LOW-ENERGY COLLISIONS OF MULTIPLY CHARGED IONS WITH ELECTRONS, ATOMS AND SURFACES

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ABSTRACT

Results are presented from recent experiments at the ORNL-ECR Multicharged Ion Research Facility which have addressed low-energy interactions of multiply charged ions with electrons, hydrogen atoms and metal surfaces. The specific processes for which results are reported are electron-impact excitation, electron capture and ion neutralization. The objective of these studies is a more detailed understanding of the mechanisms which govern the interactions of multicharged ions at low (or near-threshold) collision energies.

1. Introduction

Low-energy interactions of multiply charged ions are generally dominated by enhanced Coulomb or polarization forces, and/or by the appreciable neutralization energy that such ions carry into the interaction. This neutralization energy is equal to the sum of the binding energies of the $q$ electrons that have been removed from an atom to produce an ion of net positive charge $q$. This may be thought of as a reservoir of stored electronic potential energy for certain types of interactions. In experimental studies with low-energy ion beams, these $q$ electrons are removed from the atom in an ion source prior to acceleration. The development of advanced sources of multiply charged ions such as the electron-cyclotron-resonance (ECR) and electron-beam ion source (EBIS) now makes possible experimental studies with low-energy ions having charges of 20 or more and carrying hundreds to even thousands of electron volts of neutralization energy. During the last few years, the increasing availability of such ion sources for atomic physics research has spawned considerable activity in this area.
The large Coulomb forces between highly charged ions and other charged particles dominate long-range interactions, modifying particle trajectories, and producing large cross sections for some processes. The large neutralization energy of the ion can dominate kinetic effects in slow collisions. For multiply charged ions, the reduced screening of the nucleus due to missing electrons increases the binding energy of the outer valence electrons, but has a lesser effect on inner-shell electrons. Thus processes involving inner-shell electrons may become relatively more important as the ionic charge increases. For example, in electron-impact ionization of multiply charged ions, inner-shell excitation-autoionization can dominate direct outer-shell ionization by an order of magnitude or more in some cases\(^1\). Polarization forces due to ion-induced dipole interactions are also enhanced in multicharged ion interactions with neutral particles, since the attractive potential is proportional to the square of the ionic charge:

\[ V(r) = -\alpha q^2/2r^4 \]  

where \( \alpha \) is the dipole polarizability of the neutral particle, \( q \) is the ionic charge, and \( r \) is the inter-particle distance. This interaction is relatively weak and short-range compared to the Coulomb interaction, but can play a role in multicharged ion-neutral collisions at electron-volt energies and below.

In this paper, three recent experiments conducted at the ORNL-ECR Multicharged Ion Research Facility will be described which address these properties of multicharged ion interactions. Specifically, results will be presented for low-energy interactions of multicharged ions with electrons, atoms and metal surfaces.


In addition to being a fundamental process of intrinsic interest, electron-impact excitation of multiply charged ions is critical to radiative power loss and diagnostics of magnetic fusion plasmas. High-resolution cross-section measurements in the near-threshold region are needed to benchmark detailed close-coupling calculations, and to elucidate the role of resonances. All existing absolute excitation cross-section measurements for multiply charged ions have been based on the crossed-beams approach and on absolute intensity measurements of the radiation emitted as the excited states decay\(^1\). Such measurements are severely limited by low photon intensities and detection efficiencies (~10\(^{-4}\)), difficulties with absolute optical calibration, as well as low electron energy resolution (~2 eV). Cascade contributions from excitation of higher levels may also contribute to the measured photon emission, complicating such measurements.
A different experimental approach\textsuperscript{2} which circumvents these limitations has been developed at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado for use in conjunction with the ORNL-ECR multicharged ion source. The technique, illustrated in Fig. 1, involves merging fast beams of electrons and multiply charged ions in a uniform axial magnetic field, and detecting electron-impact excitation events via electron energy-loss spectroscopy. Trochoidal ($E \times B$) analyzers are used to merge and demerge the beams. The magnetic field ensures complete collection of inelastically scattered electrons, which are directed onto a position-sensitive detector. Detailed electron-trajectory modelling calculations are performed in order to predict the locations where both elastically and inelastically scattered electrons will strike the position-sensitive detector. A fast two-beam modulation scheme is used to separate detector counts due to scattered electrons produced in beam-beam events from those due to interactions of either beam with residual gas or surfaces. To minimize such background events, a vacuum of at least $1 \times 10^{-10}$ torr is maintained with beams present.

