



**HAL**  
open science

## Roadmap on photonic, electronic and atomic collision physics: III. Heavy particles: with zero to relativistic speeds

Friedrich Aumayr, Kiyoshi Ueda, Emma Sokell, Stefan Schippers, Hossein Sadeghpour, Frédéric Merkt, Thomas Gallagher, F Barry Dunning, Paul Scheier, Olof Echt, et al.

### ► To cite this version:

Friedrich Aumayr, Kiyoshi Ueda, Emma Sokell, Stefan Schippers, Hossein Sadeghpour, et al.. Roadmap on photonic, electronic and atomic collision physics: III. Heavy particles: with zero to relativistic speeds. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 2019, 52 (17), pp.171003. 10.1088/1361-6455/ab26ea . hal-02374535

**HAL Id: hal-02374535**

**<https://hal.science/hal-02374535>**

Submitted on 27 May 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
















L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

## Roadmap

# Roadmap on photonic, electronic and atomic collision physics: III. Heavy particles: with zero to relativistic speeds

Friedrich Aumayr<sup>1,27</sup> , Kiyoshi Ueda<sup>2,27</sup>, Emma Sokell<sup>3,27</sup> , Stefan Schippers<sup>4,27</sup> , Hossein Sadeghpour<sup>5,27</sup>, Frédéric Merkt<sup>6,7</sup> , Thomas F Gallagher<sup>8</sup>, F Barry Dunning<sup>9</sup>, Paul Scheier<sup>10</sup> , Olof Echt<sup>10</sup> , Tom Kirchner<sup>11</sup> , Stephan Fritzsche<sup>12,13,14</sup> , Andrey Surzhykov<sup>15,16</sup>, Xinwen Ma<sup>17</sup> , Roberto Rivarola<sup>18</sup>, Omar Fojon<sup>18</sup>, Lokesh Tribedi<sup>19</sup> , Emily Lamour<sup>20</sup>, José R Crespo López-Urrutia<sup>21</sup> , Yuri A Litvinov<sup>14</sup> , Vladimir Shabaev<sup>22</sup>, Henrik Cederquist<sup>23</sup>, Henning Zettergren<sup>23</sup> , Marika Schleberger<sup>24</sup>, Richard A Wilhelm<sup>1</sup> , Toshiyuki Azuma<sup>25</sup>, Philippe Boduch<sup>26</sup>, Henning T Schmidt<sup>23</sup>  and Thomas Stöhlker<sup>12,13,14</sup>

<sup>1</sup> TU Wien, Institute of Applied Physics, A-1040 Vienna, Austria

<sup>2</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

<sup>3</sup> School of Physics, University College Dublin, Dublin, Ireland

<sup>4</sup> Justus-Liebig-Universität Gießen, I. Physikalisches Institut, 35392 Giessen, Germany

<sup>5</sup> ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, United States of America

<sup>6</sup> Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland

<sup>7</sup> Department of Physics and Astronomy, Vrije Universiteit Amsterdam, 1081 HV Amsterdam, The Netherlands

<sup>8</sup> Department of Physics, University of Virginia, Charlottesville, VA 22904, United States of America

<sup>9</sup> Department of Physics and Astronomy, Rice University MS61, Houston TX 77005, United States of America

<sup>10</sup> Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, A-6020, Innsbruck, Austria

<sup>11</sup> Department of Physics and Astronomy, York University, Toronto, Ontario, M3J 1P3, Canada

<sup>12</sup> Helmholtz Institute Jena, D-07743 Jena, Germany

<sup>13</sup> Theoretisch-Physikalisches Institut, Friedrich-Schiller Universität Jena, D-07743 Jena, Germany

<sup>14</sup> GSI Helmholtz Centre for Heavy Ion Research, D-64291 Darmstadt, Germany

<sup>15</sup> Technische Universität Braunschweig, Institut für Mathematische Physik, D-38106 Braunschweig, Germany

<sup>16</sup> Physikalisches-Technische Bundesanstalt, D-38116 Braunschweig, Germany

<sup>17</sup> Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou, 730000, People's Republic of China

<sup>18</sup> Instituto de Física Rosario CONICET-UNR, 2000 Rosario, Argentina

<sup>19</sup> Tata Institute of Fundamental Research, Mumbai 400005, India

<sup>20</sup> Institut des NanoSciences de Paris, CNRS, Sorbonne University, Paris, F-75005, France

<sup>21</sup> Max-Planck-Institut für Kernphysik, D-69117 Heidelberg, Germany

<sup>22</sup> Department of Physics, St. Petersburg State University, 199034 St. Petersburg, Russia

<sup>23</sup> Department of Physics, Stockholm University, AlbaNova, SE-106 91, Stockholm, Sweden

<sup>24</sup> Universität Duisburg-Essen, Fakultät für Physik and Cenide, D-47057 Duisburg, Germany

<sup>25</sup> Atomic, Molecular, and Optical Physics Laboratory, RIKEN, Wako, 351-0198, Japan

<sup>26</sup> CIMAP-GANIL/University of Caen-Normandie UNICAEN, France

<sup>27</sup> Guest editors of the roadmap

E-mail: [aumayr@iap.tuwien.ac.at](mailto:aumayr@iap.tuwien.ac.at), [kiyoshi.ueda.a2@tohoku.ac.jp](mailto:kiyoshi.ueda.a2@tohoku.ac.jp), [emma.sokell@ucd.ie](mailto:emma.sokell@ucd.ie), [schippers@jlug.de](mailto:schippers@jlug.de)  
and [hws@cfa.harvard.edu](mailto:hws@cfa.harvard.edu)

Received 13 December 2018, revised 18 April 2019

Accepted for publication 4 June 2019

Published 9 August 2019



## Abstract

We publish three Roadmaps on photonic, electronic and atomic collision physics in order to celebrate the 60th anniversary of the ICPEAC conference. Roadmap III focusses on heavy particles: with zero to relativistic speeds. Modern theoretical and experimental approaches provide detailed insight into the wide range of many-body interactions involving projectiles and targets of varying complexity ranging from simple atoms, through molecules and clusters, complex biomolecules and nanoparticles to surfaces and crystals. These developments have been driven by technological progress and future developments will expand the horizon of the systems that can be studied. This Roadmap aims at looking back along the road, explaining the evolution of the field, and looking forward, collecting nineteen contributions from leading scientists in the field.

Keywords: heavy particles, many-body interactions, clusters, complex biomolecules

(Some figures may appear in colour only in the online journal)

## Contents

INTRODUCTION	4
RYDBERG ATOMS AND COLD COLLISIONS	6
1. High Rydberg states and ion chemistry	6
2. Resonant energy transfer with Rydberg atoms	8
3. Studies involving high- $n$ Rydberg atoms	10
4. Chemistry close to 0 K	12
COLLISIONS INVOLVING HEAVY PROJECTILES	14
5. Non-relativistic ion–atom collision theory	14
6. Correlation and polarization phenomena in relativistic ion–atom collisions	16
7. Experimental investigations on ion–atom collisions	18
8. Interference effects in ion–molecule collisions	21
9. Ion–molecule collisions—large molecules	23
10. Ion–ion collisions in the intermediate velocity regime	25
HIGHLY CHARGED IONS	27
11. Frequency metrology with trapped and stored HCIs	27
12. Highly-charged radionuclides	29
13. QED in strong fields	31
14. Interactions of HCIs with clusters	33
15. Interaction of HCIs with surfaces and 2D materials	35

<sup>28</sup> Author to whom any correspondence should be addressed.



Original content from this work may be used under the terms  
Creative Commons Attribution 3.0 licence. Any

further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

---

16. Interaction of HCIs with crystals/solids	37
17. COMs and irradiation effects in solid phase for astrophysics: radiolysis and radio-resistance of nucleobases	40
NEW FACILITIES FOR NEW CHALLENGES	42
18. Cryogenic electrostatic storage rings	42
19. Frontiers of extreme electromagnetic fields: atomic physics with HCIs at FAIR (SPARC collaboration)	44

## INTRODUCTION

Friedrich Aumayr<sup>1</sup>, Kiyoshi Ueda<sup>2</sup>, Emma Sokell<sup>3</sup>, Stefan Schippers<sup>4</sup>, Hossein Sadeghpour<sup>5</sup>

<sup>1</sup>TU Wien, Austria

<sup>2</sup>Tohoku University, Japan

<sup>3</sup>University College Dublin, Ireland

<sup>4</sup>Justus-Liebig-Universität Gießen, Germany

<sup>5</sup>Harvard University, United States of America

To celebrate the 60th anniversary of the ICPEAC conference, we publish a series of three Roadmaps on photonic, electronic and atomic collision physics. One for each of the three classes of projectile that comprise the breadth of topics encompassed by ICPEAC; *I. Light-matter interaction*; *II. Electron and antimatter interactions*; and *III. Heavy particles: with zero to relativistic speeds*. Each of the Roadmaps is intended to provide an overview of the present status of the field, how it was arrived at and address current and future challenges faced by those working in the broad area of research. As with all IOP Roadmaps, the three articles have been authored collaboratively by leading researchers in the areas and each aims to provide an impression of current trends in the respective field of research.

Roadmap III: Heavy particles is dedicated to recent advances in collisions involving heavy particles, from highly relativistic ions to extremely cold atoms and molecules, from exotic Rydberg atoms to extremely highly-charged heavy ions, from simple atoms and molecules to clusters, large biomolecules, nanoparticles, novel 2D-materials, surfaces and solids. This field of research is at the heart of ICPEAC. The present Roadmap glimpses into the future of the field by explaining important and promising theoretical and experimental trends and developments. It comprises 19 contributions by leading scientists distributed over four topic sections: topic section 1 on Rydberg atoms and cold collisions, topic section 2 on collisions involving heavy projectiles, topic section 3 on highly-charged ions and topic section 4 on new facilities for new challenges.

In topic section 1, Merkt describes the use of molecular Rydberg states for ion chemistry using three examples, PFI-ZEKE and MQDT-assisted Rydberg spectroscopy for accessing a broad range of electronic, vibrational, rotational and hyperfine levels of the cation states and/or their energy intervals and a chip-based Rydberg–Stark deflector and decelerator for ion–molecule reactions within the Rydberg molecule. Gallagher looks back on the history of resonant energy transfer with Rydberg atoms, via dipole–dipole interactions without collisional motion, and discusses their applications from quantum gates and simulators to the construction of ultralong-range molecules. Dunning describes the current status of studies involving high-Rydberg atoms and future directions such as studying the dynamics of strongly-coupled Rydberg atoms, two-electron excited states (planetary atoms) and ultralong-range Rydberg molecules. Scheier and Echt discuss future directions of research using doped helium nanodroplets (HNDs). In particular they outline

the prospects of using up to 1  $\mu\text{m}$  large, monodisperse droplets to synthesize and characterize novel structures like nanowires, Coulomb crystals or ligand-free catalysts.

In topic section 2, Kirchner sketches the path to a fully non-perturbative treatment of ion–atom collision processes. Advances in computational methods have already allowed us to answer some long-standing questions on the role of electron correlation effects in multiparticle dynamics. However, many electron systems will remain a challenge into the future. Fritzsche and Surzhykov show how high-resolution angle as well as polarization resolved studies in relativistic ion–atom collisions can lead to new insights into quantum dynamics in extremely strong fields if combined with advanced theoretical techniques. The FAIR facility will also make such polarization studies possible for negative-continuum dielectronic recombination (NCDR), a process in which a free electron is captured into a bound state of a heavy high- $Z$  ion, while an electron–positron pair is emitted. Ma discusses the future challenges for experimental investigations of ion–atom collisions. On his list are new concepts to extract relative scattering phases from two-center interference patterns in ion–molecule collisions, as well as the incorporation of photon detection into reaction microscopes. Rivarola and Fojon further elaborate on these interference effects in ion–molecule collisions. From a theoretical point of view they suggest the investigation of the role of electron correlation not only in the description of molecular orbitals but also in the molecular continuum in the exit channels. Experimentally they propose a complete mapping of all resulting particles including the orientation of the molecular target. Tribedi deals with collisions between ions and very large molecules. In the case of larger molecules or clusters, the presence of further collision partners, to which energy can be transferred, leads to the appearance of new decay mechanisms such as interatomic Coulombic decay. In his contribution, he points out that it will be a great challenge in the future to conduct collision experiments with bio-molecules in their natural (liquid) environment. Such processes play an important role in radiation therapy, as well as in the use of metallic nanoparticles to enhance the biological effectiveness of ion irradiation via collective excitation effects. With her contribution Lamour opens a window into a hitherto unexplored collision regime, the interaction of ions with ions in the intermediate velocity regime. These experiments and reliable theoretical models are still completely missing, but will become feasible with the new upcoming facilities SPIRAL2 and FAIR in France and Germany, respectively.

In topic section 3, Crespo Lopez-Urrutia bangs the drum for the use of highly charged ions (HCI) in fundamental high precision experiments. In particular, with the first demonstration of sympathetic laser cooling of HCI re-trapped in a cryogenic radio-frequency trap, and the rapid development of narrow-band lasers in the x-ray regime, extreme frequency metrology (XFM) will become possible with HCI as adequate frequency standards and excellent study cases for fundamental interactions. Litvinov sketches the possibilities for precision investigations of highly charged radionuclides. Their decay processes are extremely sensitive to the interplay

of atomic and nuclear structure and therefore promise a large potential for new discoveries, once the next generation of low-energy storage rings and traps becomes available. Shabaev explains, how high precision experiments with HCIs provide stringent tests for non-perturbative QED methods leading to the most precise determination of electron mass, nuclear magnetic moments, nuclear radii or even an independent determination of the fine structure constant. Cederquist and Zettergren describe the challenges and prospects for ion-cluster collision studies. Improved control over properties such as cluster size, charge and internal energy will be the key to a more fundamental understanding. Schleberger and Wilhelm motivate the reasons and explain the challenges for moving from irradiation of 3D bulk to novel 2D materials in HCI—surface interaction studies. Modern multi-coincidence spectroscopies are already in use to disentangle some of the basic interaction processes and the development of truly time-resolved ion scattering techniques will be the next step to study hollow atoms and 2D materials in a highly non-equilibrium state in unprecedented detail. Azuma briefly reviews the exciting phenomenon of resonant coherent excitation (RCE) in ions traveling through periodic crystals and suggests that RCE may become a new tool for high precision spectroscopy and dynamics of HCI once new high energy storage rings become available. Boduch describes the latest efforts to simulate in the laboratory the effect of cosmic rays on complex organic molecules (COMs) embedded in icy mantles on dusty grains in interstellar media

or at the surface of comets. This is of particular interest since such molecules might have reached the early Earth via comets and meteorites contributing to the formation of life.

In topic section 4, Schmidt describes the novel purely electrostatic and cryogenic ion-storage rings which have recently become operational. They allow experiments with rotationally cold ions and therefore offer unprecedented control of all internal and external degrees of freedom. Stöhlker outlines the challenging atomic physics program foreseen at FAIR. Since this future facility will offer beams of cooled HCI in energy regimes where no such experiments have so far been possible, it will substantially enlarge the research capabilities for the exploration of atomic matter within the realm of extreme and ultra-short duration electromagnetic fields.

Although the contributions to this Roadmap, outlined above, come from a few selected researchers, we believe that they are representative of many other related scientific activities. The study of collision processes with heavy projectiles is a broad field and offers great potential for new discoveries in basic and applied research in the future.

## Acknowledgments

KU acknowledges support from the five-star alliance and IMRAM project. ES thanks SFI and the EU CALIPSOplus programme for support.



## RYDBERG ATOMS AND COLD COLLISIONS

### 1. High Rydberg states and ion chemistry

*Frédéric Merkt*

ETH Zurich, Switzerland; Free University of Amsterdam, The Netherlands

*Status.* This contribution focuses on the use of high Rydberg states of neutral molecular systems to characterize the structure, dynamics and reactivity of molecular cations. Rydberg states can be defined as the states of atoms and molecules having spectral positions  $\nu_n$  that can be approximated by Rydberg's formula

$$\nu_n = E_I(\alpha^+) / h - cR_M / (n - d_l)^2. \quad (1)$$

In equation (1),  $n$  is the principal quantum number,  $d_l$  is the quantum defect of the series with electron orbital-angular-momentum quantum number  $l$ ,  $R_M$  is the mass-dependent Rydberg constant,  $E_I(\alpha^+)$  represents the series limit as  $n$  approaches infinity and thus the onset of the ionization continuum associated with the production of a singly charged ion in the quantum state  $\alpha^+$  (see figure 1(a)). Equation (1) implies independent, separable motions of the Rydberg electron and the ion core and becomes increasingly accurate as  $n$  and  $l$  increase. Most properties of Rydberg states rapidly scale with  $n$ . For instance, their polarizability scales as  $n^7$ , their electric dipole moment scales as  $n^2$ , and the minimal electric field needed for their efficient ionization scales as  $n^{-4}$  (see [1]).

Rydberg states form series that converge on the different electronic, and in the case of molecules also vibrational ( $v^+$ ) and rotational ( $N^+$ ), quantum states of the molecular ion core (see figure 1(a)). At high  $n$  values, the Rydberg electron does not influence the ion core but maintains the charge neutrality of the molecular system. The use of Rydberg states to characterize positively charged ions relies on these properties. The measurement of Rydberg series and their extrapolation yield the energy-level structure of cations [2]. The energy-level structure of cations can also be obtained by the selective pulsed field ionization (PFI) of very high Rydberg states, as illustrated in figure 1(c). With their large dipole moments (beyond 1500 Debye at  $n = 25$ ) Rydberg atoms and molecules can easily be accelerated in inhomogeneous electric fields, and numerous devices have been developed that enable the deceleration, the deflection and the reflection of beams of Rydberg atoms and molecules, and the storage of cold Rydberg atoms and molecules in electric traps [3]. These devices have considerable potential for studies of ion–molecule reactions at low temperatures.

#### *Current and future challenges*

*Precision measurements of ionization energies and ionic level structures by Rydberg series extrapolation.* High-resolution spectra of high- $n$  Rydberg states can be used to determine the series limits, and thus the ionization energies of atoms and molecules with high precision. In atomic systems with a closed-shell ion core (Li, Na, K), the extrapolation can be performed

with equation (1). Using ultracold atomic samples to suppress Doppler and transit-time broadening in combination with photoexcitation with frequency-comb-stabilized single-mode continuous-wave lasers, the ionization energy of Cs [5] was determined to be  $E_I/hc = 31\,406.467\,7325(14)$  cm<sup>-1</sup>. To reach this level of accuracy, it is necessary to measure and compensate stray electric and magnetic fields to better than 1 mV cm<sup>-1</sup> and 1 mG, respectively. Pressure shifts and shifts arising from dipole–dipole interactions with neighboring Rydberg atoms must also be quantified. The extrapolation of Rydberg series in atoms with open-shell ion cores and in molecules necessitates the consideration of interactions between series converging on different ionic states. The most reliable extrapolations are not carried out with equation (1) but using multichannel quantum defect theory (MQDT) [6, 7], which can even be used to determine the hyperfine structure of the cations [8].

Molecular hydrogen has been the test system for the application of MQDT to molecules [7]. The MQDT analysis of recent measurements of the Rydberg spectrum of H<sub>2</sub> has allowed its ionization and dissociation energies, and rotational and hyperfine intervals in H<sub>2</sub><sup>+</sup> [8, 9], to be determined with high accuracy. The most accurate measurements of Rydberg series in H<sub>2</sub> reach an accuracy of 65 kHz [10] and are precise enough to be sensitive to the finite size of the proton [11].

Future steps in precision Rydberg spectroscopy for the determination of accurate ionization energies include (i) the development of methods and light sources to record high-resolution Rydberg spectra of a broader range of molecules, (ii) the generation of corresponding cold-molecule samples, and (iii) a rigorous establishment of the uncertainties of the Rydberg-series limits extrapolated by MQDT. In future, MQDT-assisted Rydberg spectroscopy of cations is expected to contribute not only to solve problems of molecular structure and dynamics. When applied to few-electron systems, precision Rydberg spectroscopy may also contribute to test theory at its most fundamental level, improve fundamental constants or discover new effects.

#### *Ion-neutral reactions within the orbit of a Rydberg electron.*

At sufficiently high  $n$  values, the ion-core can undergo chemical reactions with neutral molecules located within the Rydberg-electron orbit. The Rydberg electron does not affect the reaction but provides charge neutrality to the reaction system and shields it from stray electric fields. Heating of the ions by uncontrolled acceleration through stray fields is thus avoided.

This opens up the prospect of studying ion-neutral reactions at very low temperatures. Instead of observing the reaction  $A^+ + B \rightarrow C^+$  (or  $C^+ + D$ ), one observes the reaction  $A^* + B \rightarrow C^*$  (or  $C^* + D$ ), where  $*$  symbolizes a high Rydberg state. In the limit where the Rydberg electron acts as a spectator, both reactions take place at the same rate [12]. This idea has recently been used to study the  $H_2^+ + H_2 \rightarrow H_3^+ + H$  reaction [13] and the radiative association reaction  $H^+ + H \rightarrow H_2^+ + h\nu$  [14] at temperatures where quantum-mechanical effects strongly affect the reaction rates (figure 2).

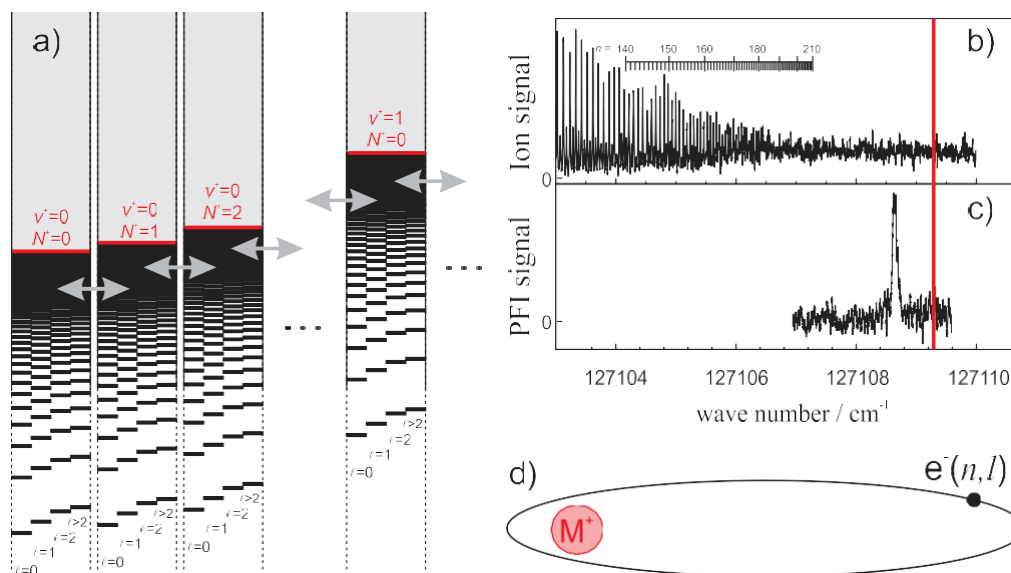


Figure 1. (a) Rydberg series converging on the different rovibrational levels (red) of a molecular ion. (b) Rydberg spectrum and (c) PFI spectrum of Ar near the  $2P_{3/2}$  ionization threshold (red bar) (from [4]). (d) Schematic representation of a molecular Rydberg state consisting of an ion core  $M^+$  surrounded by the orbit of a distant Rydberg electron.

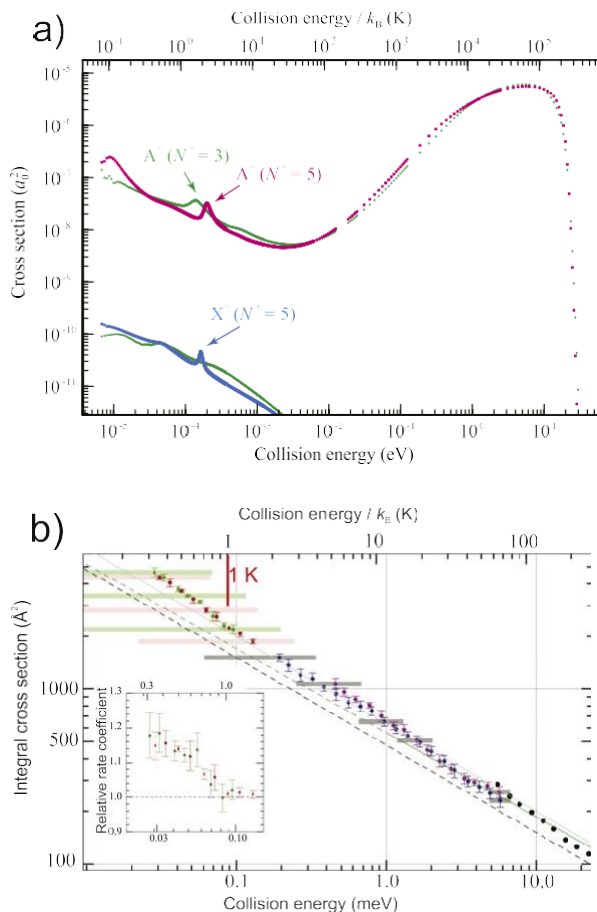


Figure 2. (a) Cross sections of the  $H^+ + H$  (green) and  $D^+ + D$  (red and blue) radiative association reactions for approach on potentials of the ground ( $X^+$ ) and first excited ( $A^+$ ) states (from [13]). (b) Cross section and relative rate coefficient of the  $H_2^+ + H_2 \rightarrow H_3^+ + H$  reaction. Black dots [15]; green dashed line [16]; black dashed line (Langevin behavior). Colored dots: merged-beam results from [14].

In the study of the  $H_2^+ + H_2 \rightarrow H_3^+ + H$  reaction, a chip-based Rydberg–Stark deflector and decelerator [13] was used to merge a beam of cold, velocity- and state-selected Rydberg  $H_2$  molecules with a supersonic beam of cold ground-state  $H_2$  molecules and to vary their relative velocity. In this way, the energy dependence of the reaction cross section could be measured at collision energies as low as  $k_B \times 300$  mK, where deviations from classical Langevin behavior were observed [13] (Inset of figure 2(b)).

The  $H^+ + H \rightarrow H_2^+ + h\nu$  reaction was studied following excitation of  $H_2$  to high ( $n \geq 200$ ) Rydberg states near the dissociative ionization threshold of  $H_2$  in a half-collision approach [14]. By observing the shape resonances of  $H_2^+$  and analyzing their role in the dissociation of the  $H_2^+$  ion core, the radiative association cross section and rate coefficient could be determined in the collision-energy range between 10 mK and  $10^5$  K [14] (figure 2(a)).

*Concluding remark.* Progress in the development of tunable narrow-band light sources, of frequency-calibration methods, of cold-molecule preparation techniques and of new devices to manipulate the translational motion of Rydberg atoms and molecules are currently opening new perspectives for investigations of ions, with applications ranging from metrology to cold ion-neutral chemistry.

### Acknowledgments

Our research is supported by the Swiss National Science Foundation (Project 200020\_172620) and the European Research Council (ERC) (Advanced Grant 743121). PM thanks the Free University of Amsterdam for a van der Waals visiting professorship.



## 2. Resonant energy transfer with Rydberg atoms

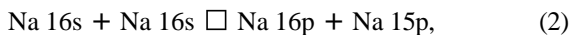
*T F Gallagher*

University of Virginia, United States of America

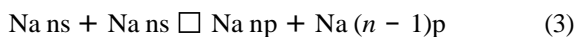
*Status.* The study of dipole–dipole interactions of Rydberg atoms began as an effort to explore systematically resonant energy transfer. A classic example of resonant energy transfer is the HeNe laser, which is based on resonant collisional energy transfer from the metastable  $2s$  states of He to the ground state of Ne, resulting in the selective population of the upper laser levels of the HeNe laser [17]. While the HeNe laser works, it does not tell us much about the sharpness of the resonance, only that the match between the He and Ne energy levels is close enough.

One approach to probing resonance in collisional energy transfer is examining fine structure changing collisions of Br with different molecular collision particles. The different frequencies of the molecular vibrational transitions straddle the Br  $5p_{1/2} \rightarrow 5p_{3/2}$  interval and provide a measure of tunability [18]. Rydberg atoms, with their  $1/n^3$  scaling of energy levels, provide a more systematic approach. Here  $n$  is the principal quantum number of Rydberg atom. A series of experiments with Xe Rydberg atoms and polar molecules, such as  $\text{NH}_3$ , showed sharp collisional resonances in which the changes in the binding energy of the Rydberg electron matched the frequencies of rotational transitions of the molecule [19]. In these collisions the impact parameters are approximately equal to the diameter of the Rydberg atom or smaller, so the interaction responsible is not simply the dipole–dipole interaction; several multipoles are involved.

An ideal way to probe a collisional resonance is to tune continuously the energy of the collision partners through resonance, and the enormous Stark shifts of Rydberg atoms provide a simple way to do so. Perhaps the most well studied example is the resonant energy transfer between two Rydberg atoms, for example the process [20]



which is tuned into resonance in fields of  $E \sim 600 \text{ V cm}^{-1}$ . In most cases static fields have been used, but the AC Stark shifts from a near resonant microwave field provide a way to alter only a few states with the field [21]. The process of equation (2), observed with a thermal atomic beam, yields sharp collisional resonances with widths of  $\sim 1 \text{ GHz}$  and cross sections of  $\sigma \sim 10^9 \text{ \AA}^2$ . The resonance widths imply that the duration, or time, of the collisions is  $\tau = 1 \text{ ns}$ , and the cross sections imply impact parameters one hundred times larger than the size of the atoms. The energy transfer is due to the dipole–dipole interaction, and it is straightforward to show that for the process



the cross section  $\sigma$  and duration  $\tau$  are given, in atomic units, by

$$s = n^4/v \quad (4)$$

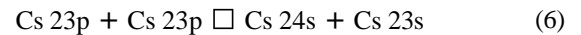
and

$$t = n^2/v^{3/2}, \quad (5)$$

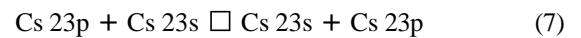
where  $v$  is the collision velocity. Compared to gas kinetic collision times of one picosecond, one nanosecond collision times are extremely long, allowing systematic study of radiative collisions, those in which photons are absorbed or emitted during the collisions [22]. Collisions in which multiple microwave photons are emitted and absorbed have been observed and characterized [23].

The experiments described above were conducted with thermal beams in which the collision velocity is determined by the velocity spread of the beam. Velocity selection has been used to produce beams with internal temperatures of 1 K, leading to collisional resonances as narrow as 1 MHz [24], and shortening the time during which the atoms can collide to less than one microsecond produces transform limited collisions, with known beginning and ending times [24].

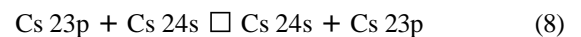
The first cold atom experiments, conducted in magneto optical traps (MOTs), were also resonant energy transfer experiments, often termed Forster resonances [25, 26]. The properties of a MOT, temperature  $T = 300 \mu\text{K}$  and density  $\rho = 10^9 \text{ cm}^{-3}$ , combined with the  $3 \mu\text{s}$  lifetime of an  $n = 20$  Rydberg atom bring the experiments into a new regime. In a MOT the typical atomic spacings and velocities are  $10^{-3} \text{ cm}$  and  $10 \text{ cm s}^{-1}$ , so in the one microsecond duration of a typical experiment the atoms move  $\sim 1\%$  of their typical spacing. In short, they are frozen in place. The atoms do not collide; instead, the interactions are between static atoms, as in an amorphous solid. In the initial experiments energy transfer resonances many MHz wide were observed. For example, the process [26]



has a width of 80 MHz. The dominant interaction is still the dipole–dipole interaction, and the observed widths of the energy transfer resonances, such as equation (6), are primarily due to pairs of atoms which are close together. However, unlike collisions, other atoms play a role. For example, the diffusive processes



and



also contribute to the widths. In addition to changing energy transfer from a binary to a many body problem, the use of cold atoms allows the Forster resonances to be examined by coherent laser spectroscopy, specifically, Ramsey interferometry [27].

