Low-energy collisions with atomic and molecular ions in a photocathode electron target

A Wolf¹, D A Orlov¹, C Krantz¹, M Lestinsky²,¹, A Shornikov¹, O Novotny¹,², J Stützel¹, H Buhr³,¹, M Mendes¹, A Petrignani¹, M Grieser¹, S Schippers⁴, A Müller⁴, F Ferro⁵ and E Lindroth⁵
¹ Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany
² Columbia Astrophysics Laboratory, Columbia University, New York, NY 10027, USA
³ Faculty of Physics, Weizmann Institute of Science, 76100 Rehovot, Israel
⁴ Institut für Atom- und Molekülphysik, Giessen University, 35392 Gießen, Germany
⁵ Atomic Physics, Fysikum, Stockholm University, Alba Nova, 10691 Stockholm, Sweden

E-mail: A.Wolf@mpi-hd.mpg.de

Abstract. Dielectronic recombination of highly charged atomic ions and dissociative recombination of molecular ions have been investigated using fast ion beams merged with cold intense electron beams (down to <1 meV beam temperature) from a GaAs photocathode. For beryllium-like germanium ions (Ge²⁸⁺) isolated fine structure Rydberg resonances (n = 9 and 14) were observed at <0.2 eV revealing configuration interaction with triply excited resonances and appearing as candidates for deriving radiative shifts of the 2s²-2s2p(⁴P₀) excitation energy.

For hydrogen fluoride ions (HF⁺) dissociative recombination with the cold electrons, producing n = 2 hydrogen atoms, was seen to occur for specific excited initial rotational levels. These levels were identified by their fragment energies down to about 4 meV and it is envisaged to measure these energies with sub-meV accuracy.

1. Introduction
Capture of low-energy electrons by atoms, molecules and their positive ions is a highly efficient process that not only changes the charge distribution in the surrounding medium, but also modifies its chemical composition by molecular fragmentation. Its relevance reaches from ionized environments over a wide temperature range (hot atomic to low-temperature molecular plasma [1, 2]) to radiation effects in biological systems [3]. The rates and final states of low-energy electron collisions are generally highly sensitive to the specific properties of the atomic or molecular systems involved; hence, they pose a large challenge for reliable predictions and require a good understanding of the underlying quantum processes and of the extent of detail needed for their theoretical description. Collision experiments under conditions defined as completely as possible are crucial for the development of this knowledge. Here we describe high resolution measurements on dielectronic recombination of atomic [4] and dissociative recombination of molecular ions [5], using an ion storage ring and a newly developed intense cold electron beam operated in merged beams geometry.
2. Fast merged beams and photocathode electron sources

Essential aspects regarding the experimental conditions are the definition of the initial state of the ions, of the collision kinematics using as highly monochromatic and well directed electrons as possible, and of the collision products, aiming at event-by-event coincidence studies. These conditions can be realized in experiments with fast overlapping beams [6]. Here, the electron and ion beam velocities are tuned to nearly match each other, defining the collision kinematics, while the high beam velocity ensures efficient observation and coincidence imaging of the collision products within a narrow cone around the beam direction. This approach requires quasi-monochromatic electron beams with intensities as high as possible, called cold since the irregular motion of the electrons in the co-moving reference frame of the beam is minimized. As described below, we have introduced GaAs photocathodes as sources for particularly cold, intense electron beams suitable for merged-beam operation. These electron beams reach temperatures of 10 K and less in the co-moving reference frame in continuous operation at the required beam intensity.

The merged-beams approach can be fruitfully combined with fast ion-beam storage techniques, in particular in ion storage rings [7]. Here, we have used photocathode electron beams [8] for low-energy collision experiments with high energy resolution [9] as well as for phase-space cooling of the stored ion beam [10]. Photocathode electron beams offer most advantages at low beam velocities, down to a few keV per nuclear mass unit (amu), which occur under typical conditions for heavy, singly charged molecular beams; however, their high monochromaticity was also used in experiments with highly charged atomic ions (beam energy of a few MeV/amu), where even the hyperfine structure splitting of dielectronic recombination resonances could be resolved [11].