A movable beam probe consisting of a phosphor screen, micro-channel plate and charge-injection-device (CID) camera is inserted into the interaction volume to quantify the three-dimensional spatial intensity distributions and overlap of the beams. Real-time spatial images of the electron and ion beams are displayed on an oscilloscope, facilitating their tuning and alignment.

Figure 1. Schematic of JILA merged-beams electron-energy-loss apparatus for the measurement of cross sections for electron-impact excitation of ions.
This apparatus was moved from JILA and installed at the ORNL-ECR facility during 1990. The first measurements on a multiply charged ion with this apparatus were reported recently\(^2\) for 3s-3p excitation of \(\text{Si}^{3+}\):

\[
e + \text{Si}^{3+}(3s \ ^2S_{1/2}) \rightarrow e + \text{Si}^{3+}(3p \ ^2P_{1/2,3/2}) - 8.88 \text{ eV}
\]  \[2\]

This system was chosen for the first measurements because cross-section calculations for Na-like ions are expected to be of high reliability, and thus a comparison of experiment and theory serves to test the validity of both. The absolute experimental cross-section measurements\(^2\) are compared in Fig. 2 to benchmark 7-state close-coupling calculations by Badnell, Pindzola, and Griffin\(^3\). The cross section for electron-impact excitation of an ion is finite at threshold, and usually reaches its largest value there. Thus an abrupt jump from zero is expected at the 8.9 eV 3s-3p threshold. For the sake of comparison, the theoretical cross section in Fig. 2 has

![Figure 2. Comparison of absolute cross-section measurements for 3s-3p excitation of \(\text{Si}^{3+}\) with 7-state close-coupling calculations by Badnell, Pindzola, and Griffin. The theoretical cross section has been convoluted with a 0.2 eV FWHM Gaussian distribution to simulate the energy resolution of the merged-beams experiment.](image-url)
been convoluted with a Gaussian electron-energy distribution of 0.2 eV (FWHM), which was selected empirically to simulate the energy resolution of the experiment. In fact, there are actually two fine-structure components in the 3s-3p excitation ($^2P_{1/2}$, $^2P_{3/2}$), and thus two expected steps in the cross section which are separated by 0.06 eV. Although the experimental energy resolution is insufficient to resolve these two steps, it may be slightly better than 0.2 eV. In any case, this represents an order-of-magnitude improvement over previous ion excitation measurements based on detection of photon emission\(^4\). The absolute agreement in cross-section magnitude between experiment and theory in the critical threshold region is seen to be very satisfactory.

Trajectory modelling of the primary electron beam, and of both elastically and inelastically scattered electrons, indicates that the merged-beams electron-energy-loss apparatus is, in principle, capable of covering almost the entire energy range presented in Fig. 2. This could not be realized in these initial measurements due to high background levels encountered as the relative energy was further increased above the excitation threshold. It is believed that this elevated background was due to components in the primary electron beam with increased transverse energy, whose trajectories either impacted the position-sensitive detector directly, or interacted with nearby surfaces. Such effects become increasingly severe as the relative energy is increased above the threshold, since the difference in energy between the primary and scattered electron beams decreases, and thus their spatial separation in the demerger is reduced.

Improvements to the electron gun and merger are in progress, based on more detailed computer trajectory-modelling calculations. It is expected that these will permit the energy range of the technique to be extended further above the excitation threshold, where strong resonance effects are predicted to occur for many ions. The structure in the theoretical cross section shown in Fig. 2 is due to such resonances. Their apparent effect has been reduced somewhat because of the convolution of the theoretical cross section with the simulated experimental electron energy distribution. These first data serve to establish the proof of principle of the merged-beams electron-energy-loss technique for excitation of multiply charged ions, and the threshold measurement demonstrates that the experimental resolution should be sufficient to uncover such resonance structures. The energy range accessible to the technique is constrained in principle only by the decreasing dispersion of elastically and inelastically scattered electrons as the energy is raised above the inelastic threshold. Future experiments will focus on fusion-relevant ion species, and will be selected in order to provide the most sensitive tests of theory.
3. Electron Capture by Multiply Charged Ions from Hydrogen Atoms Energies Below 1 eV

Low-energy electron-capture collisions involving highly ionized ions play an important role in non-equilibrium plasmas which are found both in nature and in the laboratory. Reactions of the type:

$$X^{+q} + H \rightarrow X^{+q+1} + H^+ + \Delta E$$  \[3\]

are characterized by large cross sections that depend strongly both on the electronic energy-level structure of the colliding system and on the interaction mechanism. The dominant reaction channels are those which, depending on q, are exoergic by several to tens of eV, and lead to population of excited states of the $X^{+q+1}$ product.

