Introduction

Numerous processes in nature and technology, from astronomical and terrestrial environments to chemistry and biology, depend on the internal quantum motion of atoms and molecules. There the electrons and nuclei rarely move independently, but often in strong correlation with each other. The related many-body quantum physics challenges our understanding of matter. Collisions of atoms and molecules with charged or energetic particles intercept the internal quantum motion and create new, energetically excited states that modify the molecular properties and trigger internal dynamics. Molecules change their shape, chemical bonds are weakened and, ultimately, compounds broken up. Well-controlled particle beams as well as the counting and imaging of individual particles are cutting-edge tools to disentangle the quantum mechanisms at work. Instruments developed at the MPIK can realise atomic and molecular collisions under optimised initial conditions and then analyze the products to draw conclusions about the correlated quantum motion. They particularly focus on detecting and imaging coincidence events, with several outgoing particles from one single collision. Moreover, the initial internal states of colliding particles are carefully controlled using beams of atomic, molecular and cluster ions stored in extreme isolation from the terrestrial atmosphere and even the thermal radiation of the laboratory. Certain systems are benchmarks, studied both by experiments and by the most advanced quantum theoretical methods. In other cases, molecules and matter aggregates important in natural and technical media are targeted directly.

The Electrostatic Cryogenic Storage Ring CSR

The CSR [1] is a cryogenic electrostatic ion storage ring for collisional and laser-interaction studies over long storage times with fast atomic, molecular, and cluster ion beams. The cryogenic facility offers an ambient temperature near 6 K for the stored ion beam. The ring layout was chosen to enable experiments with crossed and merged, particle and laser beams. In-ring experiments often involve detecting fast product particles released by reactive collisions of the stored ions. Along extended straight sections, the stored ions can also interact with collinear merging beams of electrons or atoms. For equal average velocities of the two merged beams, the effective collision velocities reach down to the thermal speeds in a low-temperature environment. The energy of the stored beams in CSR, up to 300 keV for singly charged ions, is sufficiently high that their velocity can be matched with the one of an electron beam even for large molecules (envisaging masses up to ~160 amu): this includes, e.g., small organic ring species. The merged beams areas of the CSR open the field of low-temperature ion reaction studies with electrons and atoms. Uniquely at CSR, such studies can be performed with ions that were stored for a long time in a low-pressure environment nearly free of blackbody radiation. Moreover, at the high ion beam velocity even neutral reaction fragments can be readily detected and imaged in event-by-event, multi-fragment coincidence mode.

CSR setup and performance. Ion beams in CSR are stored by a purely electrostatic arrangement of deflectors and focusing elements. The smallest bending radius of the deflectors is 1 m, corresponding to a field strength of 6 kV/cm at the maximum ion energy.

2.3 Atomic and Molecular Collisions
The beams for CSR were produced in its ion source area from discharge and spatter ion sources. Aside from its electronic diagnostic elements for stored ions, the CSR was equipped with detectors [2] for the fast particles produced when stored ions change their charge state or dissociate into fragments (Fig. 2). Such background reactions can be triggered by collisions of the stored ions with the molecules of the residual gas in the vacuum system. In conventional devices, even with ultra-high vacuum, they occur abundantly whenever an ion beam is present. Already in the first cryogenic beam-time of the CSR was devoted to the study of the ion-beam storage conditions and to laser interaction experiments with stored, negatively and positively charged molecules and clusters [1].

Main studies during the first cryogenic beam time were devoted to the interaction of the stored ions with a laser beam. In a negative ion, an electron can be removed by photodetachment, leading to a neutral product triggering the particle detector. In many cases, the neutral products from photodetachment served to monitor the ion intensity. By comparing this laser-induced signal to the much lower neutral background from residual gas in the absence of the laser, the residual gas density in the CSR could be constrained, yielding <140 cm⁻³ [1]. This corresponds to a pressure of <10⁻¹⁰ mbar at room temperature, improving on the design value of the CSR (10⁻¹¹ mbar) by more than a factor of 10.