3. The Heidelberg photoelectron target

The Heidelberg Test Storage Ring (TSR), suitable for beams of multicharged ions with energies of several MeV/amu and for molecular ion beams up to ~35 amu with >0.1 MeV/amu, holds a straight section free for experiments of various type [Fig. 1(a)]. The electron target [12] situated there is operated in alternance with other equipment. It offers solenoidal magnetic guiding fields...
Figure 2. Scheme of the Heidelberg photoelectron gun. V1, V2: vacuum valves; M1-M3: vacuum manipulators. Base pressures (valves closed) are given for the various regions.

(collinear to the beam direction) of typically 0.02-0.04 T for steering a cold electron beam into a ∼1.5 m long overlap region merging with the ion beam. The reactions in the overlap zone are analyzed in a collision spectrometer composed of several counting and imaging detectors for charged and neutral products.

The photoelectron gun is based [13] on a GaAs semiconductor photocathode, coated with about one monolayer of cesium and oxygen in order to achieve negative electron affinity at the surface. The electron emission process is illustrated in Fig. 1(b). Photoelectrons created by infrared absorption reach the surface with the temperature of the GaAs bulk where they are emitted towards the vacuum through a thin dipole layer created by the Cs and O coating. During the development of the source, a preparation procedure suitable for producing cold continuous electron beams was established and its influence on the longitudinal velocity distribution of the electrons was studied [13]. This was followed by a study of the transverse velocity distribution [14], which showed that the emitted electrons have the bulk temperature of the photocathode if potential barriers typical for space-charge limited emission are applied at the surface [see Fig. 1(b)]. Magnetic expansion of the electron beam reduces the transverse electron temperatures further by factors of 10–20 [15]. As a next step, cooling of the photocathode to ∼100 K was established [16] under continuous irradiation of ∼1 W of laser power, as required for producing an electron beam current of ∼1 mA. Finally, the Heidelberg photocathode electron gun was realized in a three-chamber vacuum setup (Fig. 2), which allows several photocathodes to be prepared, used and re-conditioned in closed-cycle operation. The essential procedure [17] for avoiding chemical re-cleaning of the cathodes under air is to clean the suitably heated GaAs surface by atomic hydrogen exposure, which allowed long-term operation of the photocathodes for collision experiments. The achieved operation time of a photocathode is typically 24–36 h after its insertion into the electron gun, with currents of the order of 1 mA. The most important degradation process was found to result from ions produced along the electron beam, which are magnetically guided and reaccelerated to the cathode.

4. Low-energy electron capture resonances on highly charged ions
The electron temperature achieved in the co-moving frame of the photocathode electron beam has reached values close to 0.5 meV [9] and amounts to ∼1 meV (∼10 K) under typical conditions. At low collision energy, measurements of resonant electron-ion recombination can reach an energy resolution close to this electron temperature. In this case the velocities of the two overlapping beams are very close to each other, which implies that meV changes of the collision energy are realized by much larger, easily controlled changes of the laboratory electron energy (several eV). Moreover, systematic effects from the electron space-charge have only a small effect on the collision energy between the particles and can be well kept under control by applying suitable
High-resolution measurements of recombination resonance energies offer a powerful tool for precision studies [11] of radiative energy shifts (quantum electrodynamics) and of multi-electron correlation in atomic few-electron ions with high nuclear charge. It is important to recognize that many low-energy resonances of dielectronic recombination in these systems are caused by electron capture into high Rydberg states after intra-shell excitation (and sometimes pure fine-structure excitation [19]) of the ionic core. The typical resonant capture can thus be written $A^+ + e\ell \rightarrow [(A^+)^* + nl']$, emphasizing the combination of a core excitation with the binding of a Rydberg electron. Correspondingly, it is a useful concept to consider the Rydberg binding energy and the excitation energy of the ionic core as largely independent quantities, increasingly so as the Rydberg quantum number approaches infinity. Even within a complete many-body treatment of the resonance energy, corrections from quantum electrodynamics and nuclear properties can mostly be neglected for the Rydberg binding contribution.