At collision energies in the eV range, the interaction potential energy becomes an appreciable fraction of the total available energy. Electrons of the transient quasi-molecule formed during such collisions have sufficient time to adjust to the changing interatomic field as the nuclei approach and separate. Theoretical calculations in this energy regime require sophisticated coupled-states approaches\(^5\), which often disagree with each other in their predictions of capture cross sections. Parallel quantitative theoretical and experimental determinations of cross sections for such processes can therefore yield important new information about quasimolecular structure and collision dynamics. For example, the cross section for a particular reaction channel may be enhanced at very low energies by the weak ion-induced-dipole attraction between the reactants (Eq. 1), which can permit the collision to sample potential-curve crossings which are smaller than the impact parameter\(^6\). Since this attractive force is weak, it will be significant only at very low collision velocities. This is the basis for the so-called Langevin-orbiting model\(^7\), which predicts classical orbiting trajectories for a certain critical impact parameter, and a resulting reaction cross section which varies inversely with velocity. This model successfully explains the behavior of thermal rate coefficients for many ion-molecule reactions. It cannot, however, be arbitrarily applied to electron-capture collisions\(^8\), since an active potential-curve crossing must exist at an appropriate internuclear separation in order for the capture cross section to be enhanced by such a "trajectory effect." Since the polarization potential varies as $q^2$, its influence on the collision may be felt at higher velocities as the ion charge is increased.

To address such issues, an ion-atom merged-beams apparatus has been developed at Oak Ridge National Laboratory and applied to experimental studies of electron-capture collisions of multicharged ions with hydrogen atoms at the lowest attainable energies. The technique\(^9\) is illustrated in Fig. 3. A reactant beam of ground-state H atoms is prepared by intra-cavity laser photodetachment of a 6-9 keV beam of H$^-$ ions. A beam of multicharged ions of similar velocity from the ORNL-ECR ion
source is merged electrostatically with this neutral beam in a region of ultrahigh vacuum ($P < 1 \times 10^{-10}$ T). A rotating-wire beam scanner and two scanning-slit beam probes quantify the spatial intensity distributions and overlap of the beams. An analyzing magnet demerges the beams and separates the product $H^+$ ions from the reactants. The $H^+$ products are further dispersed electrostatically and counted by a channel electron multiplier; the reactant ion and neutral beams are collected in a Faraday cup and on a secondary-emission detector, respectively. A standard fast two-beam gating scheme is used to separate beam-beam signals from backgrounds produced by collisions with residual gas.

A number of major improvements were made during the past year to the original apparatus to increase the angular acceptance for reaction products and to improve the signal-to-background ratio. This redesign included the addition of differential and active pumping in the merge path, shortening the merge path from 80 to 50 cm, and enlarging the apertures of the signal-collection lenses and the demerging magnet chamber. The signal-to-background ratio has been increased by a factor of three, permitting measurements to be made at lower energies, where the reaction rate in the apparatus becomes vanishingly small. A deflector was added just before the intersection of the $H^+$ beam with the photodetachment laser in order to remove $H$ atoms from the reactant beam which have collisionally detached on residual gas. This
and the vacuum improvements give a reactant H beam with a ground-state purity of 0.9998, compared to 0.995 for the previous arrangement. This is critical to obtaining meaningful measurements, because electron capture by multicharged ions from excited H atoms has much larger cross sections, particularly at very low collision energies. With all of these improvements, the effective dynamic energy range of the merged-beams apparatus has been extended downward by an order of magnitude to 0.1 eV/amu, which is the practical limit due to the finite divergences of the reactant beams.

