beam at 6.50 keV, and the three central electrodes were put on a bias voltage of -1278 V. In this way the center-of-mass energy was close to 0 eV for the collisions taking place in the biased section and 93 eV for collisions taking place in the non-biased drift tubes and in the pickup section.

Fig. 5 clearly demonstrates the separation of MN events of interest with \( E_{CM} \approx 0 \) eV taking place in the biased section and yielding events with \( \Delta t < 50 \) ns from those collisions taking place in the grounded sections before (right-side peak 350-450 ns) and after (peak 230-320 ns) the biased section. For the collisions at \( E_{CM} \approx 93 \) eV, the change in kinetic energies of the neutral products due to the collision’s in-elasticity is relatively insignificant and the products continue with essentially un-changed velocities towards the detector. Therefore the value of \( \Delta t \) is mainly determined by the position along the beams’ paths at which the reaction took place. This gives rise to the two-peak structure reflecting the two separated sections at which these higher energy
Figure 5. Histogram of time differences for pairs of neutral D and Li atoms formed in mutual neutralisation with the conditions described in the text. The reactions at $E_{CM} \approx 0$ eV taking place in the biased three center electrodes result in $\Delta t < 50$ ns, while reactions in the grounded sections with $E_{CM} \approx 93$ eV are easily distinguished through their much larger $\Delta t$.

collisions take place. For the biased section, on the other hand, the initial center-of-mass energy is of the order of tens of meV so that the final-state center-of-mass energy is dominated by the energy released in the reaction (1.26 eV for capture to 3s and 0.80 eV for capture to 3p). For these events the time difference is primarily determined by the amount of kinetic-energy release and the random isotropic orientation of the interatomic vector after the collision. The motivation for studying this particular collision system comes from astrophysics. The mutual neutralisation process for metal ions and H$^{-}$ in stellar atmospheres affects the line intensities in observations and a proper account of these processes is therefore essential for quantitative conclusions concerning the abundance of metals in stars. This triggered renewed theoretical efforts [30] and the soon to be published results from DESIREE will provide an experimental test of these calculations.

7. Summary and conclusions
During its first few years of operation, DESIREE has been used to study anions and their relaxation for a multitude of different systems. Atomic lifetimes have been determined, metal cluster decays have been investigated and small molecular ions have been shown to approach thermal equilibrium with the cryogenic surroundings. All these results have been made possible by the long storage lifetime and low rate of residual-gas collisions in the cryogenic extreme vacuum system. Recently, the first results of the studies of mutual neutralisation with ion beams stored in the two rings of DESIREE have been demonstrated. Also for these measurements the extreme vacuum is important to limit the background from residual-gas collisions even though such problems have been elegantly circumvented in a single-pass room-temperature experiment [31]. Experiments are now in the planning phase where DESIREE’s full potential will be reached when ro-vibrationally relaxed molecular ions are being brought to interact, thereby combining the merged-beams capability of DESIREE with the long-time storage and the cryogenic conditions. To the best of our knowledge, DESIREE is the only available tool for studies of reactions between ro-vibrationally relaxed molecular ions at low and well-controlled center-of-mass energies.
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