Precision spectroscopy of low-energy dielectronic resonances on Li-like ions has been studied at the TSR for various cases [20] and was recently much improved by using the photoelectron target in twin-beam operation together with the existing electron cooler of the TSR. For the Li-like ion Sc$^{18+}$, this yielded a very precise measurement [11] of the screened Lamb shift in the 2s–2p transition of this ion, obtaining the highest relative accuracy of all existing measurements for this transition in Li-like ions with intermediate and high $Z$. Moreover, the $n = 10$ dielectronic resonances observed appeared as clearly resolved hyperfine doublets through the interaction of the 2s core electron with the $I = 7/2$ spin of the $^{45}$Sc nucleus; this new dimension of experimental resolution also yielded an improved understanding [21] of the terms relevant for the hyperfine structure of a dielectric resonance.

Recently, these experiments were extended to next-more-complex few-electron systems featuring similar low-energy resonances, namely Ge$^{28+}$ (Be-like) [22] and Fe$^{21+}$ (B-like) [23]. From the Fe$^{21+}$ measurement [Fig. 3(a)], the resolution improvement by the photocathode electron source, compared to a previous measurement [24] with a thermionic cathode, is apparent. While the resolved structure due to $n = 7$ and 8 Rydberg resonances has not yet been unraveled in this system, the measurement on Ge$^{28+}$ [Fig. 3(b,c)] has been analyzed with the help of advanced many-body calculations. For the Be-like structure, the calculations revealed strong configuration interaction; one surprising effect are significant shifts due to the mixing of Rydberg resonances with those on the doubly excited core configuration of opposite parity (2p$^2$ vs. 2s2p).

This illustrates that the trielectric recombination process, recently found for Be-like systems in particular [25], shows substantial interference with the usual dielectric recombination channel. Thus, configuration mixing had to be accounted for among the resonances 2s2p$^2$1l and 2p$^2$7l$'$ in order to obtain a preliminary assignment of the main resonances seen [Fig. 3(c)]; the precise theoretical analysis of the resonance positions is still ongoing.

The recent theoretical progress in the assignment of the Ge$^{28+}$ low-energy recombination spectrum promises a precise determination of core excitation energies in this ion. In particular, the assignment suggests an isolated resonance Ge$^{28+} (2s^2) + e\ell \rightarrow$ Ge$^{27+} [2s2p(^3P_0) + 14d_{5/2}]$ as a candidate for the determination of the 2s$^2(^1S_0)-2s2p(^3P_0)$ transition energy in Ge$^{28+}$. To our best knowledge, there is no experimental result for the energy of this optically forbidden, $J = 0$–0 transition, for which a Lamb-shift contribution close to 1 eV is calculated [26]. For the resonance energy determination, an accuracy of the order of 0.5 meV appears feasible. Together with a reliable prediction of the core interaction with the 14d$^5/2$ Rydberg electron, this would test the quantum electrodynamics contributions in the Be-like transition on the 0.1% level, similar to the previous measurement [11] on a Li-like core.
Figure 3. Low-energy dielectronic recombination spectra of (a) \(^{56}\text{Fe}^{21+}\) [23] (B-like, 250 MeV) and (b,c) \(^{74}\text{Ge}^{28+}\) [22] (Be-like, 340 MeV) using the photocathode source. The overviews (a) and (b) show data (red lines) and predicted Rydberg series using available reference data on excitation thresholds. The broken curve in (a) shows a previous spectrum [24] with a thermionic cathode; the comparison of the absolute rates is commented in [23]. Only theoretical predictions (∼80 meV lower than observed through the \(n = 14\), high \(l\) energy) are available for the \(2s2p\) \((^3P_0)\) limit in (b). Frame (c) shows fits to the experimental resonances with a preliminary assignment. Our theoretical results for the peak positions lie within <40 meV from the fitted resonance positions (blue and green lines).