On the basis of recent calculations\textsuperscript{10} of differential cross sections for the O\textsuperscript{5+} + H(D) system, Andersson and co-workers have suggested that a disagreement of earlier merged-beams data with theory resulted from incomplete collection of the H\textsuperscript{+}(D\textsuperscript{+}) products in the 2 to 20 eV/amu energy range. This discrepancy has now been resolved by further measurements with the improved apparatus, which also permitted the energy range to be extended down to 0.14 eV/amu. These new measurements are compared with previous data and with theory in Fig. 4. The newer data are consistent within the experimental uncertainty with theory over the entire energy range, and clearly show the predicted increase at the lowest energies due to the onset of capture into the 4p and 4d states. The 10 to 30\% reduction in the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{merged_beams_figure.png}
\caption{Comparison of merged-beams cross-section measurements for electron-capture in O\textsuperscript{5+} + H(D) collisions using improved apparatus (solid points) with previous measurements and theoretical calculations.}
\end{figure}
measured cross section compared to the previous data in the 10-100 eV/amu energy range is due to the improvement in ground-state purity of the H(D) reactant beam. Previous data for $O^{3+} + H(D)$ have also been extended with the new apparatus down to 0.17 eV/amu, clearly showing the predicted contribution of capture into the 3p state at the lowest energies.$^{11}$

An upgrade of the ORNL-ECR ion source is in progress, which will increase its performance with respect to charge state and beam intensity. This will open up more highly charged collision systems for study with the merged-beams technique. Due to the enhanced polarization attraction between the reactants, such systems may exhibit "trajectory effects" or even orbiting resonances at the lowest energies accessible to the merged-beams technique. It should also be possible to study electron-capture collisions of bare ions such as $C^{6+}$ or $O^{8+}$ with hydrogen atoms. Since only one electron and two nuclei are involved, these are true three-body systems, and will provide the most fundamental tests of theory. Plans also exist to extend the merged-beams technique to the study of collisions of multicharged ions with excited hydrogen, for which cross sections are expected to be extremely large.

4. Neutralization of Multicharged Ions in Grazing Interactions with Metal Surfaces

The interaction of highly charged ions with metal surfaces has become a topic of considerable experimental investigation.$^{12-14}$ One remarkable and unexpected result of recent work has been the observation of extremely rapid neutralization of highly ionized projectiles at metal surfaces. Our understanding of such processes follows from the pioneering work of Hagstrum$^{15}$, who first proposed the so-called resonance-neutralization model nearly 40 years ago, and from work in the 1970's by Arifov, Parilis and co-workers$^{16}$. The process is illustrated in Fig. 5. As a highly charged bare (or nearly bare) ion approaches a metal surface, the potential barrier between the ion and the surface is lowered, and a negative image charge is induced at the surface. At some critical distance, electrons flow from the valence band of the metal into empty excited levels of the ion, forming so-called "hollow" or "super-excited" atoms. Classically, over some range of ionic charge $q$, this distance is estimated to be $q+7$ atomic units.$^{17}$ Of course, quantum-mechanical tunnelling through the barrier is possible at somewhat larger distances. As this "hollow" atom de-excites near the surface by Auger electron emission, electrons continue to flow from the metal to keep the ion neutralized. The emission of K X-rays$^{12}$, or of K-Auger electrons$^{13,14,18}$ may be used as a "clock" to provide information about the formation and decay of this exotic atom.

The emphasis of recent ORNL research in this area has been on elucidation of the time scales over which projectile ion neutralization occurs during grazing interactions with metal surfaces. The experimental approach is to measure the energy spectrum of projectile K-Auger electron emission as a function of the angle
of incidence of the ion on the surface, and therefore as a function of the time the projectile spends in the vicinity of the surface.

Figure 5. Formation of a "hollow" or "super-excited" N atom by the resonance neutralization of a N$^{6+}$ ion at a metal surface.

Figure 6 shows the variation of the measured yield$^{18}$ of N KLL Auger electrons with angle of incidence for 60-kev N$^{6+}$ projectiles on Au (110). In order to try to account for the measured K-Auger electron yields, a computer simulation$^{14}$ of the autoionization cascade was made using calculated atomic Auger transition rates. Radiative decay rates are negligible compared to Auger rates in this case. The cascade is assumed to start when the ion is 30 a.u. above the surface with 6 electrons resonantly captured in the n=7 shell of the N$^{6+}$ projectile, which is nearly resonant with the Fermi energy of the metal. Re-neutralization into n=7 is assumed subsequent to each autoionization step. The result of this simulation is shown in Fig. 7 for 24 keV N$^{6+}$ incident on a metal surface at an angle of 10°, and indicates that the autoionization cascade is much too slow (~100 times!) to explain the observed K-Auger yields.