Ion beam lifetime studies and Schottky noise diagnostics. Ion beam storage lifetimes in the CSR were observed (Fig. 3) to reach up to 45 min. Stored-beam signals could be observed up to three hours following a single injection. These times are largely sufficient for the envisaged experiments and almost two orders of magnitude longer than available in previous ion beam experiments at the MPIK, using the room-temperature storage ring TSR. Yet, the low residual gas densities should allow even longer storage and the mechanisms limiting the beam lifetime in these hitherto unexplored conditions are still to be understood. During the long beam lifetimes also the electronic Schottky noise of the ions could be recorded. Its spectral analysis (Fig. 4) reveals the distribution of the ion velocities in the CSR. After several minutes of storage an increase of the ion velocity spread by a diffusion of the ions in their velocity coordinates becomes visible. Further investigations on this process, potentially limiting the ion beam lifetime, are under way. Schottky-noise spectra will serve to study and optimise the phase-space cooling of the ions in the CSR using its merged electron beam.

Internal cooling of stored molecular ion beams. In the first cryogenic beam-time, the radiative cooling of small hydride ions at the low level of black-body radiation inside the CSR was investigated for two cases. Resonant near-threshold photodetachment of the astrophysically important methylidyne anion, CH⁺, was achieved by wavelength-tunable ultraviolet laser radiation. As described in Section 2.4, the resonances reveal the rotational levels J that are populated in the stored CH⁺ ions before they are hit by the laser. The relative population in the J = 0 ground state, which in a 300 K black-body field would amount to ~10% only, is seen to rise continuously up to ~60% during the 240 s of storage time in the CSR. For the lowest rotational levels accessed here, this enabled a state-by-state benchmark measurement of the CH⁺ resonant photodetachment cross section [3].

A second case studied was the near-threshold photodetachment of the hydroxyl anion, OH⁻. A probe laser set to wavelengths close to the threshold is applied to yield photodetachment signals that represent only specific ranges of rotational levels (quantum number J) in the OH⁻ ions. Normalised to the J-independent photodetachment rate from a reference laser at shorter wavelength, these signals convey the relative populations of the probed rotational levels (Fig. 5). Through spontaneous infrared emission to lower J states, signals requiring higher rotation (such as J=2) decay relatively fast, at longer times the decay is dominated by lowest J state of the range, which has the longest lifetime. The lowest excited rotational level (J=1) needs most time to decay, reaching its equilibrium population only after ~5 min of storage. After 10 min, as much as ~90% of all ions were found in the J=0 ground state. Detailed information on the rotational dependence of the photodetachment process is contained in the signals with J=2, obtained at three different probe wavelengths. These time-resolved multi-wavelength measurements allowed the relative photodetachment cross sections of the lowest J levels to be deduced on a purely experimental basis and also revealed precise rotational level lifetimes. This way the method of photodetachment thermometry using OH⁻ ions was improved in recent years to chart photodetachment efficiencies of the still uncertain theoretical predictions on state-by-state photodetachment efficiencies.
Merged and crossed beam experimental areas. In the development of the CSR experimental areas (Fig. 6), the installation of the merged electron beam of CSR is essentially complete at the end of 2016. The implemented cryogenic system involves high-temperature superconductor magnetic coils that guide slow (down to 1 eV) electrons into overlap with the ions in a linear section of the CSR orbit. Very low energy beams from a photocathode were already realised in tests at the TSR electron target. The CSR merged electron beam device awaits first operation in 2017.

Also the neutral atomic beam setup of the CSR (positions 2, 3 and 7 in Fig. 6) is completely installed and awaits first experiments. It is fed by atomic beams from a separate platform. Using a photodetachment zone with a very strong (2 kV) continuous diode laser in the injection line of CSR, fast neutral beams of hydrogen, carbon and oxygen ions can be merged with the state-controlled molecular ions circulating in the CSR. Several particle detectors were installed to analyse the products of the ion–atom interactions in the beam overlap zone:

- For detecting recoil ions and electrons released in reactions of ions stored in CSR with a weak crossed-gas jet target or with a laser beam, a reaction microscope is under design (position 4 in Fig. 6).