5. Resonant dissociative recombination of molecular ions

Molecular ions efficiently recombine with cold electrons by the radiationless exothermic process of dissociative recombination [5]. The basic mechanism driving the recombination is resonant electron capture into a doubly excited electronic potential surface of the neutral molecule occurring within the Franck-Condon zone of the ion. The doubly excited potential surface normally correlates to neutral dissociative channels of the system, which lie energetically lower reflecting the gain in electronic binding energy. Thus, the capture of an electron dissociates the molecule into neutral, often excited fragments.

Dissociative recombination is an exothermic process occurring with a high rate in the presence of cold electrons. The picture of the electronic capture to occur for stationary nuclei, neglecting their interaction with the incident electron, can explain only broad energetic structures in the cross section of the process. In contrast, especially experiments on light di- and triatomic species have revealed a rich structure of narrow resonances down to a few meV of impact energy [27]. These structures can be explained by direct energy exchange of the incident electron with the nuclei, leading into electronic Rydberg states with the molecular core carrying higher vibrational or rotational excitation than before the collision. Since these Rydberg states are predissociated by the same doubly excited neutral potential surfaces that also drive the direct dissociative recombination, the indirect process via ro-vibrationally excited Rydberg resonances leads to molecular fragmentation into neutral products in an indistinguishable way, manifesting itself by numerous Feshbach-type resonances in the cross section.

The Heidelberg photocathode electron target has been used for high-resolution measurements of the dissociative recombination cross section on the benchmark species HD\(^+\) [9, 28], and H\(_2^+\) [29], studying the low-energy resonances suitable for precision comparison with theoretical calculations of the Feshbach resonance structure. Electron temperatures down to 0.5 meV could be derived from the observed structures [9]; the electron energy distribution resulting from the electron velocity spread has a full width at half maximum (FWHM) of ∼1 meV below 10 meV.
collision energy $E$. At higher energies the FWHM grows as $\prop E^{1/2}$ through the merged-beams kinematics, reaching $\sim 4$ meV at $E = 0.1$ eV.

6. Rotationally resolved fragment energies from dissociative recombination

In addition to the cold photocathode source, the Heidelberg electron target setup is also equipped with imaging detectors capable of sensitively measuring the kinetic energy release and angular distributions of the neutral products, where the detector position lies $\sim 10–12$ m downstream of the $\sim 1.5$ m long merged-beams interaction zone [cf. Fig. 1(a)]. The photocathode electron target has largely improved the resolution in imaging measurements of the neutral products from dissociative recombination. In recent measurements, ro-vibrational Feshbach resonances in HD$^+$ dissociative recombination were investigated regarding the anisotropy of their fragment angular distributions [28] and the rotational cooling of stored HD$^+$ ions by inelastic (superelastic) collisions with cold electrons was detected and analyzed [30]. Moreover, new possibilities open up for studies of diatomic and polyatomic molecular ions through the efficient phase-space cooling of even heavy molecular ion beams enabled by the cold intense photocathode beams. In contrast to previous measurements at ion storage rings using electron cooling with a thermionic source, rapid cooling of heavy molecular ion beams could be observed, yielding stored ion beam diameters of $\sim 1$ mm after only $\sim 5$ s of electron cooling for, e.g., CF$^+$ (31 amu) [10]. Under these conditions, fragment imaging results were obtained recently on CF$^+$ and HF$^+$ [31] as well as on D$_3$O$^+$, DCND$^+$, D$_2$H$^+$ and CHD$^+$, the analysis being in progress. Here we discuss in detail the specific case of HF$^+$, where exceptionally small energy release could be observed and the different rotational levels occupied in the parent ion before the collision lead to clearly distinct contributions in the product momentum pattern.