The enormous range of the dipole–dipole interaction between Rydberg atoms has led to proposals for their use in a broad spectrum of applications, from quantum gates and simulators to the construction of ultralong range molecules [29, 30]. One of the gate notions, the dipole blockade, has proven to be widely applicable [28]. In the blockade the strong dipole–dipole or van der Waals (off resonant dipole–dipole) interaction prevents the excitation of more than one

Rydberg atom in a blockade radius, forming a superatom in each blockade zone in which one of the many atoms is in the Rydberg state, the rest remaining in the ground state. Superatoms behave like two level systems, and multiple superatoms in a sample can be observed to self organize into regular patterns [30].

While the first cold Rydberg atom experiments resembled an amorphous solid, it is possible to put Rydberg atoms into well defined arrays. The first such arrays were linear chains of three atoms, in which the excitation was observed to travel back and forth along the chain [31]. Much longer linear chains have been constructed and used to simulate many body phenomena under controllable conditions [32, 33].

*Concluding remarks.* Finally, methods of placing atoms in well defined positions in two dimensional arrays have been developed, and these arrays have been used to compare thermalization in straight (linear) and zig zag chains [34]. In the latter each atom has four, not two, nearest neighbors. The combination of the rapid advance in the ability to manipulate atoms combined with the enormous dipole–dipole interactions of Rydberg atoms suggest that there will be a continuing stream of fascinating discoveries.

## Acknowledgment

This work has been supported by the Air Force Office of Scientific Research under grant FA9550-14-1-0288.

### 3. Studies involving high- $n$ Rydberg atoms

F Barry Dunning

Rice University, United States of America

**Status.** High- $n$  Rydberg atoms possess physical characteristics quite unlike those associated with atoms in ground or low-lying excited states. They are physically very large allowing many of their properties to be discussed using the classical Bohr model of the atom. At high  $n$  the excited electron orbits far from the nucleus and its motion can be strongly perturbed by application of even modest external electric fields. In addition, as  $n$  increases the classical electron orbital period,  $T_p$ , ( $\sim 4$  ns at  $n \sim 300$ ) increases rapidly allowing high- $n$  states to be manipulated (and probed) using conventional fast pulse electronics and carefully-tailored series of electric field pulses whose characteristic times (duration and/or rise/fall times) are less than  $T_p$  [35]. Such pulse series have been used to engineer quasi-one- and two-dimensional Rydberg states and, with periodic driving, to create non-dispersive wave packets whose behavior mimics that of classical particles [36, 37]. This work has enabled ongoing studies of strongly-interacting Rydberg systems and of the production of so-called planetary atoms.

Scattering of the Rydberg electron from neighboring ground-state atoms can lead to formation of ultralong-range Rydberg molecules [38]. Such scattering can be described using a Fermi pseudopotential and results in a molecular potential that can (see inset in figure 3) support multiple vibrational levels with binding energies (typically) of a few to a few tenths of a megahertz. At sufficiently high atom densities multiple ground-state atoms can be bound to a single Rydberg atom allowing formation of not only dimers but also trimers, tetramers, (see figure 3). In a dense Bose-Einstein condensate (BEC) the Rydberg orbit can, for  $n \geq 50$ , enclose tens to hundreds of ground-state atoms [39]. Rydberg excitation introduces an ‘impurity’ into the BEC and elicits a collective response resulting in the formation of polaron-like quasiparticles comprising the impurity dressed by excitations of the background BEC [40]. Rydberg molecule production provides new opportunities for the study of particle correlations and the effects of quantum statistics.

#### Future directions and challenges

**Dynamics of strongly-coupled Rydberg systems.** Long-range interactions in many-body systems give rise to a rich variety of phenomena of fundamental importance to many areas of physics. Rydberg atoms offer advantages for the study of strongly-coupled systems because their extreme dipole moments result in strong long-range interactions whose strength can be simply controlled by manipulating the atomic states. Recent experiments show that single very-high- $n$ ,  $n \sim 300$ , Rydberg atoms can be prepared in well-defined locally-blockaded regions [41] which provides a convenient starting point for future detailed study of strongly-interacting Rydberg systems. If two atoms are prepared in reasonably-well-separated blockaded regions, a tailored series

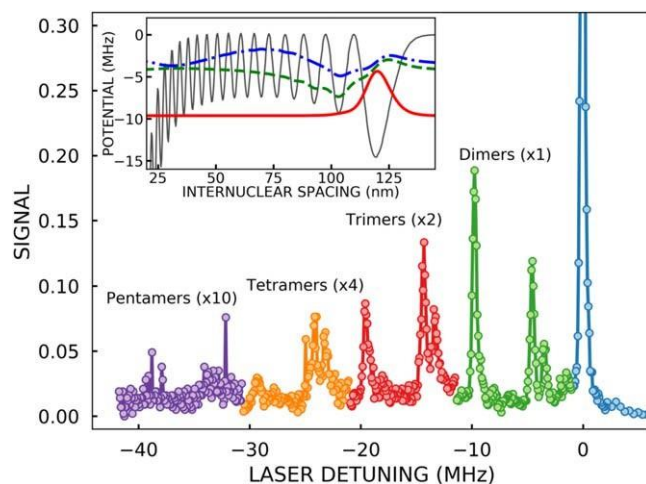


Figure 3. Rydberg excitation spectrum in the vicinity of the  $5s38s$   $^3S_1$  strontium Rydberg state. Inset—calculated molecular potential for  $5s38s$   $^3S_1$ – $5s^2$   $^1S_0$  atom pair. Wavefunctions  $RC(R)$  for the  $v = 0, 1,$  and  $2$  molecular vibrational states are included.

of short electric field pulses may be used to increase their mutual interactions by exciting them to states of much higher  $n$ , the degree of coupling being tuned by varying the final target state (and initial interatomic spacing). Given that the two atoms are excited simultaneously by the same electric field pulses, the initial conditions are particularly well-defined. Questions of interest relate to the dynamics of energy interchange and its dependence on the degree of coupling, which might be further controlled by varying the relative orientations of the states involved. For example, pairs of quasi-one-dimensional states may be formed that are oriented parallel or perpendicular to their line of centers. Excitation to Rydberg orbits whose size is comparable to the interatomic spacing leads to formation of transient Rydberg ‘molecules’ whose stability against autoionization through electron–electron scattering can be examined. Since the excited electron motions can be locked to an external periodic drive field [37, 38], long-lived configurations might exist where, due to their correlated motions, the electrons remain far apart. Initial experiments have been undertaken in an atomic beam but relative motions associated with the distribution of atomic velocities in the beam limit the time over which measurements of Rydberg–Rydberg interactions can be undertaken. Use of cold atomic gases can overcome this limitation but the optical access required for cold atom trapping presents a challenge in reducing the stray fields present in the trapping volume to the levels required,  $\sim 50 \mu\text{V cm}^{-1}$ , for study of very-high- $n$  states. To date, Rydberg studies in cold atom traps have been limited to atoms with values of  $n \leq 200$  [39]. Nonetheless, if stray fields can be controlled successfully, use of a ‘pancake-shaped’ trap and multiple blockaded regions would make possible detailed studies of interactions involving two, three, or more Rydberg atoms and their dependence on the geometrical arrangement of the atoms.

**Two-electron excited states.** Interest in two-electron excited states stems from early attempts to quantize many-electron systems using the Bohr–Sommerfeld quantization rules which met with little success due to the dynamical instability of the proposed structures. Early studies of two-electron-excited states focused on Group II elements and were limited by the dipole selection rules to states of low  $L$  which undergo rapid autoionization. However, it is now possible to engineer very-high- $n$ ,  $n \sim \ell$ , near-circular states for which the overlap between the excited Rydberg electron and inner core electrons is negligible, even if one of the inner core electrons is itself in a (lower-lying) excited state. The production of two-electron excited states in which both electrons remain far from the core ion and from each other in near classical orbits reduces the autoionization rate and admits the possibility of creating long-lived so-called ‘planetary atoms’ [42]. One possible strategy for the production of such atoms involves creation of a localized very-high- $n$ ,  $n \sim 600$ , wavepacket traveling in a near-circular Bohr-like orbit followed by excitation of a second ‘inner’ electron to a state of lower  $n$ ,  $n \sim 200$ . The ‘outer’ electron as it rotates polarizes the orbit of the ‘inner’ electron creating a dipole that rotates in step with the ‘outer’ electron and whose field preserves the localization of the ‘outer’ electron. Classical trajectory calculations suggest that such correlated motion can result in long-term stability against autoionization. Initial experiments show that autoionization rates are dramatically reduced when the ‘outer’ electron is in a high- $\ell$  state to the point that the lifetime of the two-electron-excited state is governed by radiative decay of the ‘inner’ electron [43]. However, in these experiments, undertaken in strontium, the ‘inner’ electron was only excited to the 5p state and multiple additional lasers will be required to excite it to high- $n$  states. Simulations suggest the existence of a second long-lived two-electron-excited state, termed the frozen planet configuration, which embodies very different electron dynamics and which should also be amenable to study using carefully-engineered high- $n$  Rydberg atoms [42].

**Ultralong-range Rydberg molecules.** Correlations in atomic gases become difficult to observe when their characteristic length scales fall below the wavelength of light. However, ultralong-range Rydberg molecules promise a means to investigate such correlations in this previously inaccessible regime. The wavefunction for the molecular ground vibrational state is strongly localized near the outermost well in the molecular potential (see figure 3). The probability of creating a ground-state dimer molecule therefore depends strongly on the likelihood of finding a pair of atoms with the appropriate separation. Thus measurements of dimer formation as a function of  $n$ , i.e. the position of the outermost potential well, can provide information on finding

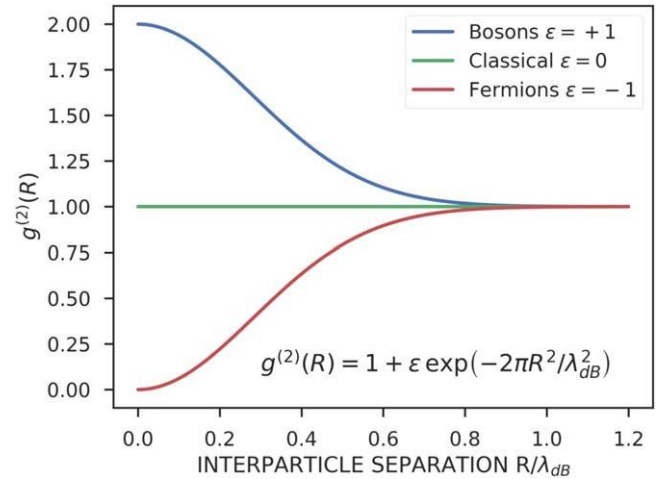


Figure 4. Pair correlation functions  $g^{(2)}(R)$  versus interparticle separation normalized to the deBroglie wavelength  $\lambda_{dB}$ .

atom pairs with different separations and hence on the pair correlation function,  $g^{(2)}(R)$ . Values of  $g^{(2)}(R)$  for thermal gases of non-interacting identical bosons, fermions, and non-identical (or classical) particles are presented in figure 4 and diverge markedly for interparticle separations,  $R$ , less than the thermal de Broglie wavelength,  $\lambda_{dB}$ . For  $T \sim 900$  nK,  $\lambda_{dB} \sim 200$  nm which corresponds to the radius of an  $n \sim 45$  s state suggesting that measurements of dimer formation over the interval  $30 \leq n \leq 45$  can be used to probe the effects of quantum statistics on  $g^{(2)}(R)$  for  $R < \lambda_{dB}$ .  $^{87}\text{Sr}$  which has a nuclear spin  $I = 9/2$  is attractive for such studies and can be conveniently optically pumped to the  $m_F = 9/2$  state to obtain a gas of identical fermions. Since the dimer formation rate depends not only on the number of ground-state atoms present but also their spatial distribution, i.e. density, a major challenge will be to account for such factors in analysis of the data. Dimer formation might also be used to examine two-atom correlations that arise in a quantum gas from resonant atom–atom scattering.

**Concluding remarks.** Although Rydberg atoms have been studied for many years, new applications continue to emerge that address important physical questions related to few- and many-body interactions.

## Acknowledgments

Research by the author and his colleagues discussed here was supported by the AFOSR, the NSF, and the Robert A Welch Foundation (Grant # C-0734).



## 4. Chemistry close to 0 K

Paul Scheier, Olof Echt

Universität Innsbruck, Austria

**Status.** Helium nanodroplets (HNDs) are readily formed by expanding helium through a nozzle into vacuum. The average droplet size can be varied by varying helium pressure and nozzle temperature. In vacuum HNDs rapidly cool by evaporation to about 0.37 K. They are superfluid and can be doped efficiently by passing the droplet beam through a pick-up cell containing a low-density vapor of atoms or molecules. The technique has led to an entirely new approach to synthesize and characterize complex systems [44, 45]. Multiple collisions with dopant species lead to the formation of clusters; their size can be controlled by varying the droplet size or the vapor pressure in the pick-up cell. Uniquely shaped species such as ultrathin metallic nanowires or nanofoam form in very large HNDs [45, 46]. Two successive pick-up cells may be used to form binary aggregates with distinct core-shell structure [47], or to study reactions.

Equally impressive are the novel ways by which doped droplets can be investigated. HNDs form an ideal matrix for spectroscopy because of the weak interaction with the dopant, optical transparency, and low temperature. Problems inherent to bulk (liquid) helium, namely agglomeration and accumulation of dopants at walls, are avoided because most dopants will preferentially reside near the center of HNDs; low dopant concentration (=1 per droplet) will avoid agglomeration. Furthermore, the weak binding of helium (bulk cohesive energy 0.62 meV) opens a path for highly sensitive action spectroscopy because absorption of a photon will cause ejection of one or more helium atoms [48]. Reaction dynamics have been followed by pump-probe spectroscopy, ion imaging and other techniques [49]. Other new venues have been explored. For example, the superfluid environment makes it possible to orient polar dopants in an external electric field, providing a molecular goniometer for electron diffraction of single molecules [50].

**Current and future challenges.** Research involving HNDs offers many tracks. Some use HNDs as vehicles to synthesize, manipulate or characterize the species of interest; others explore quantum phenomena in superfluid systems of finite dimensions or ultrafast dynamics in helium [51]. Still others seek to generate ever larger HNDs, or more intense beams of HNDs [52]. All these tracks are meritorious and actively being pursued. In this short contribution we outline the prospects of yet another, new track, namely forming intense beams of large, size-selected HNDs. Novel structures are formed upon doping very large HNDs, including nanowires, nanofoam, and granular, multi-center clusters [45, 46]. However, as discussed further below, well-defined nanostructures cannot be formed by doping unless the HNDs are large and monodisperse.

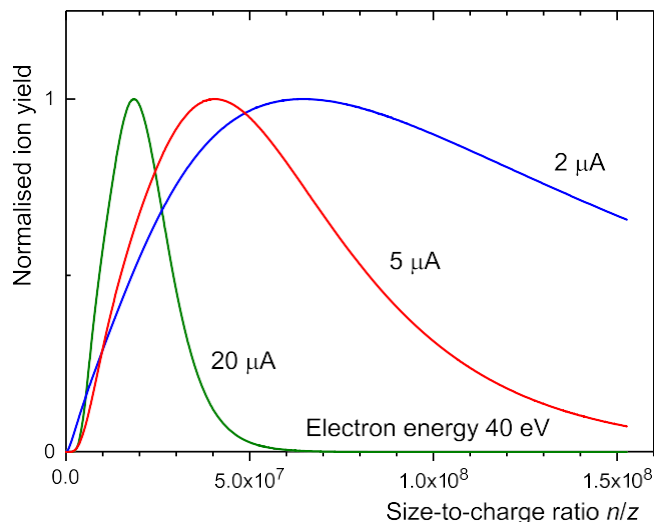


Figure 5. Mass spectrum of HNDs measured at different electron emission currents. The size-to-charge ratio  $n/z$  decreases with increasing current as  $z$  increases.

In the early years of HND research, few experimental groups had the technical means of generating HNDs containing more than a few hundred or thousand atoms. Improved designs, pumps with larger capacity, and the use of pulsed supersonic nozzles by some groups have now pushed the limit beyond  $n \approx 10^{11}$ , corresponding to droplet diameters of  $\approx 2 \mu\text{m}$  [44, 52]. At this size, new forms of matter such as core-shell clusters, nanowires or nanofoam may form inside helium doped droplets [45–47]. Moreover, these objects can be deposited on surfaces and imaged by STM or TEM; the HND provides for a disposable cushion that prevents break-up of the object upon landing.

We have recently formed and detected very large, multiply charged HNDs. Figure 5 displays the yield of HNDs cations obtained by electron ionization at 40 eV and ion deflection in an electrostatic sector field. The approach uses the fact that the velocity distribution of neutral droplets is narrow and independent of the droplet size. The deflection voltage has been converted to a mass-to-charge ratio  $n/z$ ; the ion yield has been corrected for an  $n^{2/3}$  dependence of the ionization cross section. The distributions are markedly dependent on the emission current because large droplets may collide with multiple electrons, leading to charge states  $z > 1$ . The charge state  $z$  of these ions can be explored by post-ionization or electron attachment. Values up to  $z = 19$  have been identified; the size of the charged droplets extends to  $n = 10^{12}$ .

Large, monodisperse HNDs will also enable the investigation of so-called Coulomb crystals which may form at low temperatures when several free ions, or quasi-free ions in superfluid helium, are spatially confined. In ion traps these crystals enable measurements of state-selective reaction rates in a diverse range of systems [53]. At least  $n_c = 2 \times 10^5$  atoms are needed to support two charges in a HND. The appearance of ordered charge arrangements might be detected by electron scattering. Alternatively, one may dope the HND by collisions with several charged atomic or molecular ions,

or multiply ionize droplets that have been doped with neutral multicenter clusters [45]. The charges would thus be localized at the impurities which, for sufficiently large separation, would mainly interact via Coulombic forces. Their spatial arrangement could be measured indirectly by soft-landing on a surface followed by TEM or STM imaging.

*Advances in science and technology to meet challenges.*

Controlling the growth of nanostructures requires large, monodisperse HNDs. Doping is a statistical process; for fixed  $n$  the size distribution of aggregates grown in the HND would follow Poisson statistics whose relative width decreases with average size  $\langle n_d \rangle$  as  $1/\sqrt{\langle n_d \rangle}$ . The dopant distribution would have a width of only 3% if  $\langle n_d \rangle = 10^3$ . In practice, two factors ruin narrow distributions: First, HNDs shrink upon doping. For example, a release of 2 eV, a typical cohesive energy per atom for metallic clusters, would cause the evaporation of some 3000 He. Second, the size distributions of HNDs are broad. Depending on expansion conditions they are either log-normal or bimodal [44]. The first problem is avoided if large HNDs are being doped (loss of  $3 \times 10^6$  atoms from a droplet containing  $10^8$  or more atoms would be acceptable), but the second problem necessitates the use of monodisperse HND beams. We foresee three possible ways for doing this.

1. HNDs can be efficiently ionized by electron impact. We have realized situations where droplets carry up to 19 charges due to successive collisions with electrons, and the size-to-charge ratio exceeds  $n/z = 10^8$ . Their size distributions are broad. Narrow slices of the distribution have been selected with an electric sector field but the presence of different charge states implies multimodal size distributions.
2. The production of size selected clusters has always been the holy grail of cluster science. Size selection of charged clusters by mass spectrometry wastes a large fraction of all clusters in the beam. A much less wasteful approach would be to select the singly

charged, nearly monodisperse HNDs that are ejected from highly charged droplets as a result of electrostriction combined with Coulomb repulsion. Although not in the  $n \approx 10^8$  regime that is needed to grow large, strongly bound structures, they could be used to synthesize smaller, less strongly bound systems.

3. Toennies *et al* have formed HNDs containing  $n = 10^{10}$ – $10^{12}$  atoms by expanding pressurized liquid helium through a nozzle below 4.2 K [44]. Rayleigh oscillation-induced breakup of the liquid jet produces droplets with an exceedingly narrow angular and velocity distribution but the width of the size distribution, said to be mono-disperse, was not characterized. Also, the generation of droplets much larger than needed may have undesirable side effects, namely large gas loads even if the flux of droplets is modest.

*Concluding remarks.* Research involving or merely using HNDs is a burgeoning field. New opportunities such as messenger spectroscopy of He-tagged complex ions or electron diffraction of single aligned molecules are just some of many new research directions. In this contribution we have outlined another one, namely the prospects and use of large, monodisperse droplets. With sizes between 100 nm to 1  $\mu$ m they would cover the mesoscopic regime; they could serve as vessels to synthesize and characterize, *in situ* or after deposition on surfaces, novel structures such as nanowires, Coulomb crystals, or ligand-free catalysts. Preliminary experiments by several groups have already shown the viability of this approach.

## Acknowledgments

This work was supported by the FWF (project number P31149) and the European Regional Development Fund (EFRE, project FAENOMENAL).



## COLLISIONS INVOLVING HEAVY PROJECTILES

## 5. Non-relativistic ion–atom collision theory

Tom Kirchner

York University, Canada

*Status.* One may say that the ultimate goal of non-relativistic ion–atom collision theory is the development of approaches that provide a complete and accurate description of a given collision system. Complete means that all reaction channels are taken into account simultaneously, and accurate that the numerical results explain existing experimental data and make trustworthy predictions in regions where there are none. This is difficult to achieve since in many situations of interest a number of channels, direct and rearrangement, are open and contribute at the same time. Methods for the description of *individual* channels, such as excitation, ionization, or electron transfer are usually perturbative in nature [54]. These methods have enjoyed many successes, in particular when based on distorted-wave approaches, but they are somewhat limited in scope. A full account of all, potentially competing, processes calls for a fully non-perturbative treatment implemented via advanced numerical techniques.

Despite significant progress over a long period of time [55] it is perhaps fair to say that the feat of a truly complete calculation has only recently been achieved for the prototypical one-electron proton–hydrogen collision system. A fully quantum-mechanical converged close-coupling (QM-CCC) approach has been developed and applied to this fundamental three-body problem of two Coulomb-interacting protons and one electron [56]. As an example figure 6 shows the total ionization cross section obtained from the QM-CCC method in comparison with a selection of previous non-perturbative calculations and the available experimental data. Interestingly, the overall agreement is not satisfactory in the 30–100 keV impact energy region in which the cross section maximum occurs. One may conclude that further investigation, both theoretical and experimental, is warranted before this case can be considered understood and closed [56]. This is all the more true for the study of differential cross sections, which in the past has been the domain of perturbative and classical trajectory methods, but for which fully non-perturbative calculations have started to emerge as well (see [57] and references therein).

A large body of theoretical ion–atom work, including all but the QM-CCC calculations of figure 6, makes use of the semiclassical approximation (SCA) according to which the nuclei are assumed to move classically (most often on straight-line trajectories) and only the electronic motion is treated quantum mechanically [55]. Over a wide range of impact energies the SCA is essentially exact, at least as far as cross sections that are integrated over the projectile deflection are concerned. For the case of projectile-angular differential cross sections there is a well-established procedure, called eikonal approximation [55], which re-introduces quantum mechanics into the heavy-particle scattering and often gives very accurate

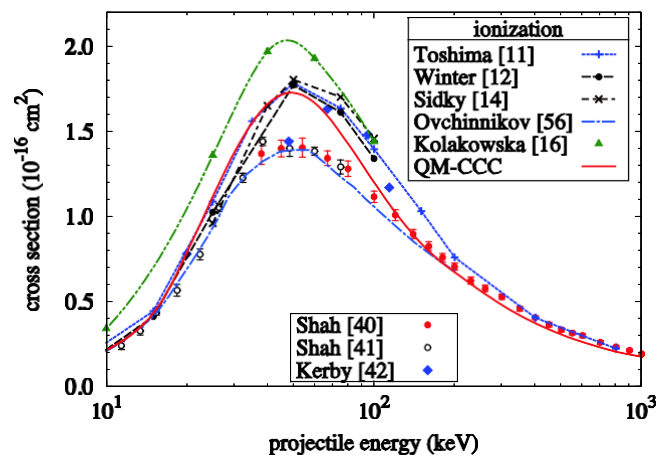


Figure 6. Total ionization cross section for proton–hydrogen collisions as a function of projectile energy. References to indicated previous works are given in [56]. Reproduced with permission from [56]. © IOP Publishing Ltd. All rights reserved.

results. In the framework of the SCA the scattering problem has similarities with the problem of laser-field induced excitation and ionization in that a time-dependent Schrödinger equation has to be solved to find the electronic wave function. Indeed some cross-fertilization between both areas in terms of method and code development has happened (see, e.g. [58]).

Most ion–atom collision problems involve few- or many-electron atoms. It has long been known that the independent-particle model (IPM) is often not sufficient to understand experimental observations in these systems. Explicit methods to deal with beyond-IPM situations are mostly restricted to two-electron systems, i.e. collisions involving helium atoms whose double ionization famously cannot be properly described without taking electron correlation effects into account (see, e.g. [58]). Recent work has shown that also three-electron problems can be studied with non-perturbative methods that are based on correlated many-electron wave functions [59]. Figure 7 shows an example: the angular-differential cross section for electron transfer from the target ground state to the projectile ground state in  $\text{He}^+–\text{He}$  collisions at 60 keV  $\text{amu}^{-1}$  impact energy [59]. While a correlated, fully non-perturbative three-electron calculation (that uses the eikonal approximation to extract the differential cross section) is in excellent agreement with the experimental data, results from previous perturbative efforts are not.

*Current and future challenges.* The above discussion suggests that there is still work to be done to reach a quantitative understanding of one-electron problems. But the bigger challenge lies in the treatment of many-electron systems given that the majority of them will remain beyond the reach of explicit methods for some time to come. Perhaps the most promising alternative approach is time-dependent density functional theory (TDDFT). The time-dependent (so-called Kohn–Sham) equations in TDDFT calculations look like IPM

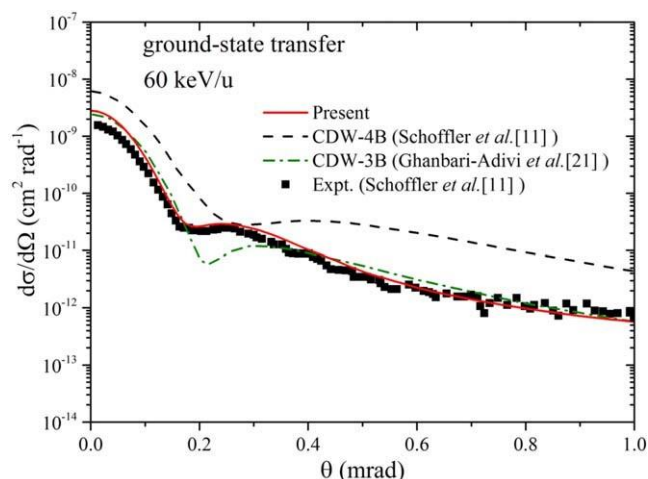


Figure 7. Angular differential cross section for ground-state transfer in  $\text{He}^+ - \text{He}$  collisions at  $60 \text{ keV amu}^{-1}$  impact energy as a function of scattering angle. References to indicated previous works are given in [59]. Reprinted figure with permission from [59], Copyright 2018 by the American Physical Society.

equations, but they involve a potential that, in its exact form, includes electron correlation effects. Similarly, the exact outcome analysis of the Kohn–Sham calculations involves a correlation integral. Both issues, correlation in the potential and correlation in the method to extract observables from the Kohn–Sham solutions, are areas of active research. Despite recent advances there is room for improvement of the current models (see, e.g. [60] and references therein).

TDDFT methods are also promising tools to deal with ion–molecule collision systems which are of relevance in the context of radiation biology [61] (see section 9 for an experimental perspective). Beyond conducting proof-of-principle studies it will be important for work in this area and in other, e.g. plasma-related applications to quantify the uncertainties of calculated cross sections. This is more challenging than it may sound given that it is straightforward (albeit perhaps tedious) to determine the numerical accuracy of a calculation. However, quantifying the uncertainties associated with the use of a particular many-body model is only poorly understood [62].

Experimental advances, most notably the development of recoil-ion momentum spectroscopy and the reaction microscope, have led to a wealth of highly-differential ion–atom and ion–molecule measurements (see section 7). They often show rich structure and probe theory and our fundamental understanding of the few-body problem on deeper levels than integrated cross section data. They may also point to aspects of the collision problem that are less well understood than assumed. A recent

example is the observation of effects that appear to be related to the coherence properties of the projectile beam [63]. This observation challenges a basic tenet of atomic collision theory in that it suggests that one can choose the set-up of an experiment such that the projectile beam is not fully coherent and the standard way of calculating a cross section does not apply.

*Advances in science and technology to meet challenges.* A large fraction of ion–atom collision theory research has been motivated by experimental studies, and this is not expected to change. Accordingly, active experimental research programs which generate accurate differential and integrated (see figure 6) data will be indispensable for progress on the theoretical side. It will be particularly useful to maintain or even expand on the breadth of the collision systems studied in the laboratory; the use of magneto-optical traps to allow for reaction-microscope studies of alkalis and the use of antiproton beams to initiate electron dynamics in a variety of atoms and molecules are important examples. Together with the ongoing advances in numerical method and code development plus the ever-increasing available computer power they will allow theorists to move forward in the areas outlined above. A few good ideas, e.g. on how to incorporate correlation effects in TDDFT models or on how to account for incomplete projectile coherence in such a way that it can be distinguished from other effects, will be required as well.

*Concluding remarks.* Ion–atom collision theory may be a mature field, but it remains highly relevant given the deep science questions it addresses and the data it produces. One can perhaps say that thanks to advances in computational methods and resources we have just started to answer some long-standing questions in a quantitative fashion, e.g. on the role of electron correlation effects in the few-particle dynamics, and can now produce (semi-) accurate data for more complex collision systems. This will continue. Moreover, similar questions are being addressed in neighboring research fields and knowledge and insights obtained from collisional studies may help answer them as well—as will progress in those areas benefit the advancement of atomic collision theory.

## Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council of Canada under Grant No. RGPIN-2014-03611. Thanks are due to the authors of [59] for providing figure 7.

## 6. Correlation and polarization phenomena in relativistic ion–atom collisions

Stephan Fritzsche<sup>1</sup> and Andrey Surzhykov<sup>2</sup>

<sup>1</sup>Helmholtz Institute Jena and Friedrich-Schiller-Universität Jena, Germany

<sup>2</sup>Technische Universität Braunschweig and Physikalisch-Technische Bundesanstalt, Germany

**Status.** Collisions of highly-charged heavy ions with atoms and electrons are central for much of our present day's knowledge about matter in strong (Coulomb) fields. Recent advances in heavy-ion accelerator and detection techniques have paved the way towards new (collision) experiments which help explore the angular distribution and polarization of energetic electrons and (x-ray) photons, emitted in such ion–atom and ion–electron collisions. Unlike measurements of total cross sections, these angle-resolved and polarization experiments provide valuable information about the dynamics of high-Z, few-electron systems in strong fields.