It is unlikely that this discrepancy is due to the neglect of additional de-excitation processes which become possible when the ion is close to the surface, or to possible enhancements of the atomic Auger rates in the proximity of the surface. Rather, the large observed K-Auger yields are more likely due to the contribution of sub-surface processes. This conclusion has been reached on the basis of extensive Monte-Carlo simulations of ion trajectories in the solid$^{18}$. Once the ion enters the solid, the L shell may be filled rapidly either by direct capture to the M shell from the Au 5p and/or valence band, followed by rapid LMM Auger decay, or by capture directly into the
Figure 6. Absolute measured projectile K-Auger electron yields for 60-keV N$^{+}$ ions incident on an Au (110) surface at five different angles.

L shell. This makes KLL emission possible with minimum delay. The simulations show that, due to the small inelastic mean free paths of the KLL electrons in the solid, the observed KLL emission originates from only the first few atomic layers of the bulk, prior to appreciable angular scattering of the projectile ion. As a result, this sub-surface KLL emission has the same Doppler signature as electron emission on the incident projectile ion trajectory. Also, when allowance is made for the different escape probabilities for LMM and KLL electrons emitted from below the surface, the anomalously low measured ratio$^{13,14,18}$ of L to K Auger electron yields is at least partially explained.
Figure 7. Calculated distribution of electrons over the principal quantum shells as a function of ion-surface distance. Atomic rates were used in the atomic ladder model for 24 keV N*' incident at 10° on a metal surface. The single K-shell electron carried by the N** ion into the interaction is not indicated.

Examining the electron yield measurements in Fig. 6 in more detail, one observes that the shape of the K-Auger peak on the low-energy side is different at the two smallest angles, suggesting the appearance of an additional feature. This feature is emphasized in Fig. 8, in which the shape of the peak at 19.5° has been subtracted from the normalized spectrum at each angle, and is attributed to above-surface neutralization. Its time evolution (i.e., dependence on ion incidence angle) is consistent with the Auger cascade model described above. Only at the smallest angles of incidence is there sufficient time available for above-surface de-excitation to contribute appreciably to the total yield of projectile K-Auger electrons. The manifestation of "hollow atoms" in multicharged ion-surface interactions is thus perhaps more subtle than was previously thought.

The upgrade of the ORNL ECR ion source will enable studies to be made of ion-surface interactions with more highly charged ions, for which the neutralization energy is substantially increased, thus providing more severe tests of evolving models for neutralization. Plans also call for construction of a new apparatus with provision for ion deceleration prior to interaction with the surface. This will allow measurements to be made for different ion incidence angles, but the same ion
velocity perpendicular to the surface (and thus interaction time). It is possible that the above- and below-surface effects would then be more clearly resolvable. Interactions with semiconductors, where a gap exists between the valence and conduction bands, is another intriguing possibility.

5. Summary

A novel merged-beams electron-energy-loss apparatus developed at JILA has been implemented at ORNL for studies of electron-impact excitation of multiply charged ions, with the first absolute cross-section measurements obtained for 3s-3p excitation of Na-like Si^{3+}. The near-threshold measurements are in excellent agreement with theory, and indicate an energy resolution of 0.2 eV for the technique.
Recent improvements to the ORNL ion-atom merged-beams apparatus have permitted measurements of absolute electron-capture cross sections for collisions of multiply charged oxygen atoms with deuterium atoms down to energies as low as 0.14 eV/amu. The data provide stringent tests of theory, and verify the predicted increase of the cross section at energies below 1 eV/amu due to the contributions of capture into the 3p and 3d levels.

In angle- and energy-resolved measurements of electrons ejected in grazing interactions of multicharged nitrogen ions with gold and copper single crystals, components have been identified in the spectrum due to both above- and below-surface emission by the ion. These data and their interpretation via computer simulations resolve some outstanding discrepancies concerning the time scale for neutralization of highly charged ions at solid surfaces.

An upgrade of the ORNL-ECR multicharged ion source is in progress which will substantially increase the capabilities and scope of studies such as those described in this paper.

6. Acknowledgments

This research was sponsored by the U.S. Department of Energy in part under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and in part under Contract No. DE-AL101-76PR16010 with the National Institute of Standards and Technology.

A.C.H.S. participated in the electron collision experiment as a Visiting Fellow at JILA and a Guest Scientist at ORNL during 1989-90. The authors are grateful to D. C. Griffin, M. S. Pindzola, and N. Badnell for permission to quote theoretical results prior to publication, and to C. Bottcher for insightful comments on this manuscript.

7. References

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