The energy levels of HF$^+$, together with the neutral product energies, are depicted in Fig. 4. The dissociation energy $D_0$ of this molecule is just a small amount larger than the ionization energy of the $n = 2$ level in hydrogen, close to 3.4 eV. Considering the interaction of HF$^+$ with cold electrons (1 meV or $\sim 10$ K temperature), efficient resonant electron capture can take place in the Franck-Condon region into the $V^1 \Sigma^+$ neutral doubly excited state of HF, which correlates to the separate atom channel of H($n = 2$) and ground-state F. However, this separate-atom level lies energetically above the lowest ro-vibrational state of the $X^2 \Pi$ ionic potential, so that ground-state HF$^+$ ions and cold electrons do not dissociate forming excited hydrogen atoms. (Instead, the captured electrons autoionize, or switch to the dissociative route ending in the hydrogen ground state.) On the other hand, dissociation into H($n = 2$) and F($^2 P_{3/2}$) can occur if the ions are rotationally excited to states $X^2 \Pi_{3/2}(J = 7/2)$ and above, which have substantial thermal population at the 300 K ambient temperature of the storage ring. Ions in states above $^2 \Pi_{3/2}(J = 7/2)$ will hence produce H and F products with distinct small energy
releases down to only a few meV.

Using 4.7-MeV HF$^+$ ions merged with the velocity-matched photocathode electron beam, the transverse momenta of the H and F products were measured by recording the transverse projected distance between coincident fragments on a multichannel-plate imaging detector 12 m from the overlap zone. The histogram of observed distances (Fig. 5) shows distinct peaks, which can be assigned to individual initial rotational HF$^+$ levels using the available data from rotational spectroscopy of this ion [32, 33]. Since the average relative velocity vector of the collisions vanishes at matched beam velocities, isotropic angular distributions have so far been assumed for analyzing the data; moreover, a fixed value of the cross section was assumed in averaging over the electron velocity distribution. In this case, the contributions for a single molecular energy release have a well-defined shape determined by the orientation angles on the low-distance side and by the beam overlap length and the electron temperature on the high-distance side. The peaks are well fitted assuming the spectroscopically measured rotational spacings. From the shape of the lowest peak, the electron temperatures were fitted to 1.7(1) meV for the data in Fig. 5 and to 1.0(1) meV for different settings expected to yield a temperature lower by $\sqrt{2}$, in reasonable agreement with the values expected under the conditions of this measurement. The kinetic energy release extracted for the lowest energetically open rotational level, $^2\Pi_{3/2}(J = 7/2)$, in this preliminary analysis amounts to 4.19(10) meV. This includes statistical errors as well as (with a safe margin) the possible systematic errors of the transverse momentum measurement.

From earlier ZEKE [34] and ion-pair production measurements [35] on HF in the vacuum ultraviolet (analyzing differences between transition energies around 16 eV), the dissociation energy of HF$^+$ can be deduced within about ±0.2 meV and used to calculate the expected energy release. (The electron affinity of F is very precisely measured [36].) A discrepancy of our measured energy release from the predicted one of $-1.67(22)$ meV (see the red arrow in Fig. 5) is under investigation. We are verifying our averaging procedure over the electron energy distribution and the fragment angles, which might require more details to be included. With further understanding of these effects, fragment imaging appears well suited for determining the molecular dissociation energy with sub-meV accuracy in a single measurement, which for analysis only needs the very precisely known ionization energy of H($n = 2$) and the similarly well known HF$^+$ rotational spectrum, and thus can verify the more indirect result where large energy intervals from separate measurements are combined.

7. Outlook

With an emission energy spread about one order of magnitude below that of conventional thermionic cathodes, photocathode electron sources offer the opportunity of producing cold

![Figure 5. Transverse fragment distance distributions for HF$^+$ with fitted components as discussed in the text. The peak positions for given initial and final levels are marked. The peak intensities roughly reflect the thermal level populations in the stored HF$^+$ beam at 300 K, with significant yields only to the F($^2P_{3/2}$) final state. The red mark and arrow denote the shift between the predicted and the measured position of the lowest peak, that represents an energy release near 4.2 meV.](image-url)
electron beams at very low laboratory energies, in the range of ∼1 to 10 eV. Such energies make it possible to apply phase-space cooling [10] and to perform merged-beams collision experiments with ion beams at keV energies in electrostatic storage rings, such as the cryogenic storage ring CSR [37] presently being set up in Heidelberg. With an estimated mass limit of ∼160 amu, merged-beams electron collisions and cooled, high-brightness beams will then become available for heavy and complex molecules, including organic compounds, with many new experimental options, such as beam accumulation and short-pulse bunching.

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