In collisions of fast bare ions with atoms, for example, initially quasi-free target electrons often recombine radiatively with ions under the emission of a photon; the time-reversed process to Einstein's well-known photoionization [64, 65]. If the electron is captured into the  $2p_{3/2}$  level of a hydrogen-like ion, it will subsequently decay by a (second) Lyman- $\alpha_1$  ( $2p_{3/2} \rightarrow 1s_{1/2}$ ) photon. This Lyman- $\alpha_1$  radiation of heavy ions appears very sensitive to both, the population of magnetic sublevels  $|2p_{3/2} \mu\rangle$ , produced in the capture process, and to the E1–M2 *multipole mixing*, i.e. the coupling of the bound electron density to the different (multipole) components of the radiation field. Indeed, combined measurements of the angular distribution and linear polarization of the characteristic Lyman- $\alpha_1$  photons help *disentangle* here the formation of the excited ionic state from the subsequent decay and to determine the M2/E1 amplitude ratio without further assumptions about the population mechanism for the  $2p_{3/2}$  state [66]. The M2/E1 amplitude ratio can be tested against quantum electrodynamics (QED) which is the fundamental theory for describing the electron dynamics of atom and ions in the presence of strong (Coulomb) fields.

Bremsstrahlung, the emission of photons due to the inelastic scattering of (quasi-) free electrons at ions and atoms, is a similarly fundamental process in relativistic collisions but with the 'capture' of the electron into the Dirac continuum. Detailed calculations of the bremsstrahlung spectra, angular distribution and polarization Stokes parameters of emitted photons, are however still a challenge to atomic theory, as they require a reliable representation of the (positive-energy) continuum for both, the initial and final electronic states as well as an accurate evaluation of 'free–free' transition amplitudes, especially at high electron and photon energies [67]. Measurements of the linear polarization of bremsstrahlung radiation with electrons of variable polarization for neutral gold atoms confirmed the need for accurate computations.

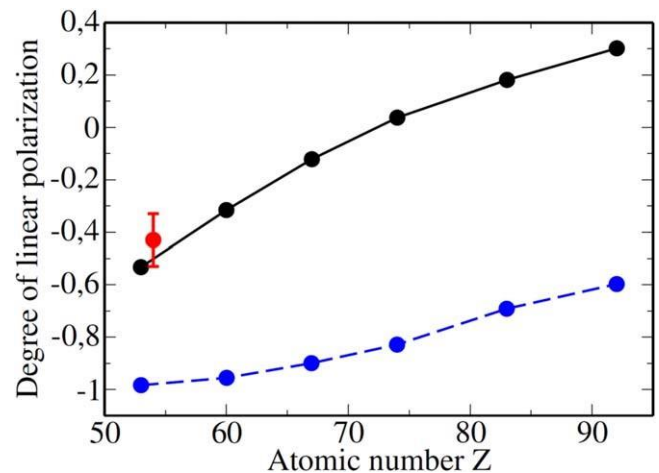


Figure 8. Degree of polarization of the  $1s\ 2s^2\ 2p_{1/2}\ J = 1 \rightarrow 1s^2\ 2s^2\ J = 0$  emission perpendicular to the incident ion beam.

Calculations with only the Coulomb repulsion (blue dashed lines) are compared with a full account of the electron–electron interaction (Coulomb+Breit; black solid line). Experimental data for the DR into beryllium-like Xe is from [68]. Reprinted figure with permission from [68], Copyright 2009 by the American Physical Society.

Distinct peaks in the observed x-ray spectra from high-Z ion–electron collisions arise especially due to the dielectronic recombination (DR) of the ions as competitive but resonant process to the radiative electron capture (EC). This resonant capture of electrons leads to the excitation of the bound electron density and often to a subsequent photon emission. Indeed, the DR in fast ion–electron collisions provides an important tool for studying the relativistic, i.e. magnetic and retardation contributions to the electron–electron interaction, known also as Breit interaction in atomic physics. To reveal details about the relativistic interactions between the electrons in the presence of strong Coulomb fields, measurements were proposed on the angular distribution and linear polarization of the  $1s\ 2s^2\ 2p_{1/2}\ J = 1 \rightarrow 1s^2\ 2s^2\ J = 0$  (electric-dipole) photon emission, following the resonant EC into initially lithium-like ions. Multi-configuration Dirac–Fock (MCDHF) calculations for this particular DR process demonstrated that the Breit interaction can dominate over the pairwise Coulomb repulsion among the electrons and may even cause a *qualitative* change of the characteristic photon emission [68]. For the DR of high-Z ions, for instance, the Breit term leads to a significant reduction of the (absolute value of) linear polarization of  $1s\ 2s^2\ 2p_{1/2}\ J = 1 \rightarrow 1s^2\ 2s^2$  line; a behavior that has meanwhile been confirmed experimentally [69], see figure 8.

**Current and future challenges.** Any detailed interpretation of fast ion–atom collision experiments requires of course a deep understanding of the underlying mechanisms and their quantum (-field) theoretical formulation. Therefore, various theoretical methods have been developed during the past two decades in order to explain such polarization and correlation phenomena in heavy-ion collisions. In particular, the density matrix theory, combined with the calculus of spherical tensors, has been found a very versatile tool to incorporate all major relativistic and

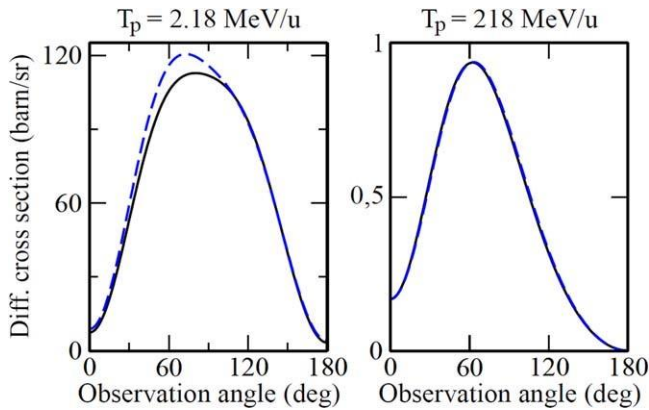


Figure 9. Angle-differential cross sections for the radiative electron capture into the  $1s^2 2s^2 ^1S_0$  state of (initially) lithium-like uranium ions  $U^{89+}$  with projectile energies of 2.18 and 218 MeV/u. Results are presented within the independent particle model (-dashed line) and MCDF approach (solid line). See [69] for further details. Reprinted figure with permission from [69] Copyright 2015 by the American Physical Society.

many-body contributions into the computational framework. The density matrix approach is naturally built upon many-electron amplitudes of the electron–electron interaction and the coupling of the electrons to the radiation field and, thus, allows quite easily to incorporate many-body and non-dipole contributions into the theoretical predictions of all *observables* of the emitted x-rays. When combined with MCDF wave functions, this approach has indeed been found versatile to explain the electronic correlations in high- $Z$  ion–electron collisions. For example, figure 9 displays the calculated angle-differential cross sections for the radiative capture of electrons into the  $1s^2 2s^2 ^1S_0$  state of (initially) lithium-like uranium  $U^{89+}$  ions with projectile energies  $T_p = 2.18$  and  $T_p = 218$  MeV/u. While the correlated motion of the electrons appears to be negligible for 218 MeV/u, it alters the angular distribution at lower energies [69].

Closely related to the ion–electron collisions from above is the (so-called) radiative double electron capture (RDEC) in which two electrons are simultaneously captured under the emission of a single energetic photon. Such an EC can occur only due to the interelectronic interactions in the continuum. Few measurements have been carried out [70] but with rather large uncertainties and until now in disagreement with theory. Further detailed angle-resolved RDEC experiments will here provide a stringent test for theory due to demand to deal with two *correlated* electrons in the continuum.

#### Advances in science and technology to meet challenges.

Recent years have seen significant progress in detecting (hard) x-rays by microcalorimeters and position as well as energy sensitive solid-state detectors, designed for advanced photon spectroscopy [71]. These detectors nowadays achieve a sub-millimeter spatial resolution as well as excellent time and energy resolution in the hard x-ray energy regime above 15 keV, and they helped advance both, x-ray polarimetry and medical imaging. Beside of EC and transfer processes, these detector advances will facilitate further QED studies and even investigations on parity-violating interactions in forthcoming years. A number of ion–atom (ion–electron) collision experiments have been proposed recently to scrutinize these interactions. For example, the parity mixing between  $1s2p_{1/2} ^3P_0$  and  $1s^2 ^1S_0$  states of helium-like ions leads to a rotation of the linear polarization of x-rays emitted in the L-shell EC [72], an experiment proposal that will likely become feasible in the near future. At FAIR, the currently built Facility for Antiproton and Ion Research in Darmstadt (Germany), such polarization measurements will be possible also for the negative-continuum dielectronic recombination (NCDR), in which a free electron is captured into a bound state of a heavy high- $Z$  ion, while the energy is released by an electron–positron pair [73]. The NCDR process provides indeed an important benchmark for theory, describing the electron and positron dynamics in quite critical fields. Special interest refers here to the formation and subsequent radiative decay of excited ionic states, and which requires a QED treatment right from the beginning.

Finally, excited ionic states are created also by Coulomb excitations of few-electron ions in collisions with target atoms and molecules. Again, the subsequent decay of these states typically results in an anisotropic angular distribution and non-vanishing polarization of the characteristic radiation. For high- $Z$  ions, these distributions of the characteristic x-ray lines will help explore especially magnetic corrections to the Coulomb interaction, i.e. further details about the Lienard–Wiechert potential.

*Concluding remarks.* Angular and polarization studies in relativistic ion–atom collisions help reveal new insights into the quantum dynamics in strong Coulomb fields [74]. Especially the comparison of high-resolution experiments with advanced theoretical techniques will provide an efficient route to further enhance our knowledge about the interaction of matter in extreme fields.



## 7. Experimental investigations on ion–atom collisions

Xinwen Ma

Chinese Academy of Sciences, People's Republic of China

**Status.** Experimental cross sections of ion–atom collisions in a wide range of impact energies play important roles in testing many-body theories and in application of astrophysics, plasma modeling, radiation damage, and ion-matter interaction, etc. The products of a collision usually consist of emitted photons, emitted electrons, recoil ions, and charge (un)changed scattered ions, and the ions may be in excited states. By detecting part of the particles in final states, experimentalists can extract essential information on collision dynamics. However, it is not just as that easy. The energies of emitted photons and outgoing electrons vary greatly depending on the collision systems and the collision energies, therefore, it is difficult to find one universal technique to detect photons, electrons and ions with sufficient resolution in one experiment. And further, due to very limited photon collection efficiency (solid angle and quantum efficiency of a detector system) compared to charged particle detection, coincidence measurements are generally difficult to apply for photons and charged particles. There are usually two types of experimental approaches for collisions studies, photon detection with high resolution and charged particles coincidence measurement. Few measurements have been reported with photon and ion in coincidence. Here the focus will be on the charged particle measurements.

Before the invention of reaction microscope [75] or COLTRIMS [76], only total cross sections and partial cross sections were obtained. Due to the powerful multiple coincidence measurements of charged particles, reaction microscope/COLTRIMS opens the way to perform multi-fold and even fully differential cross section (FDCS) studies, with reasonably good energy/momentum resolutions. The cross sections differential in scattering angle provide rich information of the impact parameter dependent collision dynamics where electron emission mechanism in a broad range of collision velocities have been studied [77].

In low to intermediate energy EC collisions, it is now possible to perform studies on quantum state-resolved charge exchange processes with high resolution. Figure 10 shows single-EC in collisions of 63 keV  $\text{Ne}^{7+}$  ions with He studied using COLTRIMS [78], where the state-resolved differential cross sections have been determined with respect to the principal quantum number, subshell levels and spin states of the captured electron. Furthermore, it is possible to explore the high resolution method to study the electron correlations in double and multiple EC processes, and give new insight into mechanisms, e.g. symmetric/asymmetric population, sequential/non-sequential processes.

At high impact energies, only few measurements of FDCSs have been done, where first Born approximation is assumed to be valid, Schulz *et al* [79] found unexpected discrepancies of electron angular distribution between theory and experiment in the perpendicular plane for single ionization

of He by 100 MeV/u  $\text{C}^{6+}$ . This ‘ $\text{C}^{6+}$  puzzle’ frustrates the community and needs to be solved in future experiments.

When more electrons are involved in a charge exchange process, electron correlation plays an important role, which is essential to understand many-body dynamics. For instance, in double-electron transfer with one electron ionized collisions of 80 keV/u  $\text{Ne}^{8+}$  on He, distinct features of the correlated processes can be well separated from the un-correlated ones [80]. With multiple coincidence technique, Gao *et al* [81] obtained fully differential data for transfer ionization process of one electron transfer with two electron ionized (five-body process). It is found that the sum electron momentum and the individual electron momenta are surprisingly strongly correlated with the total momentum transfer. Dedicated experiments for multiple ionization are expected to better understand these phenomena, and rigorous theoretical treatments are needed as well.

In the past decades, the targets used in ion collisions have been extended from simple atom to molecules and even to atomic/molecular dimers/trimers, etc. The structure information of these complex system serves as extra dimensions for the investigation of the structure involved collision dynamics. The molecular frame can be determined from the coincidence detection of charged particles produced in these processes. Consequently, the characteristic of matter wave of massive particles has also been observed at atomic scale: Fraunhofer diffraction in atomic collisions and interference in molecule involved collisions. In the works of Schmidt *et al* [82] and Zhang *et al* [83], they revealed that the interference pattern, which is in contrast to the optical double-slit experiment, resulted from the  $\pi$ -phase shift due to the parity change of molecular hydrogen ion in the collision. Later, the double-slit interference effects is used to extract the phase information in collisions with asymmetric diatomic molecules [84]. Figure 11 shows the asymmetry and shift of two-center interference patterns of  $\text{He}^{2+}$  on CO. In two different colliding energies, the scattering phase differences of  $\text{He}^{2+}$  on C compared to  $\text{He}^{2+}$  on O can be extracted.

**Current and future challenges.** Despite many successes in ion–atom collision studies, there are still challenges. To the least extent, here are some possible perspectives that one can look forwards in the near future. First, photon measurements in coincidence with charged particles. In ion collisions, photon emission from residual ions (recoils and/or scattered ions in multiply excited states) can provide additional information about the collision dynamics. However, so far sophisticated techniques where photon and charged particles are recorded in coincidence are still quite challenging.

Second, the phase information of the collision processes. Scattering phase contains important information about collision dynamics. In atomic transitions induced by the laser field, it has been shown that phase measurements show great potential in deeper understanding of the few-body problem. However, the long-range property of the Coulomb field of the projectile in ion collisions makes it nearly impossible to define the start/end point of the interactions as those of the

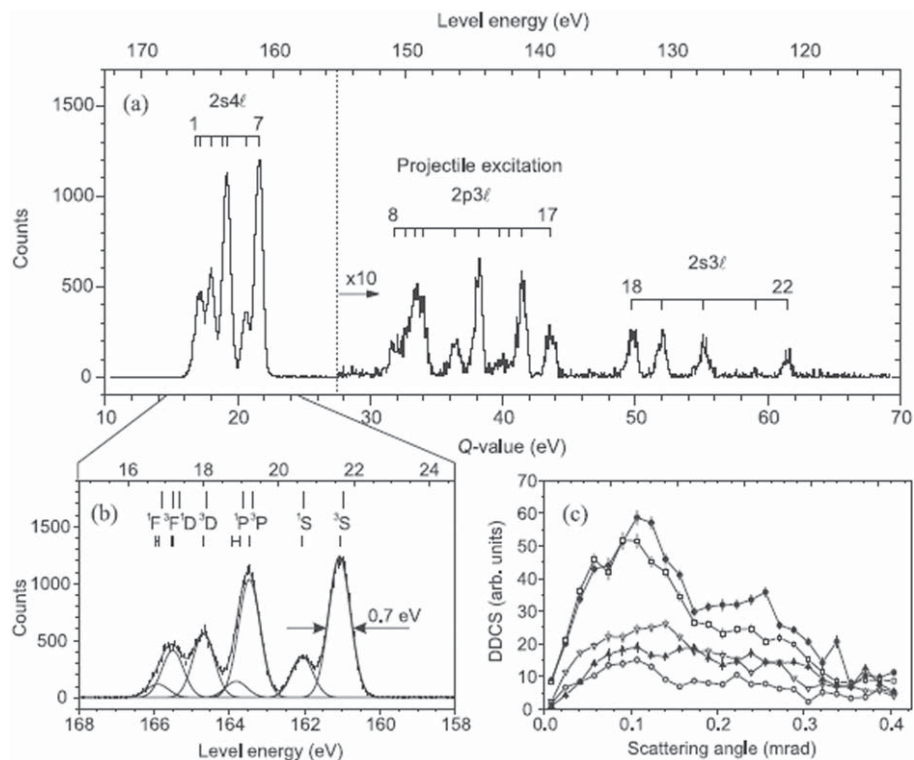


Figure 10. (a)  $Q$ -value spectrum and energy levels of  $\text{Ne}^{6+}$  following single-electron capture from He at 0.355 au velocity. (b) Decomposition of the  $2s4l$  spectrum into different subshells and spin states. (c) Differential capture cross sections [78]. Reproduced from [78]. © IOP Publishing Ltd. All rights reserved.

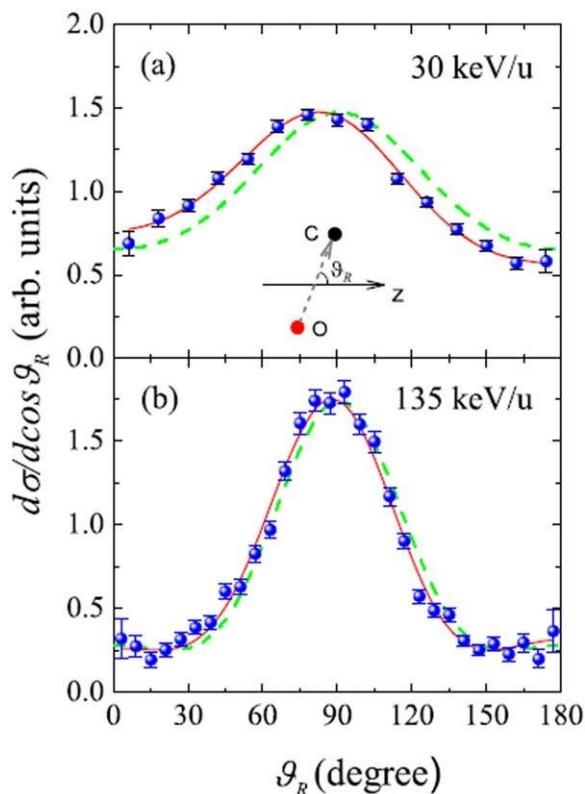


Figure 11. Relative scattering phases extraction of  $\text{He}^{2+}$  on C and O from two-center interference patterns of  $\text{He}^{2+} + \text{CO}$  double capture collisions. Reprinted figure with permission from [84]. Copyright 2018 by the American Physical Society.

photon experiments. So far there is only one successful scattering phase measurement achieved via two-center interference effects in ion collision processes [84], and it still challenges the community in finding proper ways to extract dedicated phase information of ion-atom collision dynamics.

Last but not least, electron correlation still challenges the understanding of collision dynamics. HCIs have strong Coulomb potential and thus can capture many electrons simultaneously when interacting with atoms at low and intermediate impact energies. These electrons usually populate to highly excited states and will decay via autoionization or radiation, where electron correlation plays crucial roles. High precision measurements are needed to understand the dynamics and decay process. When a HCI with relativistic velocity interacts with atoms/molecules, the interacting time is in a sub-attosecond time scale, similar to an ultrafast and strong electro-magnetic pulse, and target electrons can be kicked out instantly. This may create the ideal Heisenberg condition for studying electron correlation in an atom. On the other hand, strong electromagnetic field and relativistic will provide unprecedented extreme conditions and will lead to new phenomena in collision processes. All these investigations will challenge the present experimental technologies.

*Advances in science and technology to meet challenges.* Theoretical description of ion-atom collision dynamics is making progresses (see section 5) thanks to more experimental differential data and the rapid increase of



computation power. On the experimental side, MOTRIMS will provide much higher resolution for collision studies although only applicable to several atomic species. Some attempts have been made to incorporate photon detection in reaction microscope to get more accurate electronic level information. We are developing new ideas of scattering phase measurement, which will help to study details of collision dynamics. We pointed out a novel very fast breakup mechanism of dicationic acetylene dimers resulting from intermolecular proton transfer induced by ions [85] and even expecting breakup resulted from heavy ion transfer process in other dimers. These are important and relevant to DNA double-strand breakup induced by radiation. Furthermore, the rapid development of laser technology in recent years may help to realize laser assisted collisions studies.

In the meantime, new storage ring facilities under construction now, which will be equipped with reaction microscope and high resolution electron spectrometer, will provide HCl<sup>+</sup> with relativistic velocity, and further create excellent opportunities for investigation of collision dynamics under extreme conditions.

*Concluding remarks.* Ion–atom collision processes are by far the best choice to explore the few-body problem. First, in atomic physics the underlying Coulomb force between charged particles is precisely known and structure properties can be obtained with high accuracies, it guarantees that all discrepancies between experimental observations and theoretical predictions result from the quantum models. Second, in ion–atom collisions the number of active interacting particles can be well controlled which is essential to examine few-body processes. Few-body problem is a long-standing fundamental topic in science, more dimensions of freedoms will be accessible in experiments with the new developing technologies, and it is definitely needed to investigate the few-body dynamics in atomic collisions.

### Acknowledgments

This work was supported by the national Key R&D program of China under Grant No.2017YFA0402300.

## 8. Interference effects in ion–molecule collisions

Roberto D Rivarola and Omar A Fojón

Instituto de Física Rosario (CONICET—UNR), Argentina

*Status.* A controversy between the corpuscular or wave nature of electrons remained for centuries. Based on the oscillatory structure observed in measurements of photoabsorption cross sections of the diatomic  $N_2$  and  $O_2$  molecules, in 1966 Cohen and Fano [86] suggested that this behavior is obtained from the fact that an electron is coherently emitted from the proximities of the nuclei of the targets. This mechanism was associated with the two-slit scenario of the Thomas Young experiment [87], where the coherent superposition of electrons demonstrated the wave character of these quantum objects. The effect was measured 35 years later than the Cohen and Fano prediction but for impact of 60 MeV/u  $Kr^{34+}$  on  $H_2$  molecules [88]. In order to give visibility to the effect, experimental double differential cross sections (DDCS) as a function of the final electron velocity, at fixed emission angles, were divided by the corresponding theoretical ones for two independent effective H atoms (see figure 12; see also [89] for a case where atomic H experimental measurements were employed for comparison). Fit straight lines were drawn to enhance the visibility of the spectral structure. As a result, interference patterns were observed and a simple theoretical interpretation was given. Encouraged by this seminal work, numerous experiments and theoretical models were developed in the following years

In particular, evidences on the existence of the effect were also given for the impact of photon and electron beams, showing that the essence of this coherent behavior resided in the two-center character of the target and only depends in a secondary aspect on the projectile type (for a general review see [90]).

Usually for ion beams, perturbative approximations were employed to describe the reaction within an independent electron approximation and assuming that the residual target (including the non-ionized electrons) remains as frozen until the projectile-target interaction ends. This assumption is supported by the fact that the collision time considered is of the order of the sub-femtoseconds while the vibrational and rotational ones are much larger. Consequently, the orientation of the molecule remains fixed in space.

In general, the molecular bound orbitals are described as linear combinations of different bound states of the atoms that compose the target, and the molecular continuum in the exit channel is described by means of effective continuum states. In order to obtain DDCS the matrix elements describing the collision are integrated on the momentum transfer and then averaged over all possible molecular orientations.

Further theoretical work for  $H_2$  targets was focussed to describe the dependence of the angular distribution of emitted electrons with the molecular orientation, for impact of high energetic bare carbon ions. Thus, triple differential cross sections (TDCS) were calculated for a coplanar geometry, where the molecule, the emitted electron and the projectile velocity are all in the same plane. It was shown that the

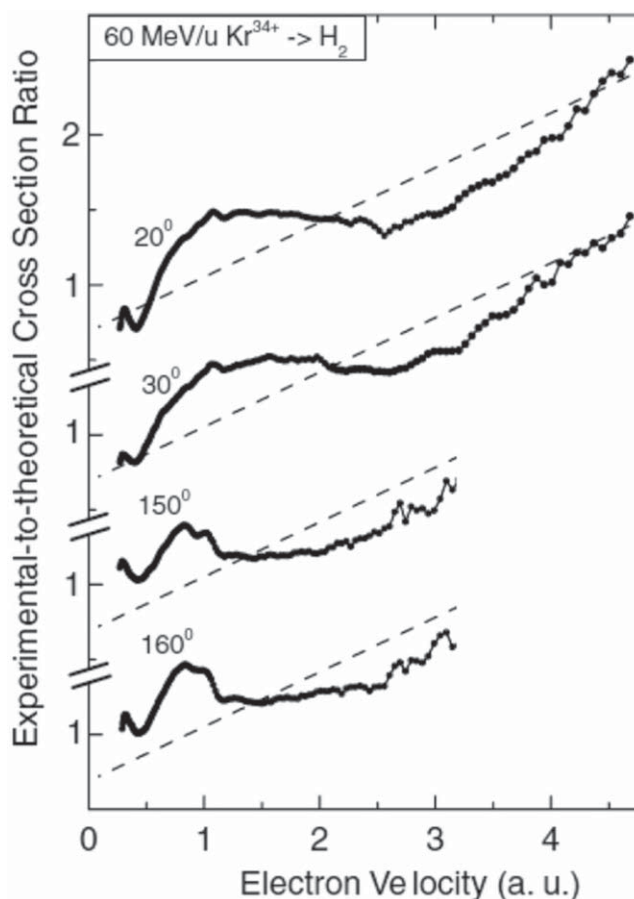


Figure 12. DDCS as a function of the electron velocity at fixed electron emission angles. See text. Reprinted figure with permission from [88] Copyright 2001 by the American Physical Society.

presence of interference patterns is favored for a molecular orientation coinciding with the one of the initial projectile velocity  $v$ . The contribution from different momentum transfers tends to shadow the corresponding oscillations as the molecule is aligned perpendicularly to  $v$ .

FDCSs were also calculated for proton beams in order to investigate the contribution of fixed values of the momentum transfer. They put in evidence that for certain kinematical conditions when the molecular orientation is perpendicular to the impact velocity, the so called recoil peak tends to disappear due to destructive interference contributions.

Concerning the influence of the molecular orientation, experimental and theoretical results of the electron spectra as a function of projectile scattering angle at fixed electron losses, suggest that for small scattering angles a transverse molecular orientation dominates whereas for large scattering ones a parallel orientation is preferred.

Further research for proton impact was extended to the case of multi-orbital targets like  $N_2$  molecules in a coplanar geometry [91]. The theoretical studies show the presence of interference patterns separately for each one of the molecular orbitals on the angular distribution of emitted electrons (see figure 13). The number of lobes revealing the apparition of coherent emission tends to increase as the electron energies

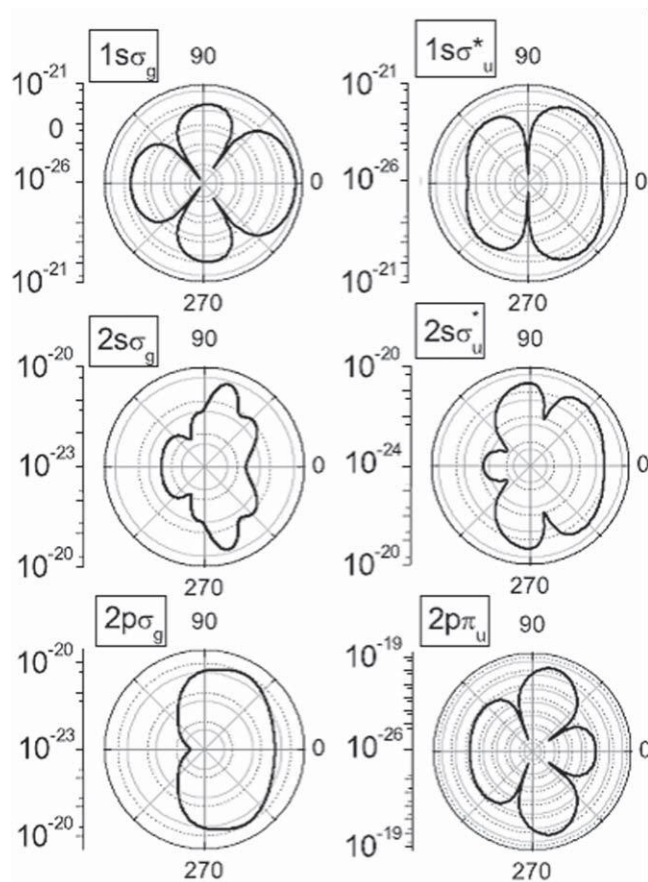


Figure 13. Angular distribution of emitted electrons for each  $N_2$  orbital at a 100 eV electron energy. Molecular orientation parallel to  $\nu$ . See text. Reproduced from [91] © IOP Publishing Ltd. All rights reserved.

increase and appear to be preferable for a molecular orientation parallel to  $\nu$  (directed to  $0^\circ$ ), as it happens for  $H_2$ . The oscillations corresponding to the different orbitals are shifted the ones with respect to the others, so that DDCS resulting from summing all their contributions do not present any signature of interference effects, as observed in existing experiments [92].

**Current and future challenges.** An important number of improvements are necessary from both theoretical and experimental sides. A tentative short list of them is given in the following.

From the theoretical aspect, it appears as relevant to investigate the role played by electron correlation not only in the description of molecular orbitals but also in an appropriate description of the molecular continuum in the exit channel, moreover in the case of multi-electron orbitals. The inclusion of vibrational and rotational movements are also necessary in the future.

Furthermore, measurements of multiple differential cross sections that take into account simultaneously the ejected

electron coordinates and the orientation of the molecule, including or not the projectile scattering angle, appear as fundamental for a more complete understanding of the effect.

The signatures of constructive and destructive interference contributions on FDCCS for different molecular orientations with respect to the momentum transfer vector, in coplanar and no-coplanar geometries, are relevant. For the case of electron impact ionization of  $H_2$ , for coplanar geometries, it is observed that under certain kinematical conditions the binary and recoil peaks may disappear, depending on the gerade or ungerade character of final residual states [93]. Recent predictions [94] for ions seem to show a similar behavior to the one obtained for electron beams. The sum over all molecular orientations allows an adequate description of the Physics involved in existing experimental TDCS and an increase of the binary peak is observed due to constructive interferences.

The influence of the symmetry character of the bound states is a main aspect to consider. For example, the inner gerade and ungerade orbitals of the  $N_2$  target show emission spectra in phase opposition. This effect has been shown to come from the mentioned symmetry character. Experimental research distinguishing the initial and final orbitals is an ambitious but useful project.

The verification of the possible existence of double frequency interference effects associated with the scattering of the ejected electron on both molecular centers is a matter of further research [95].

**Advances in science and technology to meet challenges.** As it was before mentioned a lot of theoretical work is still necessary for a more complete understanding of the Physics present in interference effects due to coherent electron emission from molecular targets. From the experimental point of view, a complete mapping of all resulting particles appears as a challenge, including the orientation of the molecular target during the collision. It could be perhaps obtained combining cold target recoil ion momentum spectroscopy (COLTRIMS) and laser techniques.

**Concluding remarks.** A brief review on the state of the art on the physical interpretation of interference effects due to coherent electron emission from molecular targets impacted by fast ion beams was presented. Future challenges for theoretical and experimental research lines are proposed.