In the CSR, the combination with the fast-beam neutral fragment detection capability and the use of state-controlled molecular anions and cations, as well as low-velocity multiply charged atomic ions, the reaction microscope will offer unique opportunities of studying atomic and molecular quantum dynamics. Even ultrafast dynamics is expected to become equalisable using femtosecond laser pulses.
Electron Collision Dynamics for Atoms, Molecules and Clusters

Electron collisions play an important role in natural environments as the upper atmosphere and interstellar space, but also in technical plasmas and in radiation biology. Here a large part of damage to living cells along the track of an energetic primary particle is assumed to be caused by slow secondary electrons. We have studied interatomic reactions which can multiply the number of slow electrons and produce several reactive ions. These experiments were done for atoms and for biologically relevant molecules in form of monomers and hydrated clusters. In addition, the study of slow electron collisions enables detailed insight into the correlated dynamics of fundamental few-body quantum systems and fosters the development of ab-initio theoretical methods.

A large number of slow electrons and two positive ions are produced (Fig. 11). The same number of charged particles is obtained in the RCT process. There, electron impact doubly ionises one atom. To the ground state, energy is transferred to a neighbour atom, ionizing it. Altogether three particles are induced in argon dimers by electron collisions [7].

In ICD one atom is ionised and left in an excited state. Subsequently, in a transition to the ground state, energy is transferred to a neighbour atom, ionizing it. Altogether three particles are induced in argon dimers by electron collisions [7].

We performed full quintuple-coincidence measurements: the energies of all the charged final-state particles were detected. As result we unambiguously distinguished ICD and RCT and traced the vibrational and relaxation dynamics as function of the energies of the collisionally ionised initial states. Such interatomic processes multiply the number of electrons and shift their energies down to the critical 1–10 eV range, where they can efficiently cause chemical degradation of biomolecules. Consequently, we extended our studies to bio-relevant species.

Fragmentation of organic molecular monomers and clusters. First studies of larger molecules focused on tetrahydrofuran (THF, C$_4$H$_8$O) [8]. This compound is an analogue of deoxyribonucleic acid (DNA). We provide a large amount of information on the electron-impact induced fragmentation of such targets. The ion spectrometer of our reaction microscope can resolve all fragments produced (Fig. 12). For each channel, also the binding energies of the ionised electron orbitals and the ion kinetic energies were measured [8]. Thus, a detailed understanding of the fragmentation dynamics is reached. E. g., we observe that the molecular structure stays intact for ionisation of the highest occupied molecular orbital (HOMO). Hydrogen emission is observed for ionisation of the next inner orbital and ring-breaking reactions are induced for ionisation of more strongly bound inner-valence orbitals.

An important motivation for this work is to observe modifications of the fragmentation dynamics when the molecule is embedded in an environment of water or other organic compounds. Therefore, we produced hydrated and pure THF cluster targets. Surprisingly, we found the fragmentation dynamics to be strongly modified for the clusters. E. g., ionisation of the THF HOMO orbital (leaving the structure intact for the monomer) here leads to a ring-breaking reaction. Also intermolecular energy transfer reactions, namely ICD, were found. The studies will be pursued further, also developing new target preparation techniques to obtain samples of larger biomolecular compounds.

Ionisation: full differential electron emission patterns. With its complete solid-angle acceptance, the reaction microscope is ideally suited to record fully differential cross sections (FDCS) for single ionisation (so-called $e^-$,$2e^-$ measurements). These critically test state-of-the-art theories. Non-perturbative models which formally solve the full many-body Schrödinger equation nowadays exactly reproduce results for the smallest systems like helium; recently even larger systems like argon came into reach. Perturbative calculations on the other hand are not exact, but give much more insight into the reaction mechanisms involved.

This was demonstrated for neon where experimental cross sections are reproduced by both the non-perturbative B-spline R-matrix model (BSR) and a perturbative distorted wave theory (3DW). In contrast, the more complex argon atom is more challenging and at the limit of both approaches (Fig. 13) [9 and references therein]. Here BSR is still doing well for the complete pattern, while 3DW is good only inside the projectile scattering plane (red frame), but fails outside this plane. This clearly demonstrates the importance of testing theory over the full solid angle of electron emission.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig13.png}
\caption{Emission pattern of a 3 eV electron after 66 eV impact on argon with 15° projectile scattering angle.}
\end{figure}
(e,2e) studies were also performed for molecules of increasing complexity. For hydrogen molecules simultaneous ionisation and excitation was studied [10]. The obtained cross sections within the molecular frame show enhanced electron emission along the molecular axis due to the non-spherical potential. A second study [2] again concerned tetrahydrofuran (THF) where TDCS were obtained at low impact energy (26 eV) for ionisation of three different molecular orbitals.

