Ions interacting with complex molecular systems: 
The effect of a surrounding environment

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Abstract. This paper highlight results from studies of keV-ion impact on complex molecules and molecular clusters, which have been carried out at the ARIBE facility in Caen (France) during the last decade. Studies of fullerenes, Polycyclic Aromatic Hydrocarbons (PAHs), and biomolecules are reviewed with focus on the effect of a surrounding environment when ions interact with weakly bound clusters of theses species. One common result is that charge and energy are rapidly shared between the individual molecules in the clusters, in contrast to e.g. weakly bound atomic clusters where the charge stay localized to a few atoms from which the electrons are removed during the collisions. Another important finding is that ion collisions may induce reactions within clusters such as e.g. proton transfer and different types of molecular growth processes. In the latter case, these processes may be driven by prompt non-statistical atom knockouts in billiard-ball like atom-atom collisions favouring highly reactive fragments. In contrast, statistical fragmentation in general yields different and less reactive fragments.

1. Introduction
During the last decades, there has been a strong development of different methods to produce pure macroscopic quantities of complex molecular systems and techniques to bring fragile systems such as e.g. biomolecules into the gas phase. Complex molecular systems have thus been extensively studied in the laboratory by means of various excitation and ionization tools such as e.g. photons, electrons, and energetic atoms/ions. When isolated molecules are excited in these interactions, the excess energy is typically redistributed across all internal degrees of freedom. This leads to statistical decay through electron emission, photon emission, or fragmentation processes on timescales exceeding the typical vibrational timescales of picoseconds. In such cases, the nature of excitation is unimportant - it is only the amount of excess energy which determines the fate of the molecules.

Studies of weakly bound clusters have also been subjects of strong research efforts. Such studies provide a bridge across the disciplines of physics and chemistry and aim to answer fundamental questions like: Do charge and energy stay localized to a few constituents in clusters which have been exposed to ionizing radiation? If not, how fast is the charge and energy communication? Is the nature of excitation important? Are the individual molecules protected from damage in the cluster environment? Are new fragmentation pathways observed in the cluster environment, which are not present for the isolated molecules? Is it possible to induce intracluster reactions and in that case what drives such processes?

In this paper, the first ever studies of collisions between keV-ions and weakly bound clusters of fullerenes, Polycyclic Aromatic Hydrocarbons (PAHs), and biomolecules are reviewed. These
pioneering experiments were carried out at the ARIBE facility in Caen (France) and have provided new insights into the above-mentioned fundamental questions. A few examples of the molecular structures used in these studies are shown in figure 1. Fullerenes are closed-cage all carbon structures where \( \text{C}_{60} \) is the most prominent family member. Due to its highly symmetric structure where all atoms experience identical chemical environments, \( \text{C}_{60} \) molecules serve as excellent model systems for complex molecular systems. Weakly bound clusters of fullerenes may be viewed as small pieces of fullerite - the solid state manifestation of \( \text{C}_{60} \). The bonds between neighbouring \( \text{C}_{60} \) are of van der Waals type with \( \text{C}_{60}-\text{C}_{60} \) binding energies of only about 0.3 eV, which means that they may rotate freely and thus to a large extent keep their individual properties in fullerite and in clusters. Individual fullerenes (\( \text{C}_{60} \) and \( \text{C}_{70} \)) have been identified in space due to their characteristic IR-emission features [1], and possible signatures of fullerite (or clusters) have also been reported recently [2]. There they may coexist with Polycyclic Aromatic Hydrocarbons (PAHs) [3], which typically consist of fused benzene rings (cf. figure 1). PAHs are believed to be ubiquitous in space [4] and are thought to be the building blocks of interstellar dust grains. These findings raise questions about how fullerenes and PAHs are formed, react, respond to energy transfers, and the role of the surrounding (cluster) environment in such processes. One part of the motivation for the studies presented in this review was to shed light on these intriguing issues, which then may contribute to a better understanding of aspects of the origin and evolution of complex molecules in space [5].

Biomolecular precursors have also been identified in space and, consequently, the possibilities that the building blocks of life came to Earth from e.g. meteorite impacts have been much debated. This illustrates that it is important to understand how stable they are, how they are destroyed and how their fragments may later react to form new molecules. In the present case, keV-ions are used as tools to investigate the inherent properties of biomolecules such as e.g. DNA/RNA (nucleobases) and peptide/protein (amino acids) building blocks (cf. figure 1). Such studies also aim to further our knowledge on radiation damage processes at the single molecular level and to systematically investigate the effects of embedding a molecule inside a cluster. The latter is crucial to mimic a more realistic natural environment as for instance in an aqueous solution.

The paper is organized as follows. In section 2, the experimental multi-coincidence mass spectrometry techniques are briefly described. Sections 3 and 4 are devoted to discussions of results for collisions with monomer and cluster targets, respectively. The results are summarized in section 5 and an outlook with possible future experiments and challenges is also given there.

2. Experimental techniques
The experiments were performed at the ARIBE facility at GANIL in Caen, France. The experimental procedure has been discussed in detail elsewhere [6] and only a brief description is
given here. Ion beams from an Electron Cyclotron Resonance (ECR) ion source are accelerated to keV energies. The ion beams are then pulsed at a repetition rate of a few kHz into microsecond long beam pulses, and interact with a broad distribution