## Acknowledgments

The authors acknowledge financial support from the Agencia Nacional de Investigaciones Científicas y Técnicas of the República Argentina through the project PICT 2015-3392. Discussions with Guillaume Laurent are acknowledged.

## 9. Ion–molecule collisions—large molecules

Lokesh C Tribedi

Tata Institute of Fundamental Research, India

**Status.** Research on heavy ion collisions with atoms, molecules, clusters and solids is a natural extension of the electron-atom collision studies. While electron induced atomic molecular collision offers an excellent tool to probe the basic structure, properties and collisional aspects of the atoms and molecules, the collisions with ions have a wider scope due to the possibility of the variation of perturbation strength on a wider scale. This allows one to deal with the collision mechanisms from weak to strong perturbation regime. With the gradual development of experimental tools, such as, accelerators, ion sources, fast-electronics and detection systems, many of the investigations are renewed due to its importance towards fundamental interest in interdisciplinary sciences: radiation-biology, plasma physics, astrophysics and astrochemistry. Besides the well-known mechanisms of molecular interactions, completely new decay process—interatomic and intermolecular Coulombic decay (ICD) has been discovered [96] in case of clusters. It is only recently that the Young-type electron interference due to spatial coherence has been observed in a molecular-double slit [97, 98] under heavy ion-collisions following the original prediction by Cohen and Fano (1966). The experimental study of electron emission from atomic H under heavy ion was crucial to identify, unambiguously, the interference oscillation. Besides this, a new approach of using forward–backward asymmetry parameter to identify the interference and the existence of a second order interference were some of the highlights. Synchrotron based photo-ionization studies by Uwe Becker *et al* [99] as well as fast e-beam induced e-emission (Tribedi *et al* PRA 2016) have revealed the spatial coherence induced oscillations for N<sub>2</sub> and O<sub>2</sub> molecules. The interference oscillation has been used to estimate the bond-length in case of simple hydrocarbon molecules.

The fragmentation dynamics of multiply charged smaller polyatomic molecular ions using high resolution recoil-ion momentum imaging is under study to identify under what condition a concerted or sequential processes are crucial [100].

A new dimension to this research is the wide spread experimental and theoretical investigation of ionization and fragmentation of biologically relevant large and complex molecules under the interaction of swift ions. A detailed and systematic investigation is likely to open new avenue towards the applications in related fields, such as, radiation biology, in particular, for hadron therapy. In heavy-ion radiation therapy, the energy loss of swift ions inside the body exhibits a maximum in the Bragg peak region. Therefore, the study of ionization or fragmentation of the nucleobases, DNA, RNA, sugar phosphate backbone or water molecule over a wide energy range, across this Bragg-peak region will be of great importance. It is now well known that the electrons of energy, even lower than the ionization threshold, are primarily responsible for the single and

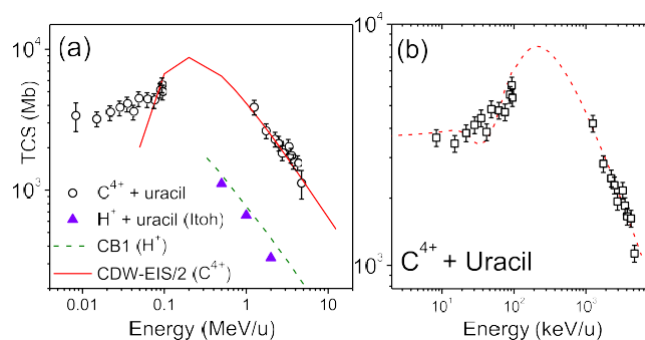


Figure 14. (a) TCS for ionization of uracil by C<sup>4+</sup> + [101] and p [102]. (b) Same data [101] along with a scaling formulation (dashed-line) by Montenegro *et al* [103].

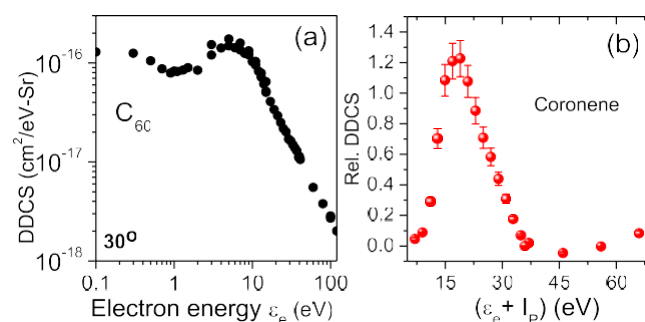


Figure 15. (a) e-DDCS for 76 MeV F<sup>9+</sup> colliding with C<sub>60</sub> [104]. (b) Relative DDCS (forward backward ratio) for Coronene under 60 MeV O<sup>8+</sup> impact [105].

double strand breaks. A detailed knowledge of the ion-induced electron emission mechanism [101, 102] is of importance for radiobiologists. One may refer to a series of experimental work by Mark *et al*; Itoh *et al*; Tribedi *et al* and Moretto-Capelle *et al*. There has been substantial progress in theoretical modeling too (e.g see Rivarola *et al*, Champion *et al* and Kirchner *et al*). One example is given in figure 14. Calculations based on the CDW-EIS model predict about twice the total ionization cross section (TCS) measured for Uracil by fast C<sup>4+</sup>-ion impact at high energy (figure 14(a)), but it overestimates by a larger factor at the peak region. Montenegro *et al* showed that the inclusion of transfer-ionization, in a scaling formulation [103] (figure 14(b)) gives excellent qualitative agreement.

Another direction of this research involves the study of plasmon excitation by detecting the plasmon electron peak in the low energy part of the e-spectrum [104] for C<sub>60</sub> (figure 15(a) as well as PAH molecules [105] (e.g. for coronene as shown in figure 15(b)). Polycyclic aromatic hydrocarbon (PAH) molecules are quite abundant in the interstellar space and, hence, attract lot of interest in astrophysics and astrochemistry. Recently observed [103] plasmon excitation peak at ~17 eV for coronene helps to explore the UV photon absorption by the PAHs in the interstellar medium. Besides PAHs, the C<sub>60</sub> fullerene and its clusters are of importance in the study of many body physics and giant plasmon excitation. The clusters of PAH are also important for nano-electronics and UV plasmonic devices. The ion collisions with such clusters and the question of instability



against fragmentation has been addressed by a few groups, e.g. at Stockholm, Caen and KVI.

A scaling law to estimate TCS for uracil, water and other large molecules are also being investigated by different authors (e.g. [103, 106] and Olson EPJD 2019).

*Current and future challenges.* From a large set of data on ion–atom and ion–molecule collisions, it appears that the theoretical techniques, based on the CDW-EIS and various versions of it, fairly explain the data-sets particularly for simple light target atoms. However, for large molecules including nucleobases the back-scattering phenomenon is yet to be understood, since one often finds deviation of theory for ejected electron emission in large scattering angles. In case of such large molecules many electron correlation, size effect or any collective effect need to be included in the models. In view of their potential applications in diverse fields like radiobiology or medical imaging there is an effort to develop Monte Carlo numerical codes of charged particle transport and energy loss. Two such approaches by Champion and Garcia can be found in EPJD 71 (130) 2017; and Rad Phys Chem 130, (371) 2017. In spite of having many measurements carried out one finds a lack of accurate experimental data on total energy loss of charged particles in water, particularly around the Bragg peak. Such measurement will automatically include the contribution of the ionization, EC and fragmentation in the total energy loss. Whether the use of water to simulate the biological medium is correct or not needs to be answered experimentally. In practical front, the challenging task is to carry out experiments which must be tuned to include the realistic environment around the target molecules. For example most of the ion–collision experiments are carried out with isolated biomolecules in vapor phase. In reality the nucleobases are parts of the DNA/RNA present in biological matters along with liquid water.

*Advances in science and technology to meet challenges.* In certain class of experiments one uses the clusters of biomolecules, water-clusters or liquid drops. For example, the study of fragmentation of clusters of 5Br-uracil indicates clustering effect, by triggering new pathways for fragmentation, e.g. the loss of the OH group (PCCP 19, 19807, (2017)). Therefore, to explore the interaction dynamics of these biologically active molecules surrounded by an environment, such as, solvent molecules, water, alcohol, or other smaller bio- molecules is an experimentally challenging task. To this end, a bio-molecular ion beam facility, comprising of an electro-spray ion source and an ion-trap with a cooling buffer-gas, capable of delivering low energy internally cold molecular-ions, could be used as injector to a storage ring. Such cross-beam experiments involving accelerators are being developed in different laboratories worldwide (e.g. Stockholm, Aarhus, RIKEN).

Metal nanoparticles are proposed to be candidates as sensitizers in cancer treatments in hadron-therapy [104]. The injection of such nanoparticles into tumors increase the biological effectiveness due to the enhancement of low energy electrons radicals. Collective plasmon excitation in the inserted metal is a possible mechanism for such enhancement [107]. In reality this is extremely challenging experiment. The initial experiments, which are in progress involve different halo-uracils as target, such as, bromouracil, iodouracil etc. In benchmark system, such as, C<sub>60</sub> it has been observed that, nearly 50% of the electron emission and hence similar fraction of energy loss can be accounted by the collective excitation alone. Such collective excitations are dealt theoretically by a few groups: Eric Suraud *et al* (Toulouse, France) and Solov'yov and co-workers (Frankfurt group) (e.g. see [105], EPJD 66, 254 (2012), JPCS 490, 012159 (2014)).

From radiation biology point of view the contribution of the ICD process, to the DNA-strand breakage needs to be investigated in more details, particularly its role in case of heavy-ion collisions.

The last, but not the least point relates to the ion–atom collisions. In case of electron emission for ion–atom or ion–molecule collisions, the deviation of the models for backward electron emission is yet to be understood. Observed double frequency in interference oscillation in backward e-emission from H<sub>2</sub> compared to the forward emission is yet to be understood. In case of interference experiment, DDCS for molecule is compared with that for the atomic DDCS. However, only in one experiment such explicit comparison was possible i.e. by using atomic H [98], but for other atomic targets, e.g. N or O atoms, such experiments are awaited.

*Concluding remarks.* The mature field of ion–molecule interaction has taken a new shape of interdisciplinary science due to constant contributions by genre of researchers across different branches of science i.e. plasma- and astrophysics, biology, chemistry and radiobiology.

New discoveries, such as, ICD in photo-ionization and e-interference in molecular double slit have kept the field vibrant. The theme of ion–molecule collision continues to offer an active area of research which enriches our basic understanding of large bio-molecules, PAH molecules, fullerenes and clusters. The future research may aim towards the interaction with biomolecules which is attached to an environment and with nano-inserted DNA/RNA molecules- which is, however, a challenging task. The development of a range of sophisticated equipment, ion-traps, ion-sources, storage-rings, ion-beam facility will continue to push the field of molecular sciences.

## Acknowledgments

I would like to thank my students, colleagues and R Rivarola and C Champion for long-standing theory-experiment collaborations.

## 10. Ion–ion collisions in the intermediate velocity regime

Emily Lamour

INSP—Sorbonne University, France

*Status.* Ion–ion collisions provide a unique scenario for testing our knowledge of fundamental electronic processes such as capture, ionization and excitation. Their study is also motivated by the fact that they are strongly correlated to the ion energy transfer in various plasma conditions.

Whereas ion–ion experiments for high-energy physics (like the experiments at CERN) are currently carried out, ion–ion collisions for atomic physics have been so far performed mainly in the context of magnetically confined plasmas [108]. There, *in the low velocity regime*, typically at center-of-mass energies of a few keV up to a few 100 keV, cross section measurements of the charge transfer process [109, 110] (by far the dominant process) were performed with light ions (up to oxygen) for collisions with bare, hydrogen- or helium-like ions, or with low-charged ions for the heavy systems like Bi and Pb, where charge states of up to  $4+$  have been used.

Investigation of *the intermediate velocity regime* (the pink area in figure 16) is more complicated due to the fact that, there, all the primary electronic processes (EC, loss and excitation) reach their optimum probability leading to the maximum of the ion stopping power and, consequently, to the strongest effects on material modifications. A few ion–plasma experiments, motivated by their consequences in the inertial confinement plasma fusion physics, have been carried out with swift heavy ions in hydrogen or deuterium low-density plasmas and, later on, in laser-generated carbon plasma of one percent solid state density. Evidences for drastic differences in ion stopping power when ions interact with either neutral or ionized matter have been clearly established (see for instance, [111]). Nevertheless, to extract direct information on elementary process modifications is almost impossible since many charge states may be present at the same time in the plasma. Likewise, in simple ion–(neutral) atom collisions, the presence of many electrons makes the determination of experimental cross sections of a single elementary collision process extremely difficult. It can be achieved only in very specific cases: for instance, taking full advantages of the spin-selectivity in excited state populations, the single  $1s \rightarrow 2p$  excitation cross section has been measured for collisions between  $13.6 \text{ MeV}/u$   $\text{Ar}^{16+}$  ions and neutral atoms (from He to Xe) [112]. From a theoretical point of view, none of the present most sophisticated available calculations is able to treat all the processes together on the same footing pointing to a fundamental issue in our understanding of elementary atomic interactions. This circumstance gives rise to a paradoxical situation where, for this velocity regime, cross sections are very hard to predict, while their knowledge is of critical importance. A significant test of theories can only be performed if the presence of numerous electrons can be avoided (beside the simplest case of a proton on hydrogen collision). Alternatively, the effect of other electrons

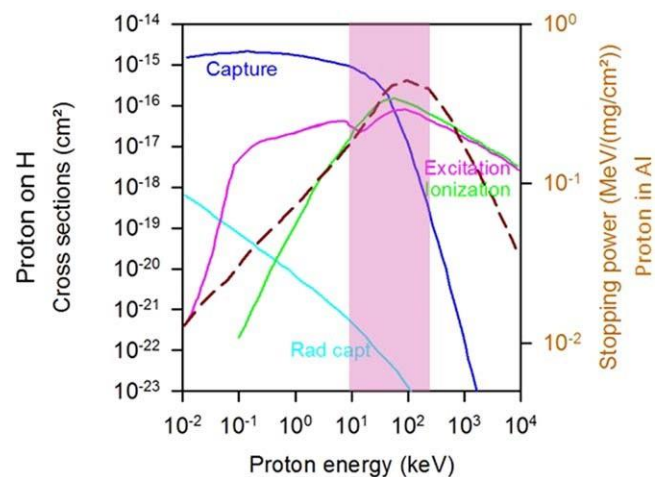


Figure 16. Cross sections of elementary atomic collision processes for the system  $p \rightarrow \text{H}$  as a function of the proton energy. The brown line is the stopping power (refer to the right y-axis) for protons in aluminum. The pink area marks the intermediate collision regime.

participating to the processes must be explored. In this context, our knowledge of *the intermediate collision regime* is really limited. There is a lack of measurements and available theoretical calculations are at their limit of validity. In other words, this regime corresponds to a real *'terra incognita'* for atomic physics.

With ion–ion collision experiments, we deal with 'clean plasmas' of well-known charge states, we have the ability to investigate a large variety of systems and the possibility to easily scan the charge state of each ion partner. Nevertheless, the realization of these experiments remains a real challenge involving several steps that have to be solved in order to perform absolute cross section measurements.

*Current and future challenges.* The intermediate regime is reached when the relative target–projectile velocity is of the same order as the ones of the active electrons in its initial state. For instance, in the case of the symmetric collision  $\text{Ar}^{Q+}$  on  $\text{Ar}^{Q+}$ , it occurs at a collision velocity around  $8 \text{ MeV}/u$ .

Besides the possibility to reach the pure three-body problem (bare ion on hydrogenic target) as a benchmark, the role of additional electrons bounded to the target and/or to the projectile –one by one– should allow quantifying several effects such as:

1. closure and/or opening of different channels: such as capture channels, that are open for bare projectiles but may be closed (or less likely) for other charge states;
2. electron–electron interactions: besides correlations, the presence of additional electrons can also directly increase (anti-screening) or decrease (screening) the mechanism probabilities;
3. multi-electron processes: often neglected, they can become as large as single processes in some cases (see, for instance [112]);



4. Coulomb forces acting on the electron cloud in the entrance and exit pathway of the collision (effect related to the total charge of the collision partners).

Therefore, these kind of studies should provide original data on the quantum dynamics of  $N$ -body systems.

So far, no experiment has been performed in this regime mainly due to experimental issues, among which the requirement of (i) very high ion beam intensities of good optical quality with a perfect charge state control of the both ion beams, (ii) the control of the overlap between the ion beams and (iii) the high energy ion detector with a good count rate capability (up to 1 MHz) that need to be, in particular, radiation resistant. Additionally, an efficient cross beam arrangement running under ultra-high vacuum conditions is needed with the possibility to slightly change the energy of the low-energy ions in the interaction zone to tag the true events from the ones coming from collisions with the remaining atoms in the residual gas. Obviously, to properly analyze the collision products, powerful charge-state dispersion systems coupled to ion detectors are required for multi-coincidence measurements.

*Advances in science and technology to meet challenges.* For the low-energy channel, an ion source connected to a beam transport line provides currently ions in the keV/ $u$  energy range. The line needs to be well-adapted to shape the beam and clean it from the non-desired charge state just prior to the collision zone (for background reduction). This beam constitutes a target of a rather dilute density (a few  $10^{14}$  cm<sup>3</sup> maximum). Therefore, for the high energy channel, very intense beams are mandatory.

The forthcoming availability of MeV energy and stable ion beams of high optical quality at French and German Large Scale Facilities, GANIL/SPIRAL2/S3 [113] and FAIR/CRYRING ([114, 117], see section 19), opens now real opportunities towards the study of the intermediate collision regime. In fact, two experimental approaches have to be considered depending on the facility used. With SPIRAL2/S3, very intense ion beams between  $10^{12}$  and  $10^{14}$  particles per second of medium  $Z$  number (from He to Ar) will be delivered allowing a ‘single-pass experiment’ arrangement. In this case, the stripping of very intense ion beams for reaching the desired charge state raises the issue of the resistance of the stripper (a thin solid foil) to the ion energy deposition. This can be overcome by using a rotating stripper so that the beam power is distributed over a much larger volume [115]. With

the CRYRING ion storage ring, the effective target density is increased simply due to the revolution frequency of the MeV/ $u$  ion beam what we call a ‘multi-pass experiment’ arrangement. CRYRING is equipped with an electron cooler operating with an ultracold electron beam, allowing to provide ion beams of very high-optical quality. With this facility, MeV/ $u$  ions heavier than the ones provided by SPIRAL2 (presumably up to U) will be stored allowing the study of asymmetric collision systems. For the heaviest ions stored at energies in the region of  $\sim 10$  MeV/ $u$  or less, we also enter the realm where the formation of a quasi-molecule during the collision with an electric field from the combined nuclear charge of  $Z_{\text{target}} + Z_{\text{projectile}} > 174$  can be formed allowing the spontaneous creation of electron–positron pairs (supercritical field) [116]. This offers the possibility to investigate the most controlled environment where fully relativistic QED calculations are required to study atomic processes in the presence of extreme electromagnetic fields (i.e. exceeding the critical Schwinger limit of  $2 \times 10^{16}$  V cm<sup>-1</sup>) [117].

*Concluding remarks.* When a few MeV/ $u$  ions collide with a few keV/ $u$  ions, a hitherto unexplored collision regime is reached: the regime where the ion energy transfer is at its maximum. There, measurements and reliable theoretical predictions are completely lacking. With the performances of the new upcoming facilities in France and Germany, a complete experimental program of ion–ion collisions is now clearly conceivable involving a large variety of collision systems with the possibility to tune both the projectile and target charge state over a wide range up to bare ion on hydrogenic target. There is no doubt that original experimental data on the quantum dynamics of  $N$ -body systems are expected.

## Acknowledgments

This work is not and will not be feasible without the full ASUR team at INSP, our colleagues from CIMAP (Caen, France) and from the Atomic Physics group at GSI and Jena University (Germany). We thank the GANIL staff and the Atomic Physics group at Giessen (Germany). This work is supported by the French National Agency under the two contracts ANR-13-IS04-0007 and 10-EQPX-0046 as well as by the Laboratory of Excellence Plas@Par (Plasma à Paris).

## HIGHLY CHARGED IONS

## 11. Frequency metrology with trapped and stored HCIs

José R Crespo López-Urrutia

Max-Planck-Institut für Kernphysik, Germany

*Status.* Arguably, all interactions in the Standard Model of physics leave their watermark on the electronic wave function. The question is, can one access those effects through precision measurements? Until now, the answer in atomic physics has often been yes; witnesses are atomic clocks, hyperfine anomalies, Mössbauer-based general relativity tests, atomic parity non-conservation and many other examples. An even wider landscape of possibilities is reviewed in [118]. For the most accurate method in science, frequency metrology, the introduction of the frequency comb as well as the use of atoms and singly charged ions as clock references [119], with laser cooling techniques bringing them into the Doppler-free motional ground state are enabling stupendous and steady gains in accuracy. With frequency ( $\nu$ ) determinations in optical transitions by far surpassing in their accuracies that of classical microwave atomic clocks, novel methods of optical frequency metrology (OFM) are starting to contribute to fundamental and applied research in manifold ways. At the level of  $\Delta\nu/\nu \approx 10^{-18}$  recently demonstrated [120], universally reproducible atomic frequency standards are also equally sensitive to various physical aspects of their environment and become the finest physical sensors available.

Until recently, HCIs stayed outside those developments, since directly laser cooling them is not possible. Fundamental studies with HCI in the field of QED in extreme fields, nuclear-size effects and the like had the advantage of the high powers of the atomic number  $Z$  with which those effects scale up with the charge state (see, e.g. [121, 122]). Astrophysics benefited from controlled spectroscopic studies in the laboratory [123], and atomic structure theory was stringently benchmarked [124]. However, HCI spectroscopy in electron beam ion traps [124], merged-beam setups and storage rings was intrinsically limited by Doppler-borne broadening and shifts to an accuracy typically worse than one part-per-million, more than ten orders of magnitude away from state-of-the-art OFM. None of the proposed techniques including the use of free-electron lasers and highly monochromatic synchrotron radiation could suppress this drawback of those devices.

Very recently, with the introduction of sympathetic laser cooling [125] in a cryogenic radio-frequency trap (see figure 17) at the Max-Planck-Institut für Kernphysik (MPIK), HCI cooling to the motional ground state has nonetheless become achievable, breaking the present barriers. In addition, this step has suddenly increased the variety of species available for OFM by a large factor, since many isoelectronic sequences in HCI possess narrow optical transitions suitable for laser excitation from the electronic ground state. Many

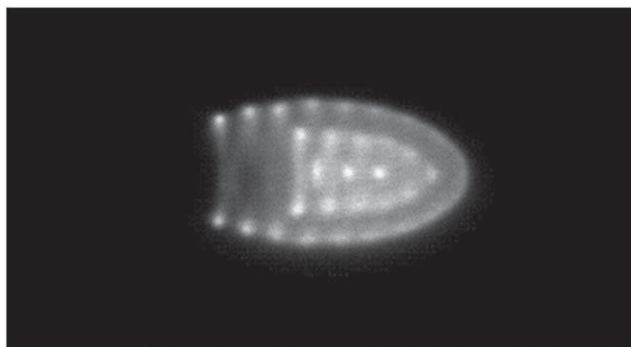


Figure 17. Invisible, a sympathetically cooled  $\text{Ar}^{13+}$  ion occupies the left side of a Coulomb crystal of laser-cooled  $\text{Be}^+$  ions. Bringing down the translational temperature of the HCI by nearly eight orders of magnitude, this key step prepares the ion for subsequent ground-state cooling followed by quantum-logic spectroscopy in a cryogenic radio-frequency trap (Image: MPIK).

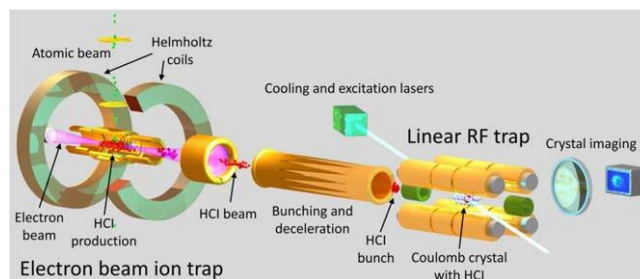


Figure 18. Frequency metrology with HCI: an electron beam ion trap emits HCI that are decelerated, bunched, and injected into a linear radio-frequency trap, where sympathetic cooling with a previously prepared Coulomb crystal of several  $\text{Be}^+$  ions takes place. Then, an ensemble of one single HCI with one single  $\text{Be}^+$  ion is prepared and cooled to its motional ground state. Resonant excitation of forbidden transitions in the HCI, and detection of those excitations by means of quantum-logic spectroscopy follow. In this method, interrogation of the Raman side-band transitions of  $\text{Be}^+$  yields the state of the HCI (Image: MPIK).

applications in fundamental research will benefit from this advance [124, 126].

Moreover, HCI have high ionization potentials and can therefore be excited by lasers from the extreme ultraviolet to the x-ray region without being photoionized, making narrow electronic transitions at such high frequencies of the electromagnetic field possible (figure 18). In this way, supported by rapid advances in the generation of narrow-band lasers in those spectral regions based on high-harmonic generation, extreme frequency metrology (XFM) will find in HCI [127] adequate frequency standards for reference and stabilization beyond the few that potential nuclear clocks could provide.

*Current and future challenges.* From a scientific point of view, the foremost task is testing the basic theories that support our understanding of nature, such as QED, general

relativity, the standard model of physics, parity non-conservation, cosmology and the Dark Matter question appear. Atomic physics and frequency metrology are already yielding deeper and deeper insights into those, and presumably an extension to higher photon energies will open new possibilities to contribute to these fields. However, our ability to benchmark theoretical developments against the most accurate results from OFM still encounters a conundrum that is both hindrance and opportunity, namely the limitations of our knowledge about the atomic nucleus. A very good example is the proton radius issue, where the superior sensitivity of laser techniques has challenged long standing high-energy electron scattering results, albeit not all problems have been solved yet. QED in stable, bound systems is the most accurate theory of physics, but further advances will require a better understanding of nuclear-size contributions to the experimentally determined atomic transition frequencies. On the other side, proposed combinations of such measurements can provide exactly that information on the nucleus, thus facilitating tests of nuclear theory and deeper benchmarking of QED. This would be more propitious than at first sight: as the primordial quantum-field theory, any improvements in its methods will lead to advances in other parts of the standard model both from the point of view of the mathematical methodology in use as well as from the better understanding of perturbations that affect measurements at high and low momentum transfer.

#### *Advances in science and technology to meet challenges.*

Exquisite methods of OFM [119] have been developed in the last decade by pioneering groups worldwide. Transferring those to the newly accessible HCI [125] will undoubtedly become a task for the next few years. Auspiciously, ground-state cooling of HCI via sympathetic cooling, and quantum-logic spectroscopy with HCI have just been achieved by a collaboration of the QUEST group (Schmidt) at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig and MPIK. This step makes HCI available for the application of OFM at the highest levels of accuracy now available. Other groups pursuing this route will also profit from it.

With this clear path for OFM with HCI already in the near future, the quest for an extension into the XFM domain is still pending [127]. Frequency combs in the VUV and XUV have already been demonstrated by a few groups. Attempts to make them available for uses with HCI are already underway. Perspectives for their application include in principle all what has already been shown to work in the optical region, plus fields of research which intrinsically require high photon energies. One interesting example for long-term research is the study of nuclear transitions unaffected by solid-state

effects, this means, using isolated HCI as targets being the carriers of the nuclei of interest. Potentially, HCI impervious to the x rays needed to excite low-lying nuclear levels, as in Mössbauer transitions, up to 100 keV could be prepared and cooled. The extremely narrow linewidths of those x-ray transitions would enable even more sensitive probes of nuclear forces and fundamental physics.

Another fruitful approach to fundamental physics with HCI is their use in high-precision Penning traps (see related references to recent work of various groups in [118, 124]). This has delivered outstanding tests of QED through studies of the bound-electron  $g$  factor and atomic mass determinations that are sensitive to the binding energies of nuclei and their surrounding electronic shell to a level which is rapidly becoming competitive with standard x-ray spectroscopy of HCI. Furthermore, in combination with rare-isotope beam facilities, Penning traps that are already workhorses of nuclear physics will also experience a stupendous push in accuracy from the application of sympathetic laser cooling techniques to the trapped HCI, and quantum logic techniques.

*Concluding remarks.* Beyond our daily perspective, HCI constitute the bulk of baryonic matter for the majority of the chemical elements in the universe. Due to their properties, they control radiation transport in stellar cores, and are the strongest spectral emitters in x-ray astrophysics from stellar coronae to black hole and active galactic nuclei environments. As isolated quantum systems, they are excellent probes for fundamental interactions with the triple advantage of strongly scaled-up QED and nuclear-size effects, simpler electronic structure than atoms, and extreme suppression of sensitivity to spurious external perturbations of the electromagnetic field. Nowadays, their use in the laboratory is becoming easier, with smaller and more practical sources showing their performance exactly for those purposes.

Now, tamed for XFM by means of re-trapping followed by sympathetic cooling, their variety will constitute an invaluable advantage for fundamental and applied research. The periodic table acquires height with the ionic charge state; on the pathways across these largely pristine ranges, new spots at high vantages will offer broad scopes and far sights of the physics landscape. Leaving them unexplored would be a lost opportunity.

## Acknowledgments

Stimulating discussions with J Berengut, K Blaum, D Budker, A Derevianko, V Flambaum, M Kozlov, M Safronova, P O Schmidt, and other colleagues driving this field with their ideas are gratefully acknowledged.

## 12. Highly-charged radionuclides

Yuri A Litvinov

GSI Helmholtz Center, Germany

*Status.* Highly-charged radionuclides (HCR) are systems with none or just a few atomic electrons, like, for instance, hydrogen- (H-like), helium- (He-like) or lithium-like (Li-like) ions. These are well-defined nucleus plus lepton(s) systems with well-defined quantum numbers. Studies of isolated HCRs shall help understanding complicated processes involving HCRs in stellar hot and dense objects.

The first major research subject with HCRs is devoted to studies of nuclear decay properties [128]. Here, decay channels known in neutral atoms can disappear, like for instance orbital EC is disabled in fully-ionized nuclides, while new decay channels may open up. One example of the latter is the bound-state beta decay ( $\beta_b$ ). Different from an ordinary  $\beta^-$  decay, the electron is not emitted into continuum but occupies one of the free bound orbitals. To date,  $\beta_b$  decay has been measured for 5 nuclides ( $^{163}\text{Dy}^{63+}$ ,  $^{187}\text{Re}^{87+}$ ,  $^{205}\text{Hg}^{80+}$ ,  $^{206,207}\text{Tl}^{81+}$ ), providing—among other important results—the first  $\beta_b/\beta^-$  ratio that can be compared to time-mirrored EC/ $\beta^+$  ratios [128]. Very demanding is the measurement of the  $\beta_b$  of  $^{205}\text{Tl}^{81+}$ , which is important for the determination of the pp-solar neutrino capture probability into the 2.3 keV state of  $^{205}\text{Pb}$  and can also be used to constrain the very end of the s-process (slow neutron capture) nucleosynthesis.