**Dissociative Electron Attachment.** Low-energy electron collisions with molecules often lead to transient negative ions which subsequently dissociate into reactive negative ions and neutral fragments. With a newly setup and commissioned apparatus, we analysed the masses and momentum vectors of the negative fragments. A cold supersonic jet target offers significantly better momentum and mass resolution compared to existing setups in other groups. So far electron attachment to molecular species ranging from NH$_3$ to complex organic compounds was investigated. Exemplarily, for NH$_3$, an interesting bond angle dynamics was found [6]. Comparing a theoretical emission pattern for the NH$_2^-$ fragment with our data it can be concluded that after electron attachment and before the dissociation, the molecular bond angle in the transient NH$_2^-$ opens up in an umbrella-mode oscillation. We studied a range of larger molecules and clusters where the fragment kinetic energies normally are small since most of the energy release goes to internal vibration and rotation. One exception was observed for the pyridine ring molecule. Here we observed a completely symmetric dissociation reaction again yielding NH$_2^-$ ions, but now including an internal rearrangement of hydrogen atoms.

*Alexander Dorn*

---

**Cooling Dynamics of Small Anionic Metal Clusters**

Radiative cooling and heating processes of small anionic metal clusters in gas phase are important observables in cluster physics. Their dynamics reveal basic characteristics about the geometrical and electronic structure of clusters. The timescales of these processes are covering many orders of magnitude. Electronically excited levels are typically depopulated within milliseconds by internal conversion. But the radiative depopolation of ro-vibrationally excited states and processes such as spontaneous electron emission are substantially slower and consequently require long observation times. The cryogenic trap for fast ion beams (CTF)—a prototype of the successful cryogenic storage ring (CSR) project [1]—is an ideal setup for the needed gas-phase spectroscopy with great time resolution.

The recent studies concentrated on anionic copper and cobalt clusters stored for several seconds in the CTF. The spontaneous electron emission process of Cu$_{4,5}^-$ produced in highly excited ro-vibrational states was studied. The measurements reveal two-component decays in contrast to the previously excepted single power-law decay. Furthermore, laser-induced electron emission was studied to observe the radiative cooling of excited clusters in the cryogenic (−15 K) environment at the CTF [11]. While for Cu$_{4,5}^-$ no cooling could be observed even after 4 minutes of storage time, the initial equilibration process of Cu$_{4,5}^-$ stops significantly before room temperature. The measurements indicated that equilibration with the trap temperature was not reached for any of the cluster species. The underlying processes are not yet fully understood.

CO$_2^-$ was used to demonstrate a novel measurement scheme continuously observing the internal energy distribution of anionic cluster systems by employing laser-induced delayed electron emission. The thermalisation of hot clusters at about 1000 K, produced in a sputter source, as well as of cold clusters at about 250 K, produced in a laser vapourisation source, with the 295 K experimental environment was followed with great time resolution (Fig. 14).

*Sebastian George*

---

**Statistical Recombination: Multi-Electron Tungsten Ions**

Ions in a plasma environment involving heavier elements can have very complicated electronic structures. A key process for hot plasma governing their abundance in various charge states is the recombination with free electrons. It dominantly proceeds by resonant capture, where electrons already bound in the ion are excited and the incident electron is temporally attached by giving up its kinetic energy. Radiative stabilisation of the resonance then leads to a high recombination cross section at low temperatures.

For the realisation of a fusion reactor (like the ITER project), predicting the abundances of highly charged ions in the plasma poses a challenging problem, especially regarding heavy elements such as tungsten. Recombination rates of ions W$^{19+}$ with intermediate charge states q = 20 are particularly difficult to predict. A second molecular (e,2e) study again concerned W$^{19+}$ where TDCS were obtained at low impact energy (26 eV) for ionisation of the W$^{19+}$ ion. Calculations using radiative recombination only (RR) and presently used data-base models (ADAS) underestimate the recombination rate by an order of magnitude or more. This experimental benchmarking helped to establish the new statistical theory and now confirms its predictive power for modelling the interactions of multi-electron in hot plasma environments.

*Claude Krantz, Oldrich Novotny, Andreas Wolf*

---

**References**