Excellent examples illustrating the importance of the interplay of atomic and nuclear structure in describing weak decays are provided by first experiments addressing allowed Gamow–Teller EC decays in H- and He-like ions [129]. The EC decay rate in H-like  $^{140}\text{Pr}^{58+}$  and  $^{142}\text{Pm}^{60+}$  ions was found to be about 50% larger than in the respective He-like ions. This result is explained by considering the conservation of the total (nucleus + leptons) angular momentum and the defined helicity of the emitted electron neutrino [129]. A surprising consequence of the latter is the disabled Gamow–Teller  $1+ \rightarrow 2+ \text{EC}$  transitions in H-like  $^{122}\text{T}^{52+}$  ions [129]. By selecting specific nuclei and transitions, forbidden decays and other subtle effects in weak decay can be addressed in the future. One specific example is  $^{111}\text{Sn}$ , where, by studying  $\beta$  decay rate in bare and H-like ions, first direct measurement of electron screening in  $\beta$  decay can be achieved [129].

Concerning the electromagnetic decays, the atomic charge state can also have a significant influence on the decay rate. It is straightforward that the de-excitation of nuclei via internal conversion (IC) is disabled in fully-ionized nuclides. A new decay mode, the bound-state internal conversion (BIC) [130], can open up in HCRs. Here, an excited nuclear state resonantly transfers its excitation energy to a bound electron which is excited to a bound atomic level at a higher energy. The time-reversed processes for IC and BIC are respectively the nuclear excitation by electron capture/transition (NEEC/T). The latter exotic decay modes are being searched for many decades. They may play an essential role in the population of nuclear excited states in

plasmas, which in turn are the reason for the so-called stellar enhancement factors in nucleosynthesis modeling. Furthermore, an effective induced de-excitation of a nuclear isomer through NEEC/T process is one of the dreams for the application of nuclear isomers for energy storage. A first observation of the NEEC process has been reported in 2018 [131] and calls for an independent verification. Suggestions for searches of other exotic decay modes, like Pauli-forbidden transitions and bound electron–positron de-excitations, have been proposed and await their realization [132].

The second research subject is DR on HCRs [129]. The DR spectra of the in-flight generated Li-like  $^{237}\text{U}^{89+}$  and  $^{234}\text{Pa}^{87+}$  ions have been obtained [133]. The resonant nature of the DR process, which is sensitive to nuclear quantum numbers, might be used to select/purify nuclides of interest from unresolved contaminants [133]. This may be employed to investigate the lowest-energy isomeric states ( $^{229}\text{Th}$ ,  $^{235}\text{U}$ ) [134]. The experimental verification of the existence of the ‘nuclear clock’ isomeric state in  $^{229}\text{Th}$  [135] makes its future extraction and trapping highly relevant. It is also interesting to measure the lifetime of  $^{229}\text{Th}$  isomeric state dependent on the atomic charge state, that is with enabled/disabled hyperfine splitting (HFS).

The last application of HCRs addressed here are the astrophysical reactions, where the nuclear reaction rate is deduced through normalizing to the significantly better known theoretical atomic K-REC cross-section. The first proton capture reactions were performed on  $^{94}\text{Ru}^{44+}$  and  $^{124}\text{Xe}^{54+}$  stable nuclides [136]. In the latter case, the center of mass energy as low as 6 MeV/u has been achieved [137] thus approaching the Gamow window of the astrophysical p-process (proton capture process). The available experimental data are scarce and such investigations are therefore highly demanded.

*Current and future challenges.* Experimentally, precision investigations on HCRs are complicated since the exotic nuclides have to be produced in a specific high atomic charge state and then be purified from inevitable contaminants [128, 129]. Furthermore, except for very short lifetimes, all experiments require HCRs to be stored for an extended period of time in a preserved atomic charge state. The experimental studies with HCRs are presently routinely conducted at heavy-ion storage rings. We note though, that there are proposals for studying decays of HCRs in electron-beam ion traps (EBITs). Therefore, the main challenges are connected with the development of trapping devices, EBITs and storage rings, connected to radioactive-ion beam facilities. Furthermore, different experiments require different energies and sophisticated beam manipulations. All experiments count on excellent quality of electron-cooled ion beams.

To keep HCRs stored, the detectors must be non-destructive or intercept reaction products at special locations defined by the storage ring ion-optics. Since the experiments are conducted on rare ion species, an essential goal is to improve sensitivity and efficiency of detectors, ideally up to ultimate sensitivity to individual ions and 100% efficiency. One example of the latter is illustrated in figure 19, where the



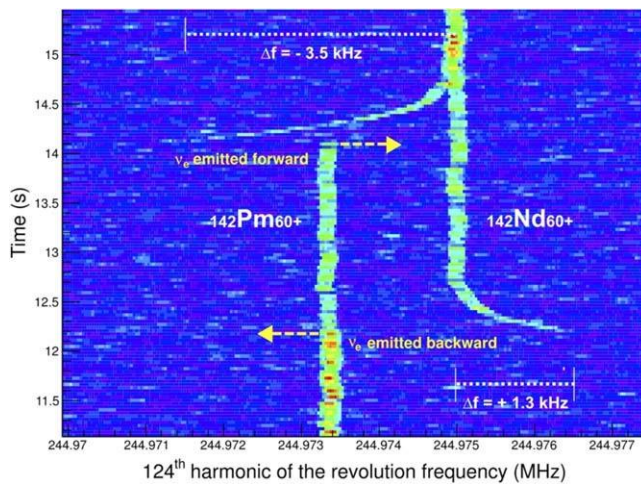


Figure 19. Two electron capture decays of H-like  $^{142}\text{Pm}^{60+}$  ions measured by a resonant Schottky detector in the ESR at GSI [129]. The disappearance of each  $^{142}\text{Pm}^{60+}$  ion and a correlated in time appearance of daughter  $^{142}\text{Nd}^{60+}$  ion is seen. The curved traces correspond to the electron cooling of the recoil energy due to the neutrino emission. The lengths of the curved traces and the sign provide information on the direction and longitudinal component of the recoil momentum [129]. Reprinted from [129] Copyright 2013, with permission from Elsevier.

novel resonant non-destructive Schottky detector is applied to detect EC decays of each stored H-like  $^{142}\text{Pm}^{60+}$  ion [129].

For the particle detectors, the electron-cooled beams have tiny sizes so as the hit area on the detectors. Furthermore, the experiments at lower energies need detectors to be located directly in the ultra-high vacuum environment of a storage ring which is often a severe technological challenge [136, 137].

The relevant center-of-mass energies for astrophysical p-process are 2–6 MeV/ $u$ . Efficient slowing down to these energies of HCRs produced at high energies is yet a challenge [117]. Ultra-pure, thin, internal gas-jet targets are needed. The handling of low-energy beams interacting with gas targets, background due to Rutherford scattering, cooling efficiency, duty cycles, etc are still to be investigated. If successful, even lower energies relevant for, e.g. rp-process (rapid proton capture process) can be envisioned. So far only proton capture reactions were addressed. However, all kinds of proton and alpha induced reactions are of high interest.

#### Advances in science and technology to meet challenges.

Presently there are only two operational heavy-ion storage rings capable of performing relevant experiments. These are the experimental storage ring (ESR) at GSI in Darmstadt and the experimental cooler-storage ring at IMPCAS in Lanzhou [128, 129]. However, both rings are designed for a routine operation at high, several hundred MeV/ $u$ , energies. Although the ESR is capable of slowing the ions down to energies as low as 3 MeV/ $u$ , there is an obvious need for dedicated low-energy storage rings. At GSI, the CRYRING@ESR project is being finalized ([117], section 19). Several pilot experiments have been approved to run in the near future.

In addition to ESR and CRYRING, the new-generation Facility for Antiproton and Ion Research (FAIR) will add collector ring and high-energy storage ring (HESR) ([128, 129], section 19). Mainly due to significantly increased secondary beam intensities from the new powerful radioactive ion-beam facility Super-FRS, various studies of decays of HCRs will become possible, especially for nuclides relevant for astrophysics. Furthermore, the HITRAP facility will enable HCRs at rest (section 19). With all these new trapping devices, GSI/FAIR will offer HCRs in a wide range of energies from about at rest (HITRAP) throughout to about 5 GeV/ $u$  (HESR) (section 19).

In China, High-Intensity Accelerator Facility (HIAF) is being planned [138]. This complex will include several storage rings and versatile experimental capabilities.

A unique project to install a low-energy storage ring at ISOLDE/CERN has been proposed [134]. Such a ring would enable a broad range of experiments with HCRs. One distinct advantage of the project is that HCRs are injected into the ring at the required energy omitting the inefficient deceleration process. In particular, the EC decay of H- and He-like  $^7\text{Be}$  would be measured, which is important for constraining the Solar neutrino flux [134]. The project is presently postponed.

A new storage ring facility R3 has been constructed behind the fragment separator at RIKEN in Japan. Atomic mass measurements and lifetimes of very exotic HCRs are planned there [138].

**Concluding remarks.** The interest in HCRs is found at the intersection of atomic, nuclear, and plasma physics. The precision investigations with HCRs allow for investigating basic phenomena under very clean experimental conditions where the atomic charge state and the corresponding quantum numbers are well-defined. Thus, the complex processes found in hot and dense plasmas can be constrained.

Addressed here are the decays of HCRs, which are extremely sensitive to the interplay of atomic and nuclear structure. Furthermore, DR and reaction studies on HCRs have huge discovery potential. Left aside are atomic mass measurements [138]. All measurements will profit dramatically from new possibilities offered by the next-generation accelerator complexes. Especially the low-energy storage rings and traps will boost the research field in near future [117, 134].

#### Acknowledgments

This short paper is dedicated to my friends Paul Kienle and Fritz Bosch who passed away much too early. It is based on previous publications of our colleagues from several storage ring collaborations. To all of them I am deeply obliged. Discussions with K Blaum, C Brandau, I Dillmann, H Geisel, J Glorius, C Kozhuharov, R Reifarh, M S Sanjari, M Steck, Th Stöckler, D Schneider, P M Walker, P J Woods, T Yamaguchi and Y H Zhang are greatly appreciated. This work is supported by the European Research Council (ERC) under the EU Horizon 2020 research and innovation programme (ERC CG 682841 'ASTRUM').

### 13. QED in strong fields

Vladimir Shabaev

St. Petersburg State University, Russia

*Status.* Basic principles of QED were formulated to the beginning of 1930s by merging quantum mechanics with special relativity. The discovery of the Lamb shift in 1947 stimulated theorists to complete the creation of QED by developing the renormalization technique. Till the beginning of 1980s tests of QED were mainly restricted to light atomic systems where the calculations were performed in the weak-field approximation, which corresponds to small values of the parameter  $\alpha Z$  ( $\alpha$  is the fine structure constant and  $Z$  is the nuclear charge number). A unique opportunity to test QED in a strong-field regime, which requires calculations without any expansion in  $\alpha Z$ , appeared when high-precision experiments with heavy few-electron ions became feasible.

High-precision tests of QED effects with HCIs were first performed for the binding energies. The ground state Lamb shift in H-like uranium, which is defined as a difference between the exact energy and the point-nucleus Dirac energy, was measured to amount 460.2(4.6) eV [139]. The comparison of this experiment with the theoretical result, 463.99(39) eV (see [140] and references therein), provides a test of QED at the strong Coulomb field on a 2% level. Higher accuracy was achieved in experiments with Li-like ions. The present status of theory [141] and experiment [142] for the  $2p_{1/2}-2s$  transition energy in Li-like uranium provides a test of QED on a 0.2% level. For both H- and Li-like uranium ions the theoretical uncertainty is presently defined by some uncalculated contributions of two-loop QED diagrams (figure 20) and by an uncertainty of the nuclear charge radius.

To date we have a number of high-precision measurements of the HFS in heavy H-like ions (see, e.g. [143] and references therein). The main goal of these experiments was to test QED in a unique combination of strong electric and magnetic fields. But, because of a large theoretical uncertainty due to the nuclear magnetization distribution correction (so called Bohr–Weisskopf effect), it turned out that the QED tests are possible only via studying a specific difference of the HFS values of H- and Li-like ions [144]. The recent measurements of this difference in Bi [143] revealed a large discrepancy between experiment and theory. This discrepancy was explained in [145] by an incorrect value of the nuclear magnetic moment which was widely used in literature. New calculations of the magnetic shielding factor and new measurements of the nuclear magnetic moment in  $^{209}\text{Bi}(\text{NO}_3)_3$  and  $^{209}\text{BiF}_6$  [145] lead to good agreement between theory and experiment. However, more precise measurements of the nuclear magnetic moments and the HFS values are needed to provide stringent QED tests.

High-precision measurements of the g factor of H- and Li-like low- and middle-Z ions (see, e.g. [146] and references therein) have provided stringent tests of the QED effects in presence of a magnetic field. Combined with the related theoretical predictions, these experiments have also provided the most precise determination of the electron mass [146].

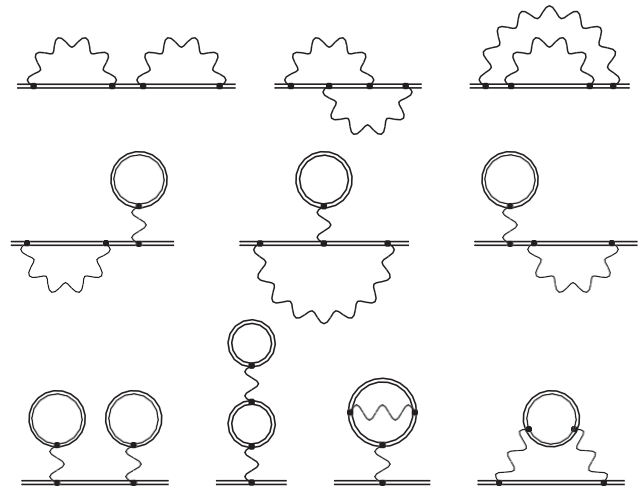


Figure 20. One-electron two-loop Feynman diagrams which contribute to the Lamb shift. The double line represents an electron propagating in the Coulomb field. The wavy line indicates a virtual photon.

Recently [147], the isotope shift of the g factor of Li-like calcium ions was measured. This experiment allowed the first test of the relativistic theory of the nuclear recoil effect on the g factor of highly charged Li-like ions.

One of the most interesting and intriguing issues of modern fundamental physics is related to tests of QED at supercritical fields. According to the QED theory, a static and spatially uniform electric field should create electron–positron pairs, provided its strength is close to the Schwinger limit,  $E = 1.3 \times 10^{16} \text{ V cm}^{-1}$ . One might expect that the desired field can be achieved using strong laser fields. Recent developments of the laser technologies have triggered a great interest to calculations of the pair production in strong fields, especially for the case of colliding laser pulses. However, the maximal field strength which can be achieved by modern lasers is by 3–4 orders of magnitude smaller than the Schwinger limit. Another access to QED at supercritical fields can be gained in Coulomb field created by an extended nucleus with the nuclear charge number exceeding the critical value,  $Z_c = 173$ . At this critical value, the 1s level should ‘dive’ into the negative energy Dirac continuum. If the 1s level was empty, its diving results in spontaneous creation of two positrons. Since there is no nuclei with so high  $Z$ , the only way to access the supercritical regime is to study low-energy collisions of heavy ions with the total nuclear charge larger than the critical value. The corresponding experiments were performed many years ago at GSI (Darmstadt). However, for a number of reasons [148], these experiments could not prove or disprove the spontaneous pair creation. Plans to return to investigations of this phenomenon at FAIR (Germany), HIAF (China), and NICA (Russia) facilities have triggered new theoretical studies of relativistic quantum dynamics at low-energy heavy-ion collisions.

*Current and future challenges.* Despite the great progress in the Lamb shift experiments with heavy few-electron ions, further work on improving the precision of the 1s Lamb shift in heavy H-like ions is needed. The nearest principal goal consists in

gaining the 1 eV accuracy in the 1s Lamb shift in H-like uranium. The Lamb shift in heavy H-like ions should be considered as the main reference point for QED tests at strong fields. This is due to the simplicity of H-like ions compared to few-electron ions as well as the simplicity of the Lamb shift compared to other QED effects. These tests are needed to prove the non-perturbative QED methods, which then can be applied to calculations of other important properties of HCIs. From the theoretical side, to improve the accuracy of the ground-state Lamb shift, the last two diagrams in figure 20 have to be calculated beyond the free-electron-loop approximation. Also the rigorous evaluations of the second-order two- and three-electron QED contributions in highly charged Be-like ions are urgently needed to meet the experimental accuracy achieved in recent measurements of the transition energies.

Accurate measurements of the HFS transition energies in H- and Li-like ions must be accompanied by independent high-precision determinations of the nuclear magnetic moments. From the theoretical side, the corresponding calculations for B-like ions including all second-order two- and more-electron contributions are required. Together with the corresponding calculations for H- and Li-like ions, these calculations can also be used for tests of QED in a combination of the strongest electric and magnetic fields.

High-precision measurements of the  $g$  factors of heavy H-, Li-, and B-like ions are anticipated in the near future at the Max-Planck Institut fuer Kernphysik (MPIK) in Heidelberg and at the HITRAP/FAIR facilities in Darmstadt. Combined with the related theoretical predictions, these measurements should provide stringent tests of QED at strong fields. It was recently shown that the study of the  $g$  factors of H- and Li-like lead ions can provide a test of the QED nuclear recoil effect on a few-percent level. This would give the first test of QED at strong-coupling regime beyond the Furry picture. Measurements of the  $g$  factor of ions with non-zero nuclear spin will result in the most precise determinations of the nuclear magnetic moments. Also an independent determination of the fine structure constant from the  $g$ -factor experiments with heavy H- and B-like ions is feasible, provided the corresponding theoretical calculations are performed to the required accuracy.

The study of QED at supercritical fields created in low-energy heavy-ion collisions demands developments of

theoretical methods which allow to investigate in all details such processes as pair production, electron excitation and ionization, charge transfer, and x-ray emission. Special attention should be paid to calculations focused on finding signatures of the 'diving' scenario which inevitably leads to the spontaneous pair production.

#### *Advances in science and technology to meet challenges.*

The progress in high-precision QED calculations of HCIs was always stimulated by the related progress in experiment. No doubts that any further substantial progress on the Lamb shift experiments with heavy ions, which is one of the main topics of a number of nowadays conferences and workshops, will motivate theorists to advance the calculations of two-loop QED contributions in ions with one and more electrons. Precise measurements of the  $g$  factors of heavy few-electron ions at MPIK in Heidelberg and at GSI/FAIR in Darmstadt will stimulate theoretical calculations of the corresponding higher-order QED and nuclear effects. The recent advances in calculations of the pair-creation probabilities in low-energy heavy-ion collisions beyond the monopole approximation give a hope for further developments of theoretical two-center methods, which are needed to study in details the quantum dynamics of electrons in strong and supercritical fields.

*Concluding remarks.* High-precision measurements with HCIs, combined with the corresponding theoretical calculations, provide stringent tests of non-perturbative QED methods. These theory and experiment can be also used for the most precise determinations of the electron mass, nuclear magnetic moments, nuclear radii, etc. They have also a potential for an independent determination of the fine structure constant. The study of quantum dynamics of electrons in low-energy heavy ion collisions can provide a unique possibility for tests of QED in supercritical regime.

#### **Acknowledgments**

This work was supported by the Russian Science Foundation (Grant No. 17-12-01097).



## 14. Interactions of HCIs with clusters

Henrik Cederquist and Henning Zettergren

Stockholm University, Sweden

*Status.* The title ‘Interactions of HCIs with clusters’ makes most ICPEAC participants think about situations where atomic ions, stripped of many of its electrons, collide with some neutral aggregation of matter—a cluster. Typically, ICPEAC-clusters have consisted of metal atoms [149], noble gas atoms [150], or small molecules [151]. Carbon clusters and in particular  $C_{60}$  have also often been used as targets. A recent trend is to study interactions with clusters of larger molecules where the bonds between the individual molecules are much weaker than within the molecules themselves.

Examples are loosely bound clusters of biomolecules [152], clusters of  $C_{60}$  [153] or PAHs—Polycyclic Aromatic Hydrocarbon molecules [154]. The interest in the latter two targets is partly motivated by astrophysical observation of characteristic emission in the micrometer wavelength region, where  $C_{60}$ , PAHs and other aromatic molecules are known—or expected to—play important roles. Here we will mainly focus on collisions between *slow* highly charged, positive, ions and neutral clusters of molecules. In this context a collision is slow when the velocity of the ion is lower than typical velocities of the outermost target electrons. As indicated in figure 21, one or several electrons may be transferred from the cluster to the ion already at large distances. The higher the charge state,  $q$ , the larger the ion-cluster distance at which electron transfer processes may occur and the larger the cluster ionization cross section. The essence of this behavior is well described by over-the-barrier models in which one considers the potential energy barrier for an electron moving in the electric field created by the ion, the active electron itself, and the ionized cluster (see [155] and references therein). These considerations become particularly simple for surfaces and spherical or close to spherical targets and it has been shown that  $C_{60}$  can be modeled as a classical metal sphere [155]. The same model also explains the high charge mobility within clusters of fullerenes and the ultrafast (sub-femtosecond) timescales for such processes [155, 156]. At a first glance, one would expect that distant electron transfer processes would lead to very little heating of the cluster, but with HCIs strong heating of individual molecules emitted from clusters have been observed [154]. This is most likely due to heating during cluster Coulomb-explosion processes [154]. In penetrating collisions, the incoming HCI is first neutralized and may then transfer considerable amounts of energy in electronic and nuclear stopping processes as it passes through the cluster. In particular, the projectile may knock out single atoms in prompt Rutherford-like atom–atom scattering processes (sub-femtosecond timescale). This gives highly reactive molecular fragments, which are likely to bind to other molecules or fragments in the cluster breakup phase (see [157] and references therein). The fast knockout processes are non-statistical in nature as the knockout atom is removed before local excitations (at the

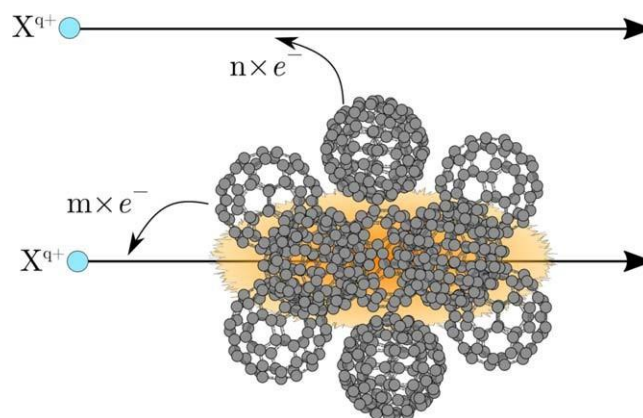


Figure 21. Schematic of distant and penetrating (close) collisions between a highly charged ion and a cluster of  $C_{60}$  fullerenes. Distant collisions lead mainly to charge transfer with little heating of the target, but in penetrating collisions much more damage can be inflicted through nuclear and electronic stopping processes.

knockout site) have time to distribute over the whole molecule. Here, a key point for the survival of molecular-growth products is that the excess energy is shared among many of the molecules in the cluster. This scenario is supported by close agreement between experimental results and classical molecular dynamics (MD) simulations assuming neutral projectiles. In these simulations, trajectories of all individual atoms in the system are followed for a few picoseconds and the agreement with the experimental results then indicate that growth products survive also on typical experimental time scales of microseconds (see [157] and references therein). Given the interest from the astrophysics community for, for example, carbon-based molecules and their formation and destruction in interstellar space, planetary atmospheres and supernova shock waves—and for understanding fundamental molecular growth processes as such—it is of great interest to study the long-term stabilities of such fragments and to study how they react with neutral, charged, and multiply charged molecules or clusters. Related to this, it will be most interesting to investigate the role of the incident ion charge in situations like the one depicted in figure 21.

*Current and future challenges.* So far, most ion-cluster collision studies have been performed with keV atomic ions colliding with thermal neutral cluster targets and where distributions of cluster sizes always have been rather wide. One challenge is thus to perform experiments with *size-selected* clusters. Such experiments will make it possible to control internal cluster temperatures and to study how size-selected clusters interact with atoms, molecules, or other clusters in completely new velocity domains using merged-beams techniques. A further challenge on the experimental side concerns spectroscopic studies of molecular growth products resulting from close interactions between clusters of molecules and ions in both high and low charge states. On the theoretical side, long-term goals are to simulate knockout driven intra-cluster reactions in a wide range of systems using



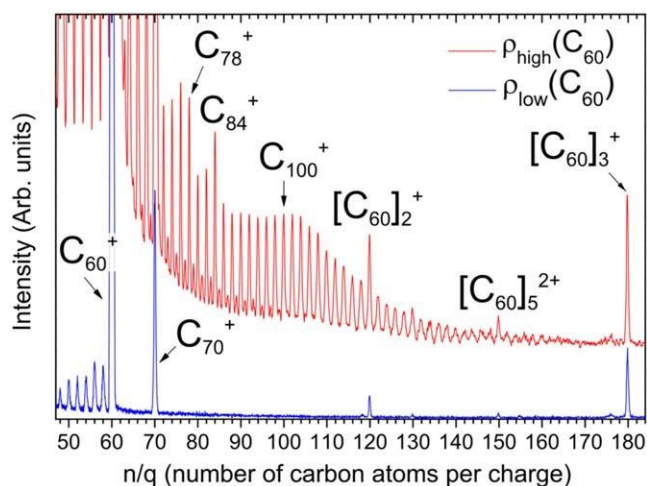


Figure 22. Mass spectra from collisions between 400 keV  $\text{Xe}^{20+}$  ions and neutral  $[\text{C}_{60}]_k$  clusters. The red data is for experimental conditions that give, on average, larger cluster sizes  $k$  than the blue data. Reprinted from [158], with the permission of AIP Publishing.

quantum mechanics instead of classical force fields, and to include the effects of electronic excitations and the incident ion charge state in the simulations. These are extremely challenging tasks but some steps in this direction have already been taken [157].

Studies of ions interacting with aggregates of carbon-based matter relates to one of the main issues in fullerene research: How are the classical fullerenes predominantly formed and why is it that  $\text{C}_{60}$  and  $\text{C}_{70}$  become so dominant in so many different types of experimental situations and in nature? In figure 22, which is adapted from [158], parts of mass spectra recorded for collisions between 400 keV  $\text{Xe}^{20+}$  and small (blue spectrum) and large (red spectrum) neutral clusters of  $k$   $\text{C}_{60}$  molecules,  $[\text{C}_{60}]_k$ , are shown. In both cases there are broad size-distributions of neutral clusters before the collision but with a larger average target cluster size in the experiment yielding the red spectrum. The much wider distribution of *reaction products* in the red spectrum is particularly striking. There are also enhanced intensities for so called magic fullerenes like, for examples,  $\text{C}_{84}^+$  and  $\text{C}_{70}^+$ . These results are consistent with a picture in which hot large giant fullerenes form in confined hot carbon plasma along projectile ion trajectories through the cluster. The  $\text{C}_{60}$  molecules that are not directly struck by the projectile mostly remain intact initially and are then either evaporated from the heated system or react with, e.g. carbon atoms or molecules from the plasma. Hot giant fullerenes may then decay by fragmentation and photon emission and some of them will shrink towards smaller sizes including, for examples,  $\text{C}_{84}^+$ ,  $\text{C}_{78}^+$ ,  $\text{C}_{70}^+$ , and  $\text{C}_{60}^+$ . Such magic fullerenes have somewhat higher stabilities than their neighbors. It has been suggested, however, that the large abundances of  $\text{C}_{60}$  in many different situations rather is due to exceptionally fast radiative cooling

processes. Products like  $[\text{C}_{60}]_3^+$  in figure 22 are due to multiple ionization of much larger  $[\text{C}_{60}]_k$  clusters followed by emissions of many intact  $\text{C}_{60}$  molecules. A current challenge is to investigate molecular growth starting from much smaller carbon-based molecular building blocks and also to study the conditions for  $\text{C}_{60}$ -formation as functions of cluster size, cluster charge, mass and velocity, a future challenge is to study how internally cold cluster ions in different charge states interact with neutrals and with other ions at subthermal and higher collision energies.

*Advances in science and technology to meet challenges.* It is of great interest to improve, e.g. the experiment behind the spectra in figure 22. As has already been indicated above, this can be done by colliding *size-selected*  $[\text{C}_{60}]_k^+$  clusters and clusters of other carbon-bearing molecules with atomic targets. This will yield cluster-size specific distributions of reaction products and, in addition, possibilities to register several reaction products in coincidence for each cluster size. Furthermore, one could prepare beams of ultracold  $[\text{C}_{60}]_k^+$  clusters inside HNDs, which would lead to a much better definition of the cluster structure than in earlier experiments. By placing a gas target on injection lines of cryogenic electrostatic ion storage devices it will become possible to study stabilities and photo-absorption properties of fragments and molecular growth products resulting from single collisions in the target gas. In some ion storage devices, it may also become possible to study interactions between internally cold complex (cluster) ions of opposite charge states using merged beams techniques. Interactions between highly charged *atomic ions* and internally cold clusters of molecules can be performed in single-pass merged beams experiments.

*Concluding remarks.* We foresee highly interesting developments where molecular growth processes, and in particular the  $\text{C}_{60}$  formation mechanism are investigated with control of cluster size, charge, internal energy, structure, and velocity for different masses of the target. In these studies, the charge will be carried into the collision by the cluster and it will be crucial to be able to handle the system charge in simulations of reaction processes. Stabilities and optical properties of molecular growth products will be studied with cryogenic electrostatic ion storage devices. In the near future, these devices will allow studies of pairwise interactions between molecular clusters using merged-beams techniques.

## Acknowledgments

This work was supported by the Swedish Research Council through Grants No. 2015-04990 and 2016-0418. Michael Gatchell, Stockholm University and Innsbruck University is gratefully acknowledged for his input and for discussions

## 15. Interaction of HCIs with surfaces and 2D materials

Marika Schleberger<sup>1</sup> and Richard A Wilhelm<sup>2</sup>

<sup>1</sup>Universität Duisburg-Essen, Germany

<sup>2</sup>TU Wien, Austria

**Status.** Nowadays, the modification of solids with ion beams represents the backbone in semi-conductor manufacturing with respect to tuning electrical properties by implantation and shaping surface structures by ion lithography. However, the ever-smaller layer thicknesses and lateral dimensions in modern electronics demands new approaches [159]. Reducing the ion's kinetic energy to confine energy deposition to only a few atomic layers seems to be a straightforward solution, but serious challenges arise from the broad energy spread of the ion sources and when it comes to beam focus at these low energies.

Slow HCIs carry an additional potential energy, which can be even larger than the kinetic energy [160]. Upon neutralization, HCI deposit a large amount of the potential energy in a shallow region at the material's surface and thus feature an ideal tool to tailor properties of surfaces and 2D materials without the need to go to ultralow kinetic energies [161]. It was shown on surfaces of wide band-gap insulators that HCI can induce extremely large sputtering yields of a few thousand atoms per ion or even induce local phase transitions on the nanoscale depending on material properties [162]. For insulators the modification mechanisms are well described by the formation of an inelastic thermal spike, surface melting, and resolidification; or by electronically stimulated desorption (DIET). In general, HCI neutralization leads to heating of the electronic subsystem of the material. A coupling between electrons and phonons heats the lattice on a later time scale. This two-temperature model (TTM) provides an extremely powerful description of the initial energy deposition processes, while details of the electrical and thermal properties of the material play a decisive role for the outcome of the ion impact. This also is the reason why metal surfaces are typically not prone to nano-structuring by HCI, because the deposited energy in the electronic subsystem dissipates in the material before electron-phonon coupling can effectively set in.

When moving towards 2D materials supported by arbitrary substrates, new phenomena already emerge as the non-perfectly matched electronic and lattice subsystems of the substrate decouple the 2D layer [163]. Quantum confinement effects for the excited electrons prevent energy dissipation in the third dimension. This points towards an even more efficient potential energy-driven process leading to modifications similar to those for bulk insulators, and the few experiments conducted so far support this assumption [164, 165]. In the purely freestanding case of 2D materials, where a substrate is entirely absent, one may expect that even metal-like materials become prone to HCI modifications due to quantum confinement effects. However, this has not yet been observed experimentally [166]. In their freestanding

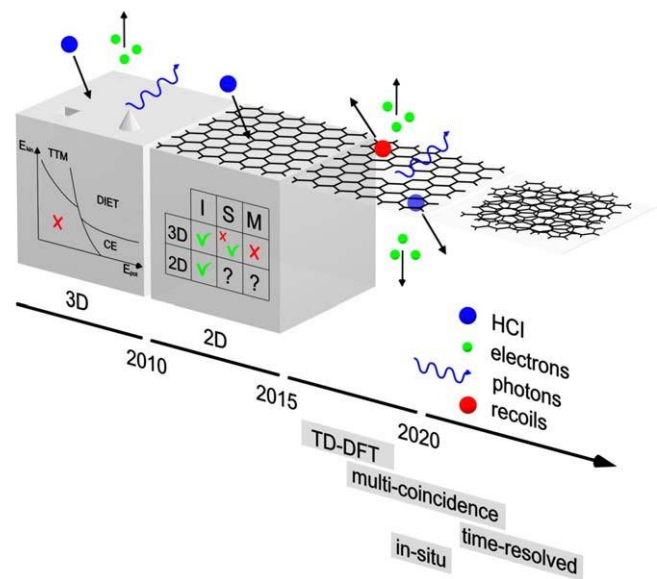


Figure 23. HCI irradiation of surfaces from bulk materials revealed efficient nanostructuring. Possible processes are surface melting (described by TTM), DIET, or Coulomb explosion (CE) depending on the ion's kinetic and potential energies. 3D insulators (I), semi-conductors (S), and metals (M) show different susceptibility to HCI driven modification, whereas further research for 2D materials is needed. In the future, more complex integrated multi-coincidence spectroscopy and *in situ* microscopy in combination with refined theoretical descriptions will reveal details on the interaction mechanisms.

state, 2D materials also constitute a perfect model system to study the material in an (ion-induced) highly non-equilibrium state in unprecedented detail [167]. While the TTM allows for a powerful description of the processes in a thermodynamic sense only, a detailed and quantifiable atomistic model is still missing due to the complexity of the neutralization processes and subsequent surface electron and atom dynamics.

**Current and future challenges.** One of the greatest challenges in HCI irradiation and spectroscopy with 2D materials lies currently in the fact that HCI beams are only available as broad beams. Additionally, the presence of surface contaminations becomes increasingly important. Because 2D materials are surface-only materials, adsorbed hydrocarbons, residuals either from wet-chemical transfer or from the growth substrate despite chemical etching, all affect available measurement techniques, i.e. scanning probe and electron microscopy, spectroscopy of the scattered/transmitted ions, sputtered target recoils, as well as emitted electrons and photons, see figure 23.

Another important problem and research issue are defects in 2D materials. Those have a great influence on the material's structural, optical, and electronic properties, and even sometimes dominate them. The presence of intrinsic defects, i.e. single and multi-atomic vacancies, small and extended rotational defects, grain boundaries, foreign atoms, creases, wrinkles, etc needs to be controlled during all steps of sample preparation, i.e. material growth, transfer onto a substrate, onto another 2D material and/or onto a supportive

grid in case of a suspended sheet. This is why currently homogeneous, defect-free 2D materials cannot easily be produced on the mm-scale.

Some 2D materials are even not stable in air, as e.g. black phosphorous or silicene, and thus require a complicated in-vacuum transfer to an HCI facility and to an analysis device. On top of this, some 2D materials are highly susceptible to damage by electronic excitations, beneficial for HCI induced modification, but hampering atomically resolved electron-based microscopy. In principle, suspended 2D materials allow direct spectroscopy of the ion still in a non-equilibrium state after transmission through the material together with the spectroscopy of emitted secondary particles i.e. sputtered atoms, electrons, and photons. Spectroscopy of (quasi-) particles from the interaction process with a suspended 2D material can give, for the first time, experimental access to the dynamics of ion-induced electronic processes on the femto-second time-scale. However, the current challenge lies in the measurement of all particle energies and momenta, ideally in coincidence, plus the determination of energy retained in the material. To probe even longer time scales, i.e. atomic dynamics in the layer after the ion transmission, a truly time-resolved ion scattering spectroscopy would be needed.

Apart from the experimental difficulties also theory faces serious challenges. The models for ion-solid interaction nowadays adequately describe equilibrium processes, whereas the impact of an HCI on a surface represents a highly perturbative non-equilibrium process. In this regime only little is known about the dynamics of the ion neutralization as well as the kinetic energy loss. However, to model and predict the energy deposition of HCI in various materials, challenges in simulating multi-electron processes must be overcome.

*Advances in science and technology to meet challenges.* To meet the challenges, the integration of HCI facilities into an ultra-high-vacuum (UHV) set-up will be necessary. Currently, some labs are pursuing this path. Further, the combination of HCI beams with electron-based microscopes would allow true *in situ* measurements minimizing the influence of surface adsorbates, even though volatile hydrocarbon molecules are always abundant even in UHV. For small area 2D materials or crystalline grains, the development of focused HCI devices with beam spot sizes well below 1  $\mu\text{m}$  will be advantageous. Some first efforts have been undertaken until now, but further development is heavily needed in this field.

To further complement spectroscopic measurements with data from emitted secondary particles, a reaction microscope

setup suitable to hold a suspended 2D sample will be necessary. To measure the energy retained in the material, a bolometer-type temperature measurement at liquid He temperature could be performed and thus making the full kinematics of energy deposition and emission by the projectile and secondary particles accessible.

To disentangle processes during the ion impact on the material such as its neutralization and primary energy deposition, from processes on much longer time scales, such as atom sputtering and thermalization, a truly time-resolved methodology is required. Whether this will rely on absolute time-resolution or on a stroboscopic technique is currently under debate.

In case of highly perturbative interaction phenomena, new theoretical methods for their description must be developed. The most promising methodologies are based on TD-DFT and hybrid models, i.e. MD simulations for large simulation cells coupled to an electronic temperature bath. While MD can capture atomic motion in large cells for an extended period of time (several nanoseconds), TD-DFT can give ab-initio information on the energy deposition into the electronic system by charge state dependent ion stopping and neutralization. Coupling TD-DFT and MD goes beyond the Born-Oppenheimer-Approximation and therefore represents a powerful tool for situations where the electronic and atomic subsystems are strongly coupled on similar time-scales [168].

*Concluding remarks.* Over recent years HCI-surface interaction studies have moved from 3D to 2D and thus increased drastically in complexity with respect to sample manufacturing, handling, analysis, and ion spectroscopic methodologies, see figure 23. The combination of an increasing number of all-UHV and *in situ* methods, 2D material complexity, as well as multi-coincidence techniques will continue in the future. While simulations will soon be able to describe HCI-surface interaction from the sub-fs to the ns time regime, the next disruptive step in experiments will be the development of truly time-resolved ion-scattering techniques.

## Acknowledgments

MS acknowledges funding by the DFG SFB1242 'Non-Equilibrium Dynamics of Condensed Matter in the Time Domain', project C5. R W acknowledges support from the DFG through project WI 4691/1-1 (no. 322051344). We want to express our gratitude to A Reichert for contributing to the visualization.



## 16. Interaction of HCIs with crystals/solids

Toshiyuki Azuma

RIKEN, Japan

**Status.** Ever since energetic heavy ions have been available, their interaction with solids has been an important topic to be explored. Energy transfer and damage to the solid are especially critical to material and biological sciences. HCIs in solids experience successive collisions with the constituent atoms of the solid, leading to the formation of tracks in the solid. This is a far cry from the single-collision conditions for ion–atom collisions in the gas phase. Nowadays a large amount of information has been compiled for ion-induced effects in solids including electronic excitation and elastic collisions. The traveling ions' behavior such as ionization, EC, and excitation has also been investigated in detail. Nevertheless, owing to the difficulty in observing the ion state in the solid *in situ*, many issues still remain unresolved.

For crystal targets, a very unique property known as channeling is available. By being guided by the crystal potential, traveling ions have a chance to pass through the open space of the crystal without hard collisions with atoms. This phenomenon has been widely applied as a powerful tool for diagnostics of crystal quality.

From the viewpoint of atomic collision physics, one of the most exciting phenomena in crystal targets is the Okorokov effect, often also called RCE. Ions passing through a periodic lattice (ordered rows or planes) of a crystal feel a time-dependent perturbation of the crystal potential. When one of the frequencies of the perturbation corresponds to the difference of internal energy levels of the ions, transitions may take place. Theoretical prediction of this effect can be traced back more than 50 years to an idea proposed by Okorokov [169]. Experimentally concrete observation was reported by Datz *et al* [170]. They observed this phenomenon by measuring the change of the charge state of H-like or He-like HCI ( $Z = 5-9$ ) in the MeV/u energy range channeling through a thin Au or Ag crystal at the resonance condition of the  $1s-2p$  transition of the HCIs. The resonantly excited electron in the  $2p$  state is more easily ionized by collisions with atoms in the crystal, leading to an enhancement of ionization under the resonance condition. The high ion energies used and the thinness of the crystals were two major reasons for the successful observation; otherwise charge exchange after resonance obscures the effect. In this experiment under the axial channeling condition, the ion energy was scanned to match the resonance condition, which was an experimentally difficult procedure for accelerator operation. They then proposed a new idea to satisfy the resonance conditions, what we now call 2D-RCE [171]. The excitation was induced by the two-dimensional periodic array of crystal strings under planar channeling conditions, where the resonance condition was achieved just by tilting the crystal with a rotating axis perpendicular to the crystal plane, enabling the precise scan of the resonance profile.

Since then, the experiments have made progress by adopting higher energy HCIs as shown in figure 24(a). In 1998 using HCIs with much higher energy, i.e. 390 MeV/u,

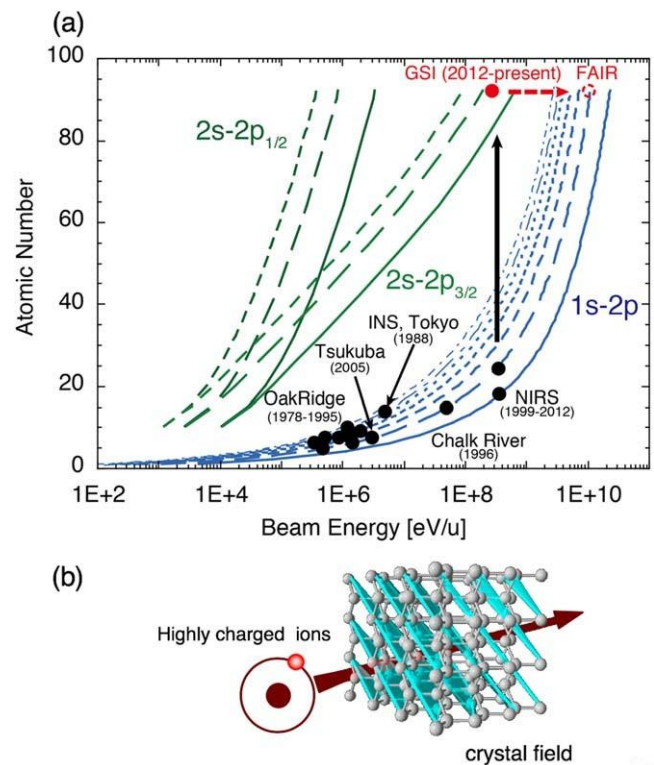


Figure 24. (a) Relationship between beam energy and atomic number required to observe the RCE process. The lines are calculated for the  $1s-2p$  transition in H-like ions, and the  $2s-2p_{1/2}$  and  $2s-2p_{3/2}$  transitions in Li-like ions. (b) Schematic view of highly charged ions passing through a periodic structure of crystals. Reprinted figure with permission from [176], Copyright 2013 by the American Physical Society.

supplied from the HIMAC synchrotron in Japan, this type of experiment was performed with H-like  $\text{Ar}^{17+}$  combined with a thin Si crystal [172]. The oscillating frequency of the periodic crystal fields in the projectile's frame are equivalent to that of about 3 keV photons. The usual atomic collision processes, especially EC, are indeed suppressed and highly resolved resonance profiles with rich structure have been observed. From a series of successive experiments clear DC-Stark effects to the excited levels due to strong static crystal electric fields of the order of GeV/cm and the corresponding evolution of the wavefunction depending on the position of the ions in the crystal were revealed. At this stage, it was recognized that not only in the channeling condition but also in the non-channeling condition, such highly energetic ions can penetrate the crystal without suffering from severe collisions anymore. Taking full advantage of this fact, a great leap in the research happened. As shown in figure 24(b), in the non-channeling condition, ions have a chance to be excited by the three-dimensional periodic array of the crystal plane, which we call 3D-RCE [173]. This phenomenon was confirmed again by H-like  $\text{Ar}^{17+}$  ions at an energy of 391 MeV/u passing through a 1  $\mu\text{m}$  thick silicon crystal, and resonance profiles observed by the charge state distribution or the x-ray emission yield are much narrower than those of planar channeling ions (2D-RCE) due to the absence of the large DC Stark shift caused by the planar potential.



The HCIs traveling through a crystal target feel a variety of periodic crystal fields including higher harmonic components simultaneously. The direction of research then naturally headed for double resonances using these different oscillating fields. The double resonance is a key technique in many fields like quantum optics or pump-probe spectroscopy in chemistry, and it has become reality in the x-ray energy region. Under the same configuration of the ion trajectory and the crystal direction, the double resonance condition of 3D-RCE can be satisfied by scanning two parameters, rotation angles of the crystal, which are in a sense analogous to two-color energy tunable x-ray laser excitation. One example of successful double resonance experiments is selective production of the doubly excited state in He-like  $\text{Ar}^{16+}$  ions [174]. The  $\text{Ar}^{16+}$  ions were resonantly excited sequentially from the ground state to the  $1s2p$  state and then the  $2p^2$  state by the (X–X) double resonance, which was confirmed by Auger electron emission. The other example is a demonstration of the Autler–Townes doublet as a novel type of coherent interaction of atoms not with photons but with a periodic crystal field [175]. It was observed by the (X–VUV) double resonance. The states strongly coupled in the VUV region were probed by the excitation in the x-ray region. The characteristic spectra are well interpreted by an analogy of the dressed atom concept often adopted for atom-photon interactions.

*Current and future challenges.* Figure 25 schematically shows that, as the energy of the HCI beam increases, the resonance peaks become sharpened due to the lack of the collisions of HCI with atoms in a crystal which are the usual origin of decoherence effects. The typical resonance width,  $\Delta E/E$ , for RCE of a few 100 MeV/u HCIs is of the order of  $10^{-3}$ . This leads to a new idea that RCE may be a new tool for high precision spectroscopy of the Lamb shift in the energy levels of HCI to check the bound state quantum electro dynamics (BS-QED). To explore this feasibility, experiments using uranium ( $Z = 92$ ) ions were started at the accelerator and storage-ring facility of the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany using the heavy-ion synchrotron (SIS) [176]. The  $2s-2p_{3/2}$  transition of 4.5 keV in 192 MeV/u Li-like  $\text{U}^{89+}$  ions was excited, and the resonance profiles were measured by the de-excitation x-ray yield. Clear resonances with a width of 4.4 eV were demonstrated. However, it was also realized that the resonance width was affected by the energy distribution of the provided ion beam. Then, narrowing of the ion velocity was achieved by introducing the electron cooling technique. The He-like  $\text{U}^{90+}$  ions extracted from SIS were injected into an ESR ion storage ring, where the stored ions merged with a mono-energetic electron beam for electron cooling. The resulting Li-like  $\text{U}^{89+}$  ions produced via EC were extracted and guided to the crystal target. As a result, the resonance width was narrowed down to 1.4 eV with a Lorentzian distribution. The next challenge in the near future is to determine the absolute energy within 1 ppm. Recent HFS measurements of Bi ions stored in the ESR ring was successful in determining the ion absolute energy by

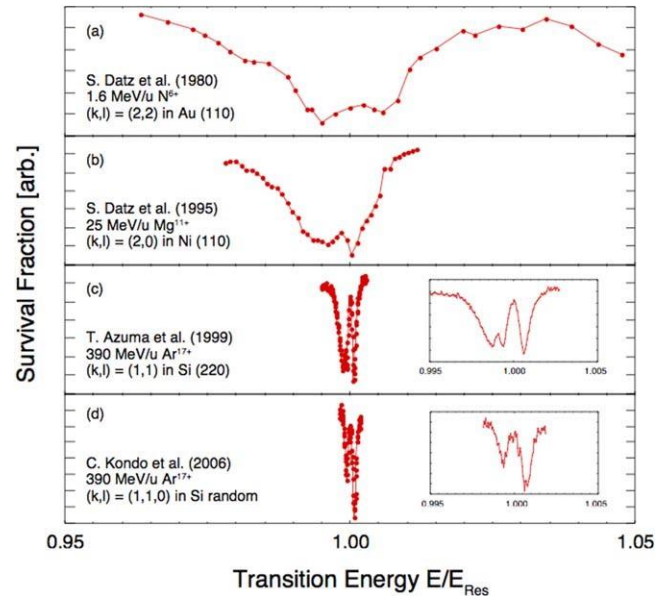


Figure 25. Narrowing of the relative resonance width  $E/E_{res}$  for the ions with higher energy.

precisely measuring the electrode voltage for the electron cooler [177]. This technique will be adopted in the coming experiments.

A new synchrotron SIS100 is under construction in the ongoing FAIR project as introduced in section 19 in this Roadmap. This will provide 1 GeV/u uranium beams, making it within reach to determine the contribution of the  $1s$  Lamb-shift ( $\sim 460$  eV) in the  $1s-2p_{3/2}$  transition of 140 keV using the RCE technique. A HESR is also planned for storing cooled beams at energies of up to a few GeV/u, and this may open a chance to perform new RCE experiments. This technique is in principle can be applied for any specific ions or transition levels. Especially, the double resonance technique will be useful to prepare metastable states. Alignment of HCIs by taking an advantage of the linearly-polarized nature of the perturbation of the crystal potential will be applied to high- $Z$  ions, where the relativistic effect like the Breit interaction plays a significant role in polarization of the emitted x-rays. Nuclear excitation of low-lying levels of nuclei including nuclear quadrupole resonance is also within scope.

Apart from RCE with high-energy ions, an alternative approach to suppress decoherence is using the surface channeling condition where ions at glancing incidence to the crystal surface experience mirror reflection above the surface to avoid the collision process with surface atoms. This idea was indeed verified by two groups [178], and extensive application of this technique is expected.

*Advances in science and technology to meet challenges.* As already described, critical new techniques and devices were introduced, when important progresses in dynamics and spectroscopy were made, like higher energy ion accelerators, electron cooling techniques, and extremely thin crystals with good quality. In the future this trend will never change.

Finally, it is also noted that, as a new approach, magnetic resonance of traveling neutral alkali atoms were achieved in the microwave frequency region using artificial periodic structures [179]. This technique also has the potential for a variety of future applications.

*Concluding remarks.* Understanding of the interaction of HCI with crystals has been deepened dramatically for the last decades far beyond a diagnostics tool for crystal quality or damage. RCE utilizing a periodic crystal field has offered a new paradigm in atomic collisions involving other research

fields. Its significance will be strengthened in the future as an alternative approach to lasers for exploring spectroscopy and dynamics of HCI.

## Acknowledgments

I would like to acknowledge valuable collaborations with Y Nakano, Y Nakai, A Hatakeyama, K Komaki, Y Yamazaki, A Demian-Bräunung, T Stöhlker, and many coworkers.

## 17. COMs and irradiation effects in solid phase for astrophysics: radiolysis and radio-resistance of nucleobases

Philippe Boduch

CIMAP-GANIL/University of Caen-Normandie UNICAEN, France

**Status.** For COMs, several theories claim that these molecules have possibly reached the early Earth via comets and meteorites [180]. Indeed, during the recent ROSETTA space mission, the simplest amino acid glycine, has been detected in the coma of comet 67P/Churyumov–Gerasimenko [181]. Additionally, analyses of carbonaceous meteorites found on Earth show a presence of COMs (e.g. nucleobases). That is a strong indication of existence of such molecules in outer space.

Concerning the formation of complex molecules, irradiation of ices containing simple molecules such as H<sub>2</sub>O, CO, NH<sub>3</sub> can lead to the formation of COMs [182, 183]. Among COMs, nucleobases are particularly important. They are a part of DNA and are essential for the emergence of life, maybe due to exogenesis. Even if nucleobases have not yet been observed directly in space, their presence on meteorites on earth is a strong indication of their existence in space environments. Thus, it is important to study irradiation effects on such molecules in order to determine their radio-resistance.

**Current and future challenges.** All the nucleobases (adenine, uracil, cytosine, guanine and thymine) have been irradiated with swift heavy ions at GANIL (Caen, France) and GSI (Darmstadt, Germany) facilities in order to determine their destruction cross sections as a function of the electronic stopping power of the projectiles. The goal of these experiments with high energy projectiles is to simulate in laboratory the effect of cosmic rays on COMs embedded in icy mantles on dusty grains in Inter Stellar Media (ISM) or at the surface of comets. The samples have been irradiated at low temperature (around 10 K) and the irradiation induced modifications are followed *in situ* by Fourier transform infrared spectroscopy (FTIR). Figure 26 shows the evolution of the cytosine column density inside the sample as a function of the local dose (deposited energy per molecule) for 4 projectiles (Ca, Ni, Xe and U). The fact that all these curves fall together strongly suggests that the local dose is a key parameter and the evolution of the cytosine sample depends mainly on the deposited energy. The same result was obtained for all of the nucleobases (for adenine, see [184]). From the evolution of the column density as a function of the fluence, it is possible to determine the destruction cross section of the nucleobases for each projectile. We distinguish 2 kinds of nucleobases: (I) purine nucleobases (guanine and adenine) formed of two heterocyclic rings, and (ii) pyrimidine nucleobases (cytosine, uracil and thymine) which are formed by just one heterocyclic ring. The corresponding destruction cross sections are of the same order of magnitude

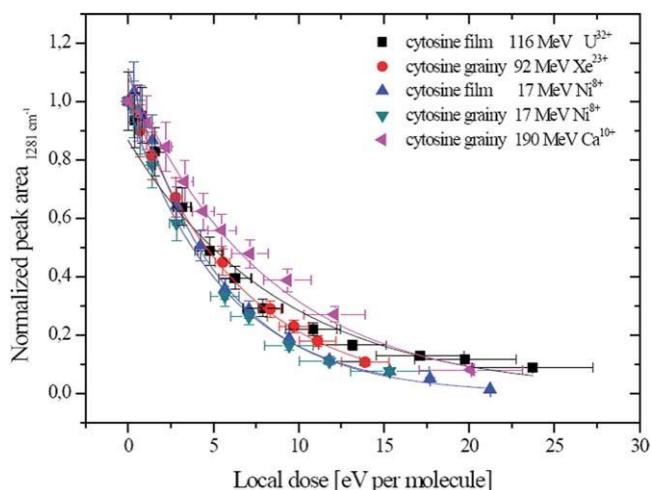


Figure 26. Evolution of the cytosine column density as a function of the local dose.

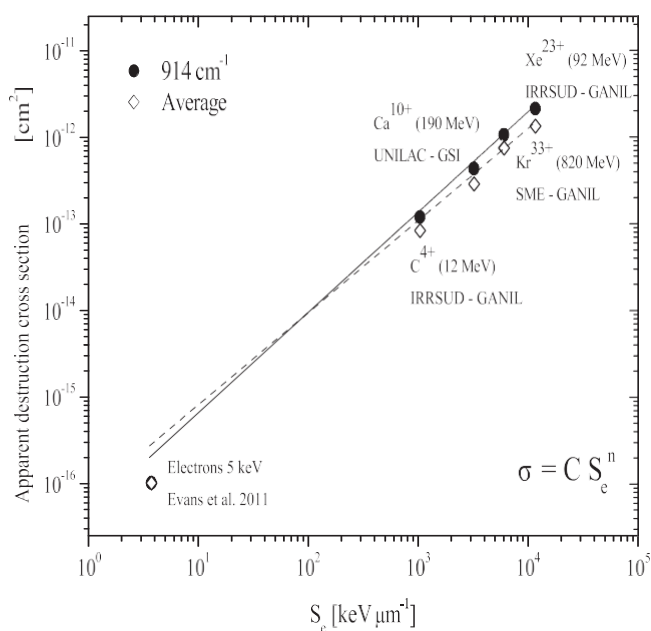


Figure 27. Destruction cross section versus the electronic stopping power  $S_e$  for adenine samples.

(between 1 and  $5 \times 10^{-13}$  cm<sup>2</sup> for the experiments performed at GSI with 190 MeV Calcium projectiles). Nevertheless, the destruction cross sections of purine nucleobases are smaller than for pyrimidine nucleobases. Guanine is the most radio-resistant nucleobase. This is in agreement with the fact that guanine is also the most abundant nucleobase detected in carbon-rich meteorites analyzed on earth ([185]). From all the experiments performed with swift heavy ions at GANIL and at GSI, it is possible to determine the evolution of the nucleobase destruction cross section as a function of the electronic stopping power. Figure 27 shows as example the results obtained for heavy ions at 2 different places (GSI and GANIL) with 2 different experimental setups for adenine, which are in good agreement. This is also the case for the

cross sections for electron beams [186]. The cross sections follow a power law with electronic stopping  $\sigma \approx A.S_e^n$  with  $n$  typically around 1.2. This law can be used for astrophysics applications in order to determine the lifetime of nucleobases in ISM. In the case of adenine, the half-life found is around 10 million years [184]. This value is directly comparable to the typical lifetime of dense clouds in the ISM, clouds which are the birth place of stellar system. These results suggest that this type of molecules has a high survival probability and could be detected in ISM in the future.

*Technology to meet challenges.* To simulate the effect of cosmic rays on complex molecules and to perform such 'online' experiments with *in situ* analysis, it is mandatory to work at very low temperature in ultrahigh vacuum conditions to ensure a controlled preparation of the targets and a clean monitoring of its evolution under irradiation, in particular for mass spectrometry. In addition, contamination by water may influence cross section and sputter yield measurements. Recently, a new ultrahigh vacuum device has been built at CIMAP-GANIL (Caen, France). The performances of this new device are described in [187]. It is equipped with three spectrometers (FTIR, UV and Quadrupole Mass Spectroscopy) and can be installed on several GANIL beam lines. This setup is open to the scientific community and will help to address new challenges about irradiation effects in ices, COMs, and other materials. These challenges are really numerous: for example, to study COMs irradiation in a more realistic situation. In ISM, grains are covered with a thin icy mantle mainly composed of H<sub>2</sub>O molecules. In these conditions, it is important to study irradiation effects on COMs trapped in a water matrix at low temperature in order to characterize the effect of the matrix. A second challenge consists in increasing the size and the complexity of the

COMs. New experiments have been started on nucleotides (nucleobase + sugar). A sample of uridine (uracil + ribose) has been recently irradiated and the associated irradiation cross section will be compared with those obtained for uracil samples. This kind of studies will be extended to more complex molecules in the future, peptides for example. For astrophysics, polycyclic aromatic hydrocarbons (PAH) are really important complex molecules. They have been detected in space and represent an important source of carbon in space (up to 30%). Since carbon is the key element in evolution of prebiotic materials [188], it would be also really interesting to study the PAH radio-resistance and the associated radiolysis products in water matrix with different percentages.

*Concluding remarks.* Nucleobases are essential for the emergence of life. The analysis of nucleobase irradiation experiments shows that these molecules are rather radio-resistant and the associated life time indicates a high survival probability in ISM. Now, recent technical developments (see e.g. [189]) allow to continue these studies in more realistic conditions with water matrix and with more complex molecules.

## Acknowledgments

This work was supported by ANR IGLIAS project, Grant No. ANR-13-BS05-0004 of the French Agence Nationale de la Recherche. The author wants to thank the CIMAP-GANIL team: J M Ramillon, C Grygiel, I Monnet, A Domaracka, C Feierstein, E Balanzat, Y Ngono Ravache, F Levesque, A N Agnihotri, G Muniz, P Ada Bibang and H Rothard, E Dartois (ISMO laboratory), M Bender and D Severin (GSI) and G Strazzulla (INAF, Catania) for their really helpful support.



## NEW FACILITIES FOR NEW CHALLENGES

## 18. Cryogenic electrostatic storage rings

Henning T Schmidt

Stockholm University, Sweden

*Status.* With the introduction of ion-storage rings in atomic and molecular physics research in the late 1980s, the option to study ensembles of ions for extended time periods exceeding the  $\mu\text{s}$  range was for the first time combined with the efficient detection of decay/collision products offered by fast beams.

While these relatively large (typically 50 m circumference) magnetic-confinement storage rings were mostly operated at MeV energies, some of the most prominent studies involved low-energy collisions between the stored ions and electrons in merged-beams configurations. The electron beams' original purpose was to cool the translational degrees of freedom of the stored ions, but at the same time they constituted an excellent target for electron-ion recombination studies. In molecular recombination the long-time storage and vibrational relaxation of the molecular ions were combined with the excellent electron-beam quality to provide unprecedented experimental conditions [190]. During the late 1990s with intense activities at the storage rings many experiments were performed, which only made use of the extended storage times and the ease with which products of interactions or spontaneous processes could be detected from an ion beam. It was realized that such experiments, which did not make use of the option of going to high (MeV) energies or to make use of electron cooling could be performed in simpler less costly devices. At the same time, a growing interest emerged in clusters and complex molecules, so that a development towards storage of higher mass particles was called for. For these new demands, a purely electrostatic ion-storage ring in an ultra-high vacuum environment was an ideal solution and this led to the development of the ELISA storage ring in Aarhus [191].

Here a single example will represent all the pioneering ELISA experiments with complex systems: In studies of hot metal cluster anions with a large spread in internal energies, it was found that the spontaneous decay monitored through neutral product detection followed a power-law rather than an exponential [192]. ELISA was followed by other electrostatic rings where spontaneous processes and processes induced by interactions with photons or electrons are studied [193].

*Current and future challenges.* The general advantage in all storage ring experiments is the combination of the temporally extended confinement, allowing the relaxation of excited state ions, and the efficient detection of reaction products. Concerning the relaxation, this is efficient for most metastable states in atomic systems with millisecond lifetimes and for vibrationally excited states of small molecular ions, where the few seconds of storage time easily available in room temperature rings are sufficient. In many cases, however, even *rotational* excitations

of molecular ions can have strong influence on the results of experimental investigations and if the fundamental properties are sought, one needs ways to accomplish control over the rotational degrees of freedom as well. The nature of this problem is two-fold. Rotational relaxation processes are generally quite slow, of the order of minutes even for the smallest molecules. Thus, very long storage times are needed. Furthermore, the excitation energies involved are so low that many rotational levels are occupied at room temperature, even if thermal equilibrium were to be attained. A central motivation behind the recently developed *cryogenic* electrostatic storage rings is that both these problems related to the rotational excitations are simultaneously addressed. Cooling the systems down to the 10 K temperature range makes the inner walls of the vacuum chambers act as efficient cryopumps for most of the gases otherwise present in the ultra-high vacuum systems. This way, residual-gas densities have been reached that are lower than one molecule per cubic millimeter. This extreme vacuum has led to storage lifetimes in cryogenic electrostatic rings of keV ion beams approaching one hour. With this, waiting for even the last steps of rotational cooling towards the ground state is within reach for many molecular systems. Evidently, the low temperature itself is also necessary for the thermally equilibrated molecular ions to have a high fraction of the population in the (few) lowest rotational levels. While the details are system dependent, the amount of rotational excitation is strongly decreased for all systems by going from room temperature to a cryogenic environment.

*Advances in science and technology to meet challenges.* Recently, three cryogenic electrostatic storage ring facilities have become operational. These are the DESIREE (Double ElectroStatic Ion-Ring ExpEriment) at Stockholm University [194], the CSR (Cryogenic Storage Ring) at the Max-Planck Institute for Nuclear Physics in Heidelberg [195] and the RICE (RIKEN Cryogenic Electrostatic ring) at RIKEN, Japan [196]. Common to these are their principle constructions with an entire separate all-cryogenic vacuum chamber surrounded by in-vacuum thermal insulation. This ensures the very high vacuum and the long storage lifetimes. The three facilities differ strongly in other respects. RICE is with its 3.0 m circumference by far the smallest one. It is well suited for studies of spontaneous processes and for laser interaction with the stored ion beams. Furthermore, there are advanced plans for merging a beam of neutrals with the stored beam to study reactions between neutrals and positive ions at low and well-controlled energies [196]. Of the three, the CSR is the biggest system with a 35.1 m circumference. This large ring is equipped with an electron cooler for merged-beams ion-electron recombination studies, a merged neutral beam is being developed, and a reaction microscope is to be included [195]. DESIREE [194] (see figure 28) is special in being a double electrostatic ring and it consists of two 8.6 m circumference ion-storage rings. The design is based on the ability to merge beams of positive and negative ions stored in

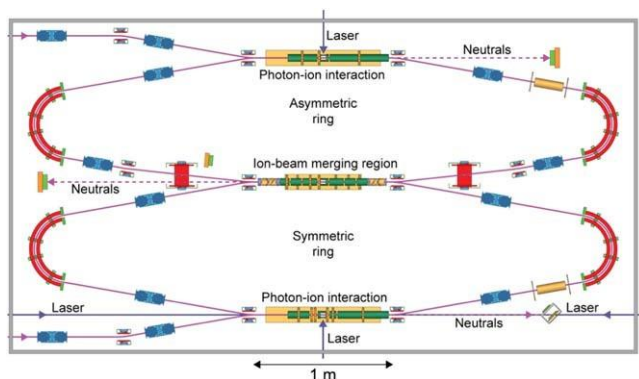


Figure 28. DESIREE [194] at Stockholm University consists of two electrostatic ion-storage rings in a common cryogenic vacuum chamber and with a common straight section where beams of opposite charge polarity can be merged. With the low internal energies that can be attained by waiting for the ions to reach thermal equilibrium and the high degree of control of the inter-particle motion obtained from the merged-beams configuration, unprecedented control of all internal and external degrees of freedom can be obtained.

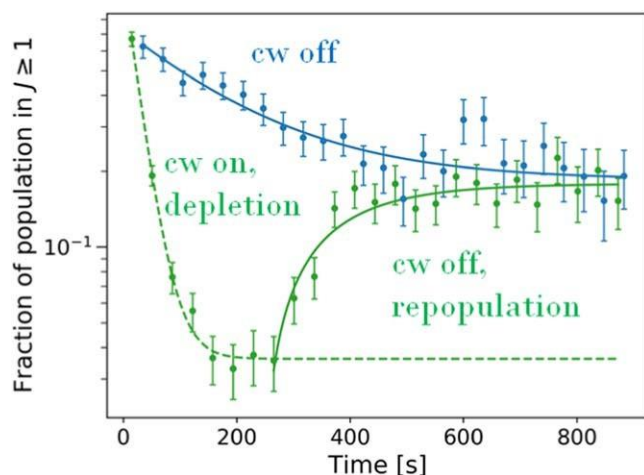


Figure 29. Measured fractions of the  $\text{OH}^-$  ions not in the rotational ground state as function of time after injection in DESIREE (blue data points and curve). The green data points and curve show the same fraction but now a cw laser beam is merged with the ion beam for the first 260 s and tuned to a wavelength where non-ground state ions only can be photodetached [197].

the two rings and measure products of mutual neutralization and related processes. The long-time storage of both beams will make it possible to study pairs of ions of complex molecules close to thermal equilibrium with the cryogenic surroundings. While the merged-beams geometry provides the opportunity to control the *inter*-molecular degrees of freedom of the collision partners, the *intra*-molecular degrees of freedom are controlled by the low temperature and the long time storage.

For all the cryogenic storage rings, the ability to demonstrate rotational cooling and to which extent thermal

equilibrium may be reached are essential. In 2017 both the CSR and DESIREE teams reported the observation of stored beams of  $\text{OH}^-$  with well over 90% of the population in the lowest ( $J = 0$ ) quantum state [197]. Figure 29 displays data from a threshold photodetachment experiment in DESIREE. By comparing signal rates for wavelengths just above and just below the threshold for ground state photodetachment and using prior knowledge of the photodetachment cross sections, the fraction of  $\text{OH}^-$  ions *not* in the  $J = 0$  ground rotational level was deduced as function of time after ion injection. For the data set shown in green, the population of ions in excited rotational levels was reduced artificially by depletion through selective photodetachment. For the first 260 s after injection, this depletion laser was on resulting in an asymptotic excitation fraction of  $3.6\% \pm 0.3\%$  corresponding to a rotational temperature of  $12.3 \pm 0.2$  K. After the laser light was blocked at  $t = 260$  s the excitation fraction increased by absorption of thermal photons from the  $13.5 \pm 0.5$  K temperature surroundings and by collisions with the few residual-gas molecules left. Finally an asymptotic excitation fraction of  $18.1\% \pm 0.9\%$ , corresponding to a rotational temperature of  $20.6 \pm 0.5$  K, was reached. These results and similar findings in CSR holds great promise for future experiments in the here mentioned and any future cryogenic storage ring systems for experiments where cold molecular ions interact with light, electrons, neutral particles or other ions [194–197].

In parallel to the electrostatic ion-storage ring developments, compact electrostatic ion-beam traps have been developed in which fast-moving ions are confined between two opposing focusing electrostatic mirrors. Here we mention the recent studies from the Weizmann institute of ultraslow isomerization in  $\text{C}_{70}$  molecular ions [198] and the first experiment with a cryogenic electrostatic storage device in which the  $\text{He}^-$  lifetime was accurately measured [199].

**Concluding remarks.** Novel cryogenic electrostatic ion-storage rings have become operational and cooling of the rotational degrees of freedom has been demonstrated. New insights from experiments with rotationally cold ions interacting with photons, electrons, neutral atoms and other cold ions are expected in the very near future.

## Acknowledgments

I want to acknowledge all colleagues at Stockholm University and elsewhere working on electrostatic ion-rings and traps for all their wonderful work, which is far beyond what can be represented here. I thank the Swedish Research council for its support for the DESIREE infrastructure (2017-00621) and my individual research grant (2018-04092).

## 19. Frontiers of extreme electromagnetic fields: atomic physics with HCIs at FAIR (SPARC collaboration)

Thomas Stöhlker

Friedrich-Schiller-University Jena, Germany; Helmholtz Institute Jena, Germany; GSI Darmstadt, Germany

*Status.* The international Facility for Antiproton and Ion Research FAIR [200–202], currently under construction, will allow for a broad variety of experiments over a wide ranges of ion energy and ion intensity. The intensities can be varied from single ions up to highest particle densities at energies ranging from rest in the laboratory up to the highly relativistic collision domain, corresponding to the strongest and shortest electromagnetic field pulses available. Moreover, stable and exotic nuclei up to the heaviest ones are available in any arbitrary charge state, enabling the extension of atomic physics research across virtually the full range of atomic matter. Of particular interest for atomic physics, FAIR is unique in its ability to deliver these highly intense, brilliant beams with excellent momentum definition. For this purpose, a unique portfolio of trapping and storage facilities will be available at FAIR covering ion energies, that span more than 10 orders of magnitude (figure 30). This will enable experiments with cooled ions aiming at exploring the atomic structure and electron dynamics in the realm of the extreme electromagnetic fields close to, and even beyond, the Schwinger limit. In order to cope with these challenges, the SPARC collaboration (Stored Particle Atomic physics Research Collaboration) has been formed. SPARC has over 430 members and is dedicated to scientifically exploit the unique discovery potential of FAIR [201, 202], in close interaction between experiment and theory.

Accelerator-based atomic physics has opened new, widely unexplored fields of research. Heavy-ion storage cooler rings, such as the ESR at GSI, have provided a first access to basic processes associated with strong electromagnetic fields in collisions of heavy, HCIs. Experiments with stored and cooled one- and few-electron high- $Z$  ions interacting with atomic targets, (polarized) electrons, or laser photons uniquely reveal the effects of relativity, electron correlations and QED on the dynamics and structure of elementary atomic systems in the presence of extremely strong fields. These research activities focus on the structure and dynamics of atomic matter subject to extreme electromagnetic fields and ultrafast electromagnetic interactions, in particular those described by non-perturbative QEDs. On the side of fundamental interactions, we conduct highly sensitive tests of atomic structure theory based on various experimental approaches such as precision measurements of the  $1s$  Lamb shift [139],  $1s$  hyperfine structure [143], bound-state  $g$ -factor [146] and mass measurements of heavy few-electron ions. In case of electrons bound to the strong Coulomb fields of heavy nuclei, experiments on quantum dynamics of electrons subject to extreme fields has been studied. This was achieved

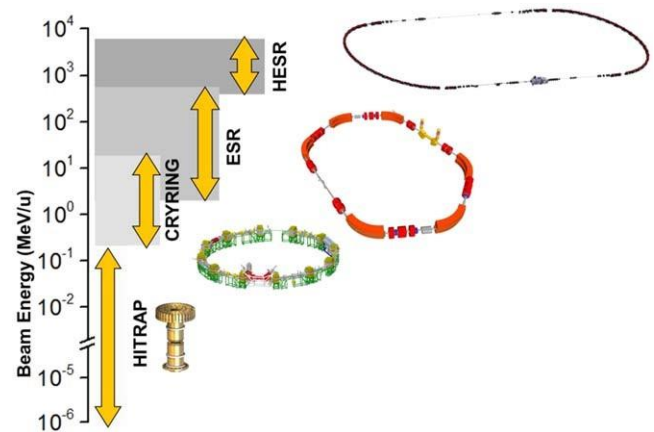


Figure 30. Main FAIR facilities for storage and trapping within the SPARC collaboration, covering more than 10 orders of magnitude in particle kinetic energies [202]. Reprinted from [202], Copyright 2015, with permission from Elsevier.

by precision studies of DR [203], photon-correlation studies for radiative EC (see section 6) [204], state-selective excitation and EC studies [205], as well as of correlated electron dynamics of atoms interacting with the intense [206], ultra-short fields of high- $Z$  relativistic ions. Moreover, atomic physics techniques have been applied to yield the most precise test of time dilatation by using stored and cooled  $\text{Li}^+$  ions at the ESR storage ring [207]. Last but not least, concerning the intersection of atomic and nuclear physics, novel decay modes of nuclei have been discovered, such as the bound-state  $\beta$ -decay, which may play an important role in nuclear astrophysics and more specifically in nuclear synthesis (see section 12) [208].

*Current and future challenges.* The storage and trapping facilities of FAIR will substantially enlarge the research capabilities for the exploration of atomic matter within the realm of extreme and ultra-short electromagnetic fields, and has key features that offer a range of new and challenging research opportunities. The investigations will focus on atomic structure, e.g. new concepts for QED in extreme fields (see section 13), collision studies at moderate and highly relativistic energies (ionization, capture and pair production) (see section 6), to generate insights into correlated many-body dynamics via ultra-short and super-intense field pulses ( $<10^{-18}$  s), and avenues towards the discovery of new electromagnetic interaction processes. Further examples include laser spectroscopy exploiting the large Doppler boost (both in the photon frequency and time domain) associated with relativistic ions, RCE of ions passing through crystal lattices at a relativistic speed (see section 16), as well as precision x-ray spectroscopy [209]. Furthermore, experiments at the border between atomic and nuclear physics will be performed with an emphasis on rare nuclear decay modes only possible for nuclei in high atomic charge states. At the same time, SPARC will apply these accurate atomic-physics techniques as powerful tools for the determination of nuclear parameters such as nuclear radii and moments, and of fundamental constants (see section 12). More specifically,



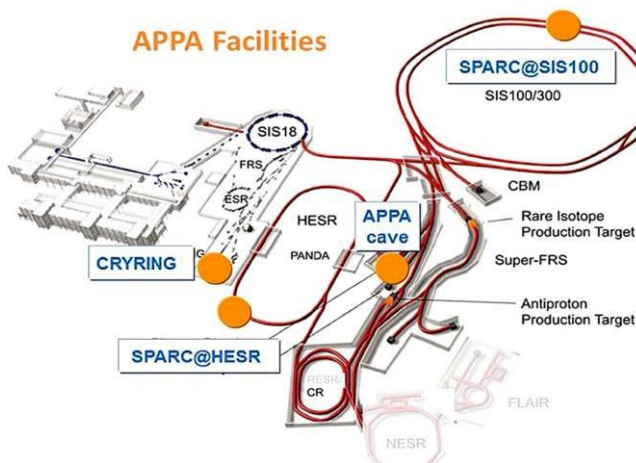


Figure 31. Overview of FAIR accelerators and storage rings. Current/future SPARC involvement in addition to ESR and HITRAP is indicated by orange dots [202]. Reprinted from [202], Copyright 2015, with permission from Elsevier.

SPARC will exploit the research potential of the following four research facilities at FAIR (see also figure 31).

**HITRAP [210]:** HCIs (up to bare uranium) from the ESR storage ring will be extracted into the HITRAP facility, where they are decelerated and cooled. The cold ions are delivered to a broad range of atomic physics experiments at very low energies or even in ion traps (see section 11). This facility is ready for operation and is waiting for first beams.

**CRYRING [211]:** A low-energy storage ring, dedicated to precision experiments with HCIs that has already proven its potential in a multitude of experiments at Stockholm. CRYRING has been transferred to GSI/FAIR and ions decelerated in the ESR will be provided to CRYRING for experiments. A unique feature of CRYRING is its ultra-cold electron cooler. CRYRING is currently being commissioned and will be available for experiments in 2019.

**ESR [201, 202]:** The ESR is the most versatile storage ring with respect to beam energies, acceptance, various beam manipulations, and detection instrumentation. It allows for electron, stochastic, and laser cooling of beams of stable and exotic nuclei. Moreover, beams for HITRAP and CRYRING will be prepared and provided (decelerated) by the ESR.

**HESR [201, 202]:** The HESR will give access for the very first time to cooled, HCIs up to a  $\gamma$ -factor of 6 for precision experiments in atomic physics and neighboring fields.

#### *Advances in science and technology to meet challenges.*

Storage and cooling are essential for the discussed studies, and the development and improvement of the corresponding dedicated tools for particle storage, preparation and detection are part of the current technical challenges. Within the SPARC collaboration, there are numerous efforts to improve instrumentation including devices for deceleration and cooling of ions in storage rings and particle traps, non-destructive detection of ions and their reactions, and

spectrometers in the optical and x-ray regimes. Newly developed calorimetric low-temperature detectors for spectroscopy of Lyman x-rays of HCIs which yield a high energy resolution that is comparable to crystal spectrometers and at the same time exhibit a large wavelength acceptance have been implemented and tested in first experiments at the ESR storage ring. Techniques for cooling of ions from keV to  $\mu\text{eV}$  energies (i.e. by more than 8 orders of magnitude) and crystallization within seconds have been devised by application in Penning traps [212].

For laser spectroscopy, a power-scalable nonlinear compression scheme which will provide few-cycle pulses at up to 1 kW of average power has been developed [213]. Thus, efficient high harmonic generation up to the water window will be feasible as well as an isolated attosecond pulse generation. A portable XUV source for experiments at heavy-ion storage rings at GSI/FAIR will be setup and installed at CRYRING [211]. At a later stage, such a system will serve as a light source for experiments at the HESR. Single- and multi-species ion crystals as presently produced in Penning traps will be used for sympathetic cooling of externally produced HCIs (HITRAP and EBIT at FAIR) and will allow us to perform high-precision optical spectroscopy of magnetic dipole transitions as probes of QED calculations in the magnetic sector. Future activities related to micro-calorimeter detectors will focus on large pixel arrays, e.g. 1000 pixels, and the optimization of the electronic read-out schemes. Furthermore, besides Metallic Magnetic Calorimeters [214], Superconducting Tunnel Junctions detectors with their high count-rate capability and unique performance at XUV photon energies will be considered.

**Concluding remarks.** The SPARC collaboration is pursuing a challenging atomic physics program in the realm of strong electromagnetic fields, exploiting the present and future trapping and storage facilities of GSI/FAIR. The focus is on collision experiments of HCIs with atoms, electrons, and photons as well as spectroscopic studies in the x-ray, optical and microwave domains. Beside experiments on stable ions, also experiments at the border between atomic, nuclear and astro-physics will be conducted. Since the future FAIR facility will offer beams of cooled HCIs in energy regimes where no such experiments were possible so far, the SPARC research physics programs exhibit a high discovery potential especially considering the advances in experimental equipment.




## Acknowledgments

The support by FAIR, BMBF, Helmholtz Association, Max-Planck-Society, EU, and DFG is acknowledged. Moreover, special thanks to the members of the SPARC collaboration for the excellent cooperation.



## ORCID iDs

Friedrich Aumayr  <https://orcid.org/0000-0002-9788-0934>  
 Emma Sokell  <https://orcid.org/0000-0002-7063-7205>  
 Stefan Schippers  <https://orcid.org/0000-0002-6166-7138>  
 Frédéric Merkt  <https://orcid.org/0000-0002-4897-2234>  
 Paul Scheier  <https://orcid.org/0000-0002-7480-6205>  
 Olof Echt  <https://orcid.org/0000-0002-0970-1191>  
 Tom Kirchner  <https://orcid.org/0000-0002-6644-3379>  
 Stephan Fritzsche  <https://orcid.org/0000-0003-3101-2824>  
 Xinwen Ma  <https://orcid.org/0000-0001-9831-0565>

Lokesh Tribedi  <https://orcid.org/0000-0002-9282-9734>  
 José R Crespo López-Urrutia  <https://orcid.org/0000-0002-2937-8037>  
 Yuri A Litvinov  <https://orcid.org/0000-0002-7043-4993>  
 Henning Zettergren  <https://orcid.org/0000-0002-2493-4161>  
 Richard A Wilhelm  <https://orcid.org/0000-0001-9451-5440>  
 Henning T Schmidt  <https://orcid.org/0000-0002-8209-5095>

## References

- [1] Gallagher T F 1994 *Rydberg Atoms* (Cambridge: Cambridge University Press)
- [2] Merkt F, Willitsch S and Hollenstein U 2011 High-resolution photoelectron spectroscopy *Handbook of High-Resolution Spectroscopy* vol 3 ed M Quack and F Merkt (Chichester: Wiley) pp 1617–54
- [3] Hogan S D, Seiler C and Merkt F 2009 Rydberg-state-enabled deceleration and trapping of cold molecules *Phys. Rev. Lett.* **103** 123001
- [4] Seiler R, Hollenstein U, Greetham G M and Merkt F 2001 Rydberg-state-resolved zero-kinetic-energy photoelectron spectroscopy *Chem. Phys. Lett.* **118** 10024–33
- [5] Deiglmayr J, Herburger H, Saßmannshausen H, Jansen P, Schmutz H and Merkt F 2016 Precision measurement of the ionization energy of Cs I *Phys. Rev. A* **93** 013424
- [6] Seaton M J 1983 Quantum defect theory *Rep. Prog. Phys.* **46** 167–257
- [7] Jungen C 2011 Elements quantum defect theory *Handbook of High-resolution Spectroscopy* vol 1 ed M Quack and F Merkt (Chichester: Wiley)
- [8] Schäfer M, Raunhardt M and Merkt F 2010 Millimeter-wave spectroscopy and multichannel quantum-defect-theory analysis of high Rydberg states of xenon: the hyperfine structure of  $^{129}\text{Xe}^+$  and  $^{131}\text{Xe}^+$  *Phys. Rev. A* **81** 032514
- [9] Haase C, Beyer M, Jungen C and Merkt F 2015 The fundamental rotational interval of para- $\text{H}_2^+$  by MQDT-assisted Rydberg spectroscopy of  $\text{H}_2$  *J. Chem. Phys.* **142** 064310
- [10] Cheng C *et al* 2018 Dissociation energy of the hydrogen molecule at  $10^{-9}$  accuracy *Phys. Rev. Lett.* **121** 013001
- [11] Beyer M, Hölsch N, Agner J A, Deiglmayr J, Schmutz H and Merkt F 2018 Metrology of high- $n$  Rydberg states of molecular hydrogen with  $\Delta\nu/\nu = 2 \times 10^{-10}$  accuracy *Phys. Rev. A* **97** 012501
- [12] Pratt S T, Dehmer J L, Dehmer P M and Chupka W A 1994 Reactions of Rydberg states of molecular hydrogen *J. Chem. Phys.* **101** 882–90
- [13] Allmendinger P, Deiglmayr J, Schullian O, Höveler K, Agner J A, Schmutz H and Merkt F 2016 Observation of enhanced rate coefficients in the  $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$  reaction at low collision energies *J. Chem. Phys.* **145** 244316
- [14] Beyer M and Merkt F 2018 Half-collision approach to cold chemistry: shape resonances, elastic scattering and radiative association in the  $\text{H}^+ + \text{H}$  and  $\text{D}^+ + \text{D}$  collision systems *Phys. Rev. X* **8** 031085
- [15] Glenwinkel-Meyer T and Gerlich D 1997 Single and merged beam studies of the reaction  $\text{H}_2^+(v = 0, 1; j = 0, 4) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$  *Isr. J. Chem.* **4** 343–52
- [16] Sanz-Sanz C, Aguado A, Roncero O and Naumkin F 2013 Non-adiabatic couplings and dynamics in proton transfer reactions of  $\text{H}^+$  systems: application to  $\text{H}^+ + \text{H} \rightarrow \text{H} + \text{H}^+$   $n$  collisions *J. Chem. Phys.* **143** 234303
- [17] Javan A, Bennet W R Jr and Herriot D R 1962 Population inversion and continuous optical maser oscillation in a gas discharge containing a He–Ne mixture *Phys. Rev. Lett.* **6** 106–10
- [18] Houston P L 1981 Electronic to vibrational energy transfer from excited halogen atoms in *Advances in Chemical Physics* vol 47 ed I Prigogine and S A Rice (New York: Wiley)
- [19] Smith *et al* 1978 Discrete energy transfer in collisions of Xe (nf) Rydberg atoms with  $\text{NH}_3$  molecules *Phys. Rev. Lett.* **40** 1362–5
- [20] Safinya *et al* 1981 Resonant Rydberg-atom–Rydberg-atom collisions *Phys. Rev. Lett.* **47** 405–8
- [21] Bouhlouli-Zanjani P *et al* 2007 Enhancement of Rydberg atom interactions using ac Stark shifts *Phys. Rev. Lett.* **98** 203205
- [22] Falcone R W *et al* 1977 Observation of laser induced inelastic collisions *Phys. Rev. A* **15** 1333–5
- [23] Pillet P *et al* 1987 Radiative Rydberg-atom–Rydberg-atom collisions in the strong field regime *Phys. Rev. A* **36** 1132–47
- [24] Thomson D S, Renn M J and Gallagher T F 1990 Transform limited collisions of K Rydberg atoms *Phys. Rev. Lett.* **65** 3273–6
- [25] Anderson W R, Veale J R and Gallagher T F 1998 Resonant dipole–dipole energy transfer in a nearly frozen Rydberg gas *Phys. Rev. Lett.* **80** 249–52
- [26] Mourachko I *et al* 1998 Many body effects in a frozen Rydberg gas *Phys. Rev. Lett.* **80** 253–6
- [27] Nipper J *et al* 2012 Highly resolved measurements of Stark tuned forster resonances between Rydberg atoms *Phys. Rev. Lett.* **108** 113001
- [28] Lukin M D *et al* 2001 Dipole blockade and quantum information processing in mesoscopic atomic systems *Phys. Rev. Lett.* **87** 037901
- [29] Kiffner M *et al* 2012 Dipole–dipole coupled double-Rydberg molecules *Phys. Rev. A* **86** 031401(R)
- [30] Schauss P *et al* 2012 Observation of spatially ordered structures in a two dimensional Rydberg gas *Nature* **491** 87–91
- [31] Barredo D *et al* 2015 Coherent excitation transfer in a Spin chain of three Rydberg atoms *Phys. Rev. Lett.* **114** 113002
- [32] Endres M *et al* 2016 Atom by atom assembly of defect free one dimensional cold atom arrays *Science* **354** 1024–7
- [33] Bernien H *et al* 2017 Probing many-body dynamics on a 51-atom quantum simulator *Nature* **551** 579–84
- [34] Kim H *et al* 2018 Detailed balance of thermalization dynamics in Rydberg atom quantum simulators *Phys. Rev. Lett.* **120** 180502
- [35] Dunning F B, Mestayer J J, Reinhold C O, Yoshida S and Burgdörfer J 2009 Engineering atomic Rydberg states with pulsed electric fields *J. Phys. B: At. Mol. Opt. Phys.* **42** 022001
- [36] Mestayer J J, Wyker B, Dunning F B, Yoshida S, Reinhold C O and Burgdörfer J 2009 Creation of non-dispersive Bohr-like wave packets *Phys. Rev. A* **79** 033417

- [37] Wyker B, Ye S, Dunning F B, Yoshida S, Reinhold C O and Burgdörfer J 2012 Creating and transporting Trojan wave packets *Phys. Rev. Lett.* **108** 043001
- [38] Bendowsky V, Butscher B, Nipper J, Shaffer J P, Löw R and Pfau T 2009 Observation of ultralong-range Rydberg molecules *Nature* **458** 1005
- [39] Schlagmüller M *et al* 2016 Ultracold chemical reactions of a single Rydberg atom in a dense gas *Phys Rev X* **6** 031020
- [40] Camargo F *et al* 2018 Creation of Rydberg polarons in a Bose gas *Phys. Rev. Lett.* **120** 083401
- [41] Yoshida S, Burgdörfer J, Zhang X and Dunning F B 2017 Rydberg blockade in a hot atomic beam *Phys. Rev. A* **95** 042705
- [42] Tanner G, Richter K and Rost J-M 2000 The theory of two-electron atoms: between ground state and complete fragmentation *Rev. Mod. Phys.* **72** 497
- [43] Fields G, Zhang X, Dunning F B, Yoshida S and Burgdörfer J 2018 Autoionization of very-high- $n$  strontium Rydberg states *Phys. Rev. A* **97** 013429
- [44] Toennies J P and Vilesov A F 2004 Superfluid helium droplets: a uniquely cold nanomatrix for molecules and molecular complexes *Angew. Chem., Int. Ed.* **43** 2622–48
- [45] Mauracher A, Echt O, Ellis A M, Yang S, Bohme D K, Postler J, Kaiser A, Denifl S and Scheier P 2018 Cold physics and chemistry: Collisions, ionization and reactions inside helium nanodroplets close to zero K *Phys. Rep.* **751** 1–90
- [46] Gode S, Irsig R, Tiggesbäumker J and Meiwes-Broer K H 2013 Time-resolved studies on the collapse of magnesium atom foam in helium nanodroplets *New J. Phys.* **15** 015026
- [47] Schnedlitz M, Lasserus M, Meyer R, Knez D, Hofer F, Ernst W E and Hauser A W 2018 Stability of core-shell nanoparticles for catalysis at elevated temperatures: structural inversion in the Ni-Au system observed at atomic resolution *Chem. Mater.* **30** 1113–20
- [48] Kuhn M *et al* 2016 Atomically resolved phase transition of fullerene cations solvated in helium droplets *Nat. Commun.* **7** 13550
- [49] Mudrich M and Stienkemeier F 2014 Photoionisation of pure and doped helium nanodroplets *Int. Rev. Phys. Chem.* **33** 301–39
- [50] He Y T, Zhang J and Kong W 2016 Electron diffraction of  $\text{CBr}_4$  in superfluid helium droplets: a step towards single molecule diffraction *J. Chem. Phys.* **145** 034307
- [51] Ancilotto F, Barranco M, Coppens F, Eloranta J, Halberstadt N, Hernando A, Mateo D and Pi M 2017 Density functional theory of doped superfluid liquid helium and nanodroplets *Int. Rev. Phys. Chem.* **36** 621–707
- [52] Sliter R, Gomez L F, Kwok J and Vilesov A 2014 Size distributions of large He droplets *Chem. Phys. Lett.* **600** 29–33
- [53] Heazlewood B R and Softley T P 2015 Low-temperature kinetics and dynamics with Coulomb crystals *Annu. Rev. Phys. Chem.* **66** 475–95
- [54] Belkić Dž 2008 *Quantum Theory of High-energy Ion-Atom Collisions* (Boca Raton, FL: CRC Press)
- [55] Bransden B H and McDowell M R C 1992 *Charge Exchange and the Theory of Ion-Atom Collisions* (Oxford: Clarendon)
- [56] Abdurakhmanov I B, Kadyrov A S, Avazbaev S K and Bray I 2016 Solution of the proton-hydrogen scattering problem using a quantum-mechanical two-center convergent close-coupling method *J. Phys. B: At. Mol. Opt. Phys.* **49** 115203
- [57] Abdurakhmanov I B, Bailey J J, Kadyrov A S and Bray I 2018 Wave-packet continuum-discretization approach to ion-atom collisions including rearrangement: application to differential ionization in proton-hydrogen scattering *Phys. Rev. A* **97** 032707
- [58] Borbély S, Feist J, Tókési K, Nagele S, Nagy L and Burgdörfer J 2014 Ionization of helium by slow antiproton impact: total and differential cross sections *Phys. Rev. A* **90** 052706
- [59] Gao J W, Wu Y, Wang J G, Sisourat N and Dubois A 2018 State-selective electron transfer in  $\text{He}^+$ -He collisions at intermediate energies *Phys. Rev. A* **97** 052709
- [60] Baxter M and Kirchner T 2016 Time-dependent density-functional-theory studies of collisions involving He atoms: extension of an adiabatic correlation-integral model *Phys. Rev. A* **93** 012502
- [61] Covington C, Hartig K, Russakoff A, Kulpins R and Varga K 2017 Time-dependent density-functional-theory investigation of the collisions of protons and  $\alpha$  particles with uracil and adenine *Phys. Rev. A* **95** 052701
- [62] Chung H-K, Braams B J, Bartschat K, Császár A G, Drake G W F, Kirchner T, Kokouline V and Tennyson J 2016 Uncertainty estimates for theoretical atomic and molecular data *J. Phys. D: Appl. Phys.* **49** 363002
- [63] Schulz M 2017 The role of projectile coherence in the few-body dynamics of simple atomic systems *Adv. At. Mol. Opt. Phys.* **66** 507–43
- [64] Eichler J and Stöhlker T 2007 Radiative electron capture in relativistic ion-atom collisions and the photoelectric effect in hydrogen-like high-Z systems *Phys. Rep.* **439** 1–99
- [65] Fritzsche S, Indelicato P and Stöhlker T 2005 Relativistic quantum dynamics in strong fields *J. Phys. B: At. Mol. Opt. Phys.* **38** S707
- [66] Weber G *et al* 2010 Direct determination of the magnetic quadrupole contribution to the Lyman- $\alpha_1$  transition in a hydrogenlike ion *Phys. Rev. Lett.* **105** 243002
- [67] Yerokhin V A and Surzhykov A 2010 Electron-atom bremsstrahlung: double-differential cross section and polarization correlations *Phys. Rev. A* **82** 062702
- [68] Fritzsche S, Surzhykov A and Stöhlker T H 2009 Dominance of the Breit interaction in the x-ray emission of highly charged ions following dielectronic recombination *Phys. Rev. Lett.* **103** 113001
- [69] Jörg H, Hu Z, Bekker H, Blessenohl M A, Hollain D, Fritzsche S, Surzhykov A, Crespo Lopez-Urrutia J R and Tashenov S 2015 Linear polarization of x-ray transitions due to dielectronic recombination in highly charged ions *Phys. Rev. A* **91** 042705
- [70] Simon A, Warczak A, ElKafrawy T and Tanis J A 2010 Radiative double electron capture in collisions of  $\text{O}^{8+}$  ions with carbon *Phys. Rev. Lett.* **104** 123001
- [71] Bellazini R, Costa E, Matt G and Tagliaferri G (ed) 2010 *X-ray Polarimetry: A New Window in Astrophysics* (Cambridge: Cambridge University Press)
- [72] Gunst J, Surzhykov A, Artemyev A, Fritzsche S, Tashenov S, Maiorova A, Shabaev V M and Stöhlker T 2013 Parity-nonconservation effects on the radiative recombination of heavy hydrogenlike ions *Phys. Rev. A* **87** 032714
- [73] Artemyev A N, Beier T, Eichler J, Klasnikov A E, Kozhuharov C, Shabaev V M, Stöhlker T and Yerokhin V A 2003 Negative-continuum dielectronic recombination for heavy ions *Phys. Rev. A* **67** 052711
- [74] Lestinsky M *et al* 2016 Physics book: CRYRING@ESR *Eur. Phys. J. Spec. Top.* **225** 797–882
- [75] Ullrich J, Moshhammer R, Dorn A, Dörner R, Schmidt L P H and Schmidt-Böcking H 2003 *Rep. Prog. Phys.* **66** 1463–545
- [76] Dörner R, Mergel V, Jagutzki O, Spielberger L, Ullrich J, Moshhammer R and Schmidt-Böcking H 2000 *Phys. Rep.* **330** 95–192
- [77] Mergel V *et al* 1997 *Phys. Rev. Lett.* **79** 387–90
- [78] Fischer D, Feuerstein B, DuBois R D, Moshhammer R, Crespo López-Urrutia J R, Draganic I, Lörch H, Perumal A N and Ullrich J 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 1369–77

- [79] Schulz M, Moshhammer R, Fischer D, Kollmus H, Madison D H, Jones S and Ullrich J 2003 *Nature* **422** 48
- [80] Zhang R T *et al* 2016 *Phys. Rev. A* **93** 032709
- [81] Gao Y, Zhang S F, Schulz M, Zhu X L, Zhang R T, Feng W T, Guo D L, Zhao D M and Ma X 2017 *J. Phys. B: At. Mol. Opt. Phys.* **50** 10LT01
- [82] Schmidt L P H, Schössler S, Afaneh F, Schöffler M, Stiebing K E, Schmidt-Böcking H and Dörner R 2008 *Phys. Rev. Lett.* **101** 173202
- [83] Zhang S F, Fischer D, Schulz M, Voitkiv A B, Senftleben A, Dorn A, Ullrich J, Ma X and Moshhammer R 2014 *Phys. Rev. Lett.* **112** 023201
- [84] Gao Y *et al* 2018 *Phys. Rev. A* **97** 020701(R)
- [85] Xu S *et al* 2018 Damaging intermolecular energy and proton transfer processes in alpha-particle-irradiated hydrogen-bonded systems *Angew. Chem., Int. Ed.* **57** 17023
- [86] Cohen H D and Fano U 1966 Interference in the photo-ionization of molecules *Phys. Rev.* **150** 30–3
- [87] Young T 1807 *A Course of Lectures on Natural Philosophy and the Mathematical Arts* (London: Johnson J)
- [88] Stolterfoht N *et al* 2001 Evidence of interference effects in electron emission from H<sub>2</sub> colliding with 60 MeV/u Kr<sup>34+</sup> ions *Phys. Rev. Lett.* **87** 023201
- [89] Misra D, Khadane U, Singh Y P, Tribedi L C, Fainstein P D and Richard P 2004 Interference effect in electron emission in heavy ion collisions with H<sub>2</sub> detected by comparison with the measured electron spectrum from atomic hydrogen *Phys. Rev. Lett.* **92** 153201
- [90] Ciappina M F, Fojón O A and Rivarola R D 2014 Coherent electron emission from simple molecules by impact of energetic charged particles *J. Phys. B: At. Mol. Opt. Phys.* **47** 042001
- [91] Tachino C A, Martín F and Rivarola R D 2012 Theoretical study of interference effects in single electron ionization of N<sub>2</sub> molecules by proton impact *J. Phys. B: At. Mol. Opt. Phys.* **45** 025201
- [92] Baran J L, Das S, Járαι-Szabó F, Póra K, Nagy L and Tanis J A 2008 Suppression of primary electron interferences in the ionization of N<sub>2</sub> by 1–5 MeV/u protons *Phys. Rev. A* **78** 012710
- [93] Fojón O A, Stia C R and Rivarola R D 2011 Erasing the traces of classical mechanics in ionization of H<sub>2</sub> by quantum interferences *Phys. Rev. A* **84** 032715
- [94] Tachino C E and Rivarola R D 2019 Fully differential cross sections for ionization of H<sub>2</sub><sup>+</sup> by ion impact: classical and quantum effects *J. Phys. B: At. Mol. Opt. Phys.* **52** 065203
- [95] Stolterfoht N *et al* 2004 Frequency doubling of interference structures in electron emission interferences from H<sub>2</sub> by 68-MeV/u Kr<sup>33+</sup> impact *Phys. Rev. A* **69** 012701
- [96] Cederbaum L S, Zobeley J and Tarantelli F 1997 Giant intermolecular decay and fragmentation of clusters *Phys. Rev. Lett.* **79** 4778–81
- [97] Stolterfoht N *et al* 2001 Evidence for interference effects in electron emission from H<sub>2</sub> colliding with 60MeV/u Kr<sup>34+</sup> ions *Phys. Rev. Lett.* **87** 023201
- [98] Misra D, Kadhane U, Singh Y P, Tribedi L C, Fainstein P D and Richard P 2004 Interference effect in electron emission in heavy ion collisions with H<sub>2</sub> detected by comparison with the measured electron spectrum from atomic hydrogen *Phys. Rev. Lett.* **92** 153201
- [99] Ilchen M *et al* 2014 Angular momentum sensitive two-center interference *Phys. Rev. Lett.* **112** 023001
- [100] Neumann N *et al* 2010 Fragmentation dynamics of CO<sup>3+</sup> investigated by multiple electron capture in collisions with slow highly charged ions *Phys. Rev. Lett.* **104** 103201
- [101] Agnihotri A N *et al* 2012 Ionization of uracil in collisions with highly charged carbon and oxygen ions of energy 100 keV to 78 MeV *Phys. Rev. A* **85** 032711
- [102] Itoh A, Iriki Y, Imai M, Champion C and Rivarola R D 2013 Cross sections for ionization of uracil by MeV-energy-proton impact *Phys. Rev. A* **88** 052711
- [103] Montenegro E C, Sigaud G M and DuBois R D 2013 Projectile and target scaling of the total ionization cross sections of atoms and molecules *Phys. Rev. A* **87** 012706
- [104] Kelkar A H, Gulyás L and Tribedi L C 2015 Angle-differential observation of plasmon electrons in the double-differential cross-section spectra of fast-ion-induced electron ejection from C<sub>60</sub> *Phys. Rev. A* **92** 052708
- [105] Biswas S and Tribedi L C 2015 Plasmon-mediated electron emission from the coronene molecule under fast ion impact *Phys. Rev. A* **92** 060701(R)
- [106] Bhattacharjee S, Biswas S, Monti J M, Rivarola R D and Tribedi L C 2017 Double differential cross section for ionization of H<sub>2</sub>O molecules by 4 MeV/u C<sup>6+</sup> and Si<sup>13+</sup> ions *Phys. Rev. A* **96** 052707
- [107] Verkhovtsev A V, Korol A V and Solov'yov A V 2015 Revealing the mechanism of the low-energy electron yield enhancement from sensitizing nanoparticles *Phys. Rev. Lett.* **114** 063401
- [108] Bräuning H, Diehl A, von Diemar K, Theiß A, Trassl R, Salzborn E and Hofmann I 2002 *Laser and Particle Beams* vol 20 (Cambridge: Cambridge University Press) p 493
- [109] Diehl A, Bräuning H, Trassl R, Hathiramani D, Theiß A, Kern H, Salzborn E and Hofmann I 2001 Charge transfer and ionization in collisions between multiply charged noble gas ions *J. Phys. B: At. Mol. Opt. Phys.* **34** 4073
- [110] Chen C Y, Cocke C L, Giese J P, Melchert F, Reiser I, Stöckli M, Sidky E and Lin C D 2001 Studies of charge exchange in symmetric ion–ion collisions *J. Phys. B: At. Mol. Opt. Phys.* **34** 469
- [111] Cayzac W *et al* 2017 Experimental discrimination of ion stopping models near the Bragg peak in highly ionized matter *Nat. Commun.* **8** 15693
- [112] Vernhet D, Adoui L, Rozet J, Wohrer K, Chetoui A, Cassimi A, Grandin J, Ramillon J and Cornille M 1997 Multielectron processes in heavy ion–atom collisions at intermediate velocity *Phys. Rev. Lett.* **79** 3625
- [113] Dechery F *et al* 2015 Toward the drip lines and the superheavy island of stability with the super separator spectrometer S3 *Eur. Phys. J. A* **51** 66
- [114] Herfurth F *et al* 2018 Commissioning of the low energy storage ring facility CRYRING@ESR *Proc. COOL2017* (<https://doi.org/10.18429/JACoW-COOL2017-THM13>)
- [115] Stodel C *et al* 2015 High intensity targets stations for S3 *J. Radioanal. Nucl. Chem.* **305** 761–7
- [116] Artemyev A N, Surzhykov A, Indelicato P, Plunien G and Stöhlker T 2010 Finite basis set approach to the two-centre Dirac problem in Cassini coordinates *J. Phys. B: At. Mol. Opt. Phys.* **43** 235207
- [117] Lestinsky M *et al* 2016 Physics book: CRYRING@ESR *Eur. Phys. J. Spec. Top.* **225** 797–882
- [118] Safronova M S, Budker D, DeMille D, Kimball D F J, Derevianko A and Clark C W 2018 Search for new physics with atoms and molecules *Rev. Mod. Phys.* **90** 025008
- [119] Ludlow A, Boyd M, Ye J, Peik E and Schmidt P O 2015 Optical atomic clocks *Rev. Mod. Phys.* **87** 7
- [120] Huntemann N, Sanner C, Lipphardt B, Tamm C and Peik E 2016 Single-ion atomic clock with 3 × 10<sup>-18</sup> systematic uncertainty *Phys. Rev. Lett.* **116** 063001
- [121] Karshenboim S G 2005 Precision physics of simple atoms: QED tests, nuclear structure and fundamental constants *Phys. Rep.* **422** 1
- [122] Beiersdorfer P 2010 Testing QED and atomic-nuclear interactions with high-Z ions *J. Phys. B: At. Mol. Opt. Phys.* **43** 074032
- [123] Beiersdorfer P 2003 Laboratory x-ray astrophysics *Ann. Rev. Astron. Astrophys.* **41** 343



- [124] Ong A, Berengut J C and Flambaum V V 2014 Optical transitions in highly charged ions for detection of variations in the fine-structure constant
- Crespo López-Urrutia J R and Harman Z 2014 Emission and laser spectroscopy of trapped highly charged ions in electron beam ion traps
- Tan J N and Mohr P J 2014 Test of theory in Rydberg states of one-electron ions *Fundamental Physics in Particle Traps* vol 256 (*Springer Tracts in Modern Physics*) ed W Quint and M Vogel (Berlin: Springer) pp 293–402
- [125] Schmöger L *et al* 2015 Coulomb crystallization of highly charged ions *Science* **347** 6227
- [126] Kozlov M G, Safronova M S, Crespo López-Urrutia J R and Schmidt P O 2018 Highly charged ions: optical clocks and applications in fundamental physics *Rev. Mod. Phys.* **90** 045005
- [127] Nauta J, Borodin A, Ledwa H A, Stark J, Schwarz M, Schmöger L, Micke P, Crespo López-Urrutia J R and Pfeifer T 2017 *Nucl. Instrum. Methods Phys. Res. B* **408** 285
- [128] Litvinov Y A and Bosch F 2011 Beta decay of highly charged ions *Rep. Prog. Phys.* **74** 016301
- [129] Bosch F, Litvinov Y A and Stöhlker T 2013 Nuclear physics with unstable ions at storage rings *Prog. Part. Nucl. Phys.* **73** 84–140
- [130] Phillips W R, Ahmad I, Baner D W, Glagola B G, Henning W, Kutschera W, Rehm K E, Schiffer J P and Wang T F 1989 Charge-state dependence of nuclear lifetimes *Phys. Rev. Lett.* **62** 1025–8
- [131] Chiara C J *et al* 2018 Isomer depletion as experimental evidence of nuclear excitation by electron capture *Nature* **554** 216–8
- [132] Cerjan C J *et al* 2018 Dynamic high energy density plasma environments at the national ignition facility for nuclear science research *J. Phys. G: Nucl. Part. Phys.* **45** 033003
- [133] Brandau C *et al* 2013 Probing nuclear properties by resonant atomic collisions between electrons and ions *Phys. Scr.* **T156** 014050
- [134] Griesser M *et al* 2012 Storage ring at HIE-ISOLDE *Eur. Phys. J. Spec. Top.* **207** 1–117
- [135] Thielking J, Okhapkin M V, Glowacki P, Meier D M, von der Wense L, Seiferle B, Düllmann C E, Thierolf P G and Peik E 2018 Laser spectroscopic characterization of the nuclear-clock isomer  $^{229\text{m}}\text{Th}$  *Nature* **556** 321–5
- [136] Mei B *et al* 2015 First measurement of the  $^{96}\text{Ru}(p,\gamma)^{97}\text{Rh}$  cross section for the p process with a storage ring *Phys. Rev. C* **92** 035803
- [137] Glorius J *et al* 2019 Approaching the gamow window with stored ions: direct measurement of  $^{124}\text{Xe}(p,\gamma)$  in the ESR storage ring *Phys. Rev. Lett.* **122** 092701
- [138] Zhang Y H, Litvinov Y A, Uesaka T and Xu H S 2016 Storage ring mass spectrometry for nuclear structure and astrophysics research *Phys. Scr.* **91** 073002
- [139] Gumberidze A *et al* 2005 Quantum electrodynamics in strong electric fields: the ground-state Lamb shift in hydrogenlike uranium *Phys. Rev. Lett.* **94** 223001
- [140] Yerokhin V A and Shabaev V M 2015 Lamb shift of  $n = 1$  and  $n = 2$  states of hydrogen-like atoms,  $1_{\pi}$ ,  $Z_{\pi}$ , 110 *J. Phys. Chem. Ref. Data* **44** 033103
- [141] Kozhedub Y S, Andreev O V, Shabaev V M, Tupitsyn I I, Brandau C, Kozhuharov C, Plunien G and Stöhlker T 2008 Nuclear deformation effect on the binding energies in heavy ions *Phys. Rev. A* **77** 032501
- [142] Beiersdorfer P, Chen H, Thorn D B and Traebert E 2005 Measurement of the two-loop Lamb shift in lithiumlike  $\text{U}^{89+}$  *Phys. Rev. Lett.* **95** 233003
- [143] Ullmann J *et al* 2017 High precision hyperfine measurements in bismuth challenge bound-state strong-field QED *Nat. Commun.* **8** 15484
- [144] Shabaev V M, Artemyev A N, Yerokhin V A, Zherebtsov O M and Soff G 2001 Towards a test of QED in investigations of the hyperfine splitting in heavy ions *Phys. Rev. Lett.* **86** 3959–62
- [145] Skripnikov L V *et al* 2018 New nuclear magnetic moment of  $^{209}\text{Bi}$ : resolving the bismuth hyperfine puzzle *Phys. Rev. Lett.* **120** 093001
- [146] Sturm S, Köhler F, Zatorski J, Wagner A, Harman Z, Werth G, Quint W, Keitel C H and Blaum K 2014 High-precision measurement of the atomic mass of the electron *Nature* **506** 467–70
- [147] Köhler F *et al* 2016 Isotope dependence of the Zeeman effect in lithium-like calcium *Nat. Commun.* **7** 10246
- [148] Greiner W, Müller B and Rafelski J 1985 *Quantum Electrodynamics of Strong Fields* (Berlin: Springer)
- [149] Chandezon F, Guet C, Huber B A, Jalabert D, Maurel M, Monnard E, Ristori C and Rocco J C 1995 Critical sizes against Coulomb dissociation of highly charged sodium clusters obtained by ion impact *Phys. Rev. Lett.* **74** 3784
- [150] Tappe E, Flesch R, Rüh I E, Hoekstra R and Schlathöfer T 2002 Charge localization in collision-induced multiple ionization of van der Waals clusters with highly charged ions *Phys. Rev. Lett.* **88** 143401
- [151] Adoui L *et al* 2009 Ionization and fragmentation of water clusters by fast highly charged ions *J. Phys. B: At. Mol. Opt. Phys.* **42** 075101
- [152] Markush P *et al* 2016 The role of the environment in the ion induced fragmentation of uracil *Phys. Chem. Chem. Phys.* **18** 16721
- [153] Manil B, Maunoury L, Huber B A, Jensen J, Schmidt H T, Zettergren H, Cederquist H, Tomita S and Hvelplund P 2003 Highly charged clusters of fullerenes: charge mobility and appearance sizes *Phys. Rev. Lett.* **91** 215504
- [154] Holm A I S *et al* 2010 Ions colliding with cold polycyclic aromatic hydrocarbon clusters *Phys. Rev. Lett.* **105** 213401
- [155] Zettergren H, Schmidt H T, Cederquist H, Jensen J, Tomita S, Hvelplund P, Lebius H and Huber B A 2002 Static over-the-barrier model for electron transfer between metallic spherical objects *Phys. Rev. A* **66** 032710
- [156] Zettergren H, Schmidt H T, Reinhard P, Cederquist H, Jensen J, Hvelplund P, Tomita S, Manil B, Rangama J and Huber B A 2007 Even–odd effects in the ionization cross section of  $[\text{C}_{60}]_2$  and  $[\text{C}_{60}\text{C}_{70}]$  dimers *Phys. Rev. A* **75** 051201
- [157] Gatchell M and Zettergren H 2016 Knockout driven reactions in complex molecules and their clusters *J. Phys. B: At. Mol. Opt. Phys.* **49** 162001
- [158] Zettergren H *et al* 2010 Magic and hot giant fullerenes formed inside ion irradiated weakly bound  $\text{C}_{60}$  clusters *J. Chem. Phys.* **133** 104301
- [159] Arden W, Brillouet M, Coge P, Graef M, Huizing B and Mahnkopf R 2010 More-than-Moore White Paper [http://itrs2.net/uploads/4/9/7/7/49775221/irc-itrs-mtm-v2\\_3.pdf](http://itrs2.net/uploads/4/9/7/7/49775221/irc-itrs-mtm-v2_3.pdf)
- [160] Wilhelm R A, Gruber E, Schweska J, Heller R, Fascko S and Aumayr F 2018 Neutralization dynamics of slow highly charged ions in 2D materials *Appl. Sci.* **8** 1050
- [161] Schleberger M and Kotakoski J 2018 2D material science: defect engineering by particle irradiation *Materials* **11** 1885
- [162] Heller R, Fascko S, Wilhelm R A and Möller W 2009 Defect mediated desorption of the  $\text{KBr}(001)$  surface induced by single highly charged ion impact *Phys. Rev. Lett.* **101** 096102
- [163] Margapoti E, Asmar M M and Ulloa S E 2016 The effects of substrates on 2D crystals *Adv. 2D Mater.* (Hoboken, NJ: Wiley) pp 67–113
- [164] Hopster J, Kozubek R, Ban-d'Etat B, Guillous S, Lebius H and Schleberger M 2014 Damage in graphene due



- to electronic excitation induced by highly charged ions *2D Mater.* **1** 101011
- [165] Kozubek R, Ernst P, Herbig C, Michely T and Schleberger M 2018 Fabrication of defective single layers of hexagonal boron nitride on various supports for potential applications in catalysis and DNA sequencing *ACS Appl. Nano Mater.* **1** 3765
- [166] Gruber E *et al* 2016 Ultrafast electronic response of graphene to a strong and localized electric field *Nat Commun.* **7** 13948
- [167] Wilhelm R A, Gruber E, Schweska J, Kozubek R, Madeira T I, Marques J P, Kobus J, Krasheninnikov A V, Schleberger M and Aumayr F 2017 Interatomic coulombic decay: the mechanism for rapid deexcitation of hollow atoms *Phys. Rev. Lett.* **119** 103401
- [168] Horsfield A P, Bowler D R, Fisher A J, Todorov T N and Sánchez C G 2004 Beyond Ehrenfest: correlated non-adiabatic molecular dynamics *J. Phys.: Condens. Matter* **16** 8251
- [169] Okorokov V V 1964 Coherent excitation of optical spectra of atoms passing through a crystal *JETP Lett* **2** 111–3
- [170] Datz S, Moak C D, Crawford O H, Krause H F, Dittner P F, Gomez del Campo J, Biggerstaff J A, Miller P D, Hvelplund P and Knudsen H 1978 Resonant coherent excitation of channeled ions *Phys. Rev. Lett.* **40** 843
- [171] Datz S, Dittner P F, Krause H F, Vane C R, Crawford O H, Forster J S, Ball G S, Davies W G and Geiger J S 1995 Resonant coherent excitation of  $N^{6+}$  and  $Mg^{11+}$  in planar channeling: anisotropies in ionization probabilities and x-ray emission *Nucl. Instrum. Methods Phys. Res. B* **100** 272–8
- [172] Komaki K, Azuma T, Ito T, Takabayashi Y, Yamazaki Y, Sano M, Torikoshi M, Kitagawa A, Takada E and Murakami T 1998 Resonant coherent excitation of 390 MeV/u Ar ions planar channeled in Si crystals *Nucl. Instrum. Methods Phys. Res. B* **146** 19–28
- Azuma T, Ito T, Komaki K, Yamazaki Y, Sano M, Torikoshi M, Kitagawa A, Takada E and Murakami T 1999 Impact parameter dependent resonant coherent excitation of relativistic heavy ions planar channeled in crystals *Phys. Rev. Lett.* **83** 528–31
- [173] Kondo C, Masugi S, Nakano Y, Hatakeyama A, Azuma T, Komaki K, Yamazaki Y, Murakami T and Takada E 2006 Three-dimensional resonant coherent excitation of nonchanneling ions in a crystal *Phys. Rev. Lett.* **97** 135503
- [174] Nakano Y, Suda S, Hatakeyama A, Nakai Y, Komaki K, Takada E, Murakami T and Azuma T 2012 Selective production of the doubly excited  $2p2$  ( $1D$ ) state in He-like  $Ar^{16+}$  ions by resonant coherent excitation *Phys. Rev. A* **85** 020701(R)
- [175] Nakai Y, Nakano Y, Azuma T, Hatakeyama A, Kondo C, Komaki K, Yamazaki Y, Takada E and Murakami T 2008 Dressed atoms in flight through a periodic crystal field: X-VUV double resonance *Phys. Rev. Lett.* **101** 113201
- [176] Nakano Y *et al* 2013 Resonant coherent excitation of the lithiumlike uranium ion: a scheme for heavy-ion spectroscopy *Phys. Rev. A* **87** 060501(R)
- [177] Ullmann J *et al* 2015 An improved value for the hyperfine splitting of hydrogen-like  $^{209}Bi^{82+}$  *J. Phys. B: At. Mol. Opt. Phys.* **48** 144022–30
- [178] Kimura K, Ida H, Fritz M and Mannami H 1996 Resonant coherent excitation of surface channeled ions *Phys. Rev. Lett.* **76** 3850
- Auth C, Mertens A, Winter H, Borisov A G and García de Abajo F J 1997 Resonant coherent excitation of fast hydrogen atoms in front of a LiF(001) surface *Phys. Rev. Lett.* **79** 4477–80
- [179] Hatakeyama A, Enomoto Y, Komaki K and Yamazaki Y 2005 Motion-induced magnetic resonance of Rb atoms in a periodic magnetostatic field *Phys. Rev. Lett.* **95** 253003
- Nagata Y, Kurokawa S and Hatakeyama A 2017 Magnetic resonance of rubidium atoms passing through a multi-layered transmission magnetic grating *J. Phys. B: At. Mol. Opt. Phys.* **50** 105002
- [180] Ehrenfreund P and Charnley S B 2000 Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early Earth *Annu. Rev. Astron. Astrophys.* **38** 427–83
- [181] Altwegg K *et al* 2016 Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov–Gerasimenko *Sci. Adv.* **2** e1600285
- [182] Rothard H, Domaracka A, Boduch P, Palumbo M E, Strazzulla G, da Silveira E F. and Dartois E 2017 Modification of ices by cosmic rays and solar wind *J. Phys. B: At. Mol. Opt. Phys.* **50** 062001 (Topical Review)
- [183] Pilling S, Seperuelo Duarte E, da Silveira E F, Balanzat E, Rothard H, Domaracka A and Boduch P 2010 Radiolysis of ammonia-containing ices by energetic, heavy and highly charged ions inside dense astrophysical environments *Astron. Astrophys.* **509** A87
- [184] Vignoli Muniz G S, Mejía C F, Martínez R, Augé B, Rothard H, Domaracka A and Boduch P 2017 Radioresistance of adenine to cosmic rays *Astrobiology* **17** 298–308
- [185] Callahan M P, Smith K E, Cleaves H J II, Ruzicka J, Stern J C, Glavin D P, House C H and Dworkin J P 2011 Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases *Proc. Natl Acad. Sci. USA* **108** 13995–8
- [186] Evans N L, Bennett C J, Ullrich S and Kaiser R I 2011 On the interaction of adenine with ionizing radiation: mechanical studies and astrobiological implications *Astrophys. J.* **730** 69
- [187] Augé B, Been T, Boduch P, Chabot M, Dartois E, Madi T, Ramillon J M, Ropars F, Rothard H and Voivenel P 2018 IGLIAS: a new experimental set-up for low temperature irradiation studies at large irradiation facilities *Rev. Sci. Instrum.* **89** 075105
- [188] Ehrenfreund P and Cami J 2010 Cosmic carbon chemistry: from the interstellar medium to the early earth *Cold Spring Harb. Perspect. Biol.* **2** a002097
- [189] Allodi M A *et al* 2013 Complementary and emerging techniques for astrophysical ices processed in the laboratory *Space Sci. Rev.* **180** 101–75
- [190] Larsson M and Orel A 2008 *Dissociative Recombination of Molecular Ions* (Cambridge: Cambridge University Press)
- [191] Møller S P 1997 ELISA, an electrostatic storage ring for atomic physics *Nucl. Instrum. Methods Phys. Res. A* **394** 281–6
- [192] Hansen K, Andersen J U, Hvelplund P, Møller S P, Pedersen U V and Petrunin V V 2001 Observation of a  $1/t$  decay law for hot clusters and molecules in a storage ring *Phys. Rev. Lett.* **87** 123401
- [193] Schmidt H T 2015 Electrostatic storage rings for atomic and molecular physics *Phys. Scr.* **T166** 014063
- [194] Schmidt H T *et al* 2013 First storage of ion beams in the double electrostatic ion-ring experiment: DESIREE *Rev. Sci. Instrum.* **84** 055115
- [195] von Hahn R *et al* 2016 The cryogenic storage ring CSR *Rev. Sci. Instrum.* **87** 063115
- [196] Nakano Y, Enomoto Y, Masunaga T, Menk S, Bertier P and Azuma T 2017 Design and commissioning of the RIKEN cryogenic electrostatic ring (RICE) *Rev. Sci. Instrum.* **88** 033110
- [197] Ball P 2017 FOCUS: the coolest molecular ion beams *Physics* **10** 93
- [198] Saha K, Chandrasekaran V, Heber O, Iron M A, Rappaport M L and Zajfman D 2018 Ultraslow isomerization in photoexcited gas-phase carbon cluster  $C_{10}$  *Nat. Commun.* **9** 912

- [199] Reinhard P *et al* 2009 Precision lifetime measurements of He<sup>-</sup> in a cryogenic electrostatic ion-beam trap *Phys. Rev. Lett.* **103** 213002
- [200] Durante M *et al* 2019 *Phys. Scr.* **94** 29
- [201] Stöhlker T, Litvinov Y, Bräuning-Demian A, Lestinsky M, Herfurth F, Maier R, Prasuhn D, Schuch R, Steck M and for the SPARC Collaboration 2014 SPARC collaboration: new strategy for storage ring physics at FAIR *Hyperfine Interact.* **227** 45–53
- [202] Stöhlker T *et al* 2015 APPA at FAIR: From fundamental to applied research *Nucl. Instrum. Methods Phys. Res. B* **365** 680–5
- [203] Brandau C, Kozhuharov C, Lestinsky M, Müller A, Schippers S and Stöhlker T 2015 Storage-ring experiments on dielectronic recombination at the interface of atomic and nuclear physics *Phys. Scr.* **2015** 014022
- [204] Tashenov S *et al* 2006 First measurement of the linear polarization of radiative electron capture transitions *Phys. Rev. Lett.* **97** 223202
- [205] Gumberidze A *et al* 2013 Electron- and proton-impact excitation of hydrogenlike uranium in relativistic collisions *Phys. Rev. Lett.* **110** 213201
- [206] Hagmann S *et al* 2013 Few-body quantum dynamics of high-*Z* ions studied at the future relativistic high-energy storage ring *Phys. Scr.* **2013** 014086
- [207] Botermann B *et al* 2015 Test of time dilation using stored Li<sup>+</sup> ions as clocks at relativistic speed *Phys. Rev. Lett.* **113** 120405
- [208] Bosch F, Litvinov Y A and Stöhlker T 2013 Nuclear physics with unstable ions at storage rings *Prog. Part. Nucl. Phys.* **73** 84
- [209] Nakano Y *et al* 2013 Resonant coherent excitation of the lithiumlike uranium ion: a scheme for heavy-ion spectroscopy *Phys. Rev. A* **87** 060501
- [210] Kluge H J *et al* 2008 HITRAP: a facility at GSI for highly charged ions *Adv. Quantum Chem.* **53** 83
- [211] Lestinsky M *et al* 2016 Physics book: CRYRING@ESR *Eur. Phys. J. Spec. Top.* **225** 797–882
- [212] Murböck T, Schmidt S, Birkl G, Nörtershäuser W, Thompson R C and Vogel M 2016 Rapid crystallization of externally produced ions in a Penning trap *Phys. Rev. A* **94** 043410
- [213] Rothhardt J, Hädrich S, Demmler S, Krebs M, Winters D F A, Kühl T, Stöhlker T, Limpert J and Tünnermann A 2015 Prospects for laser spectroscopy of highly charged ions with high-harmonic XUV and soft x-ray sources *Phys. Scr.* **2015** 014030
- [214] Hengstler D *et al* 2015 Towards FAIR: first measurements of metallic magnetic calorimeters for high-resolution x-ray spectroscopy at GSI *Phys. Scr.* **2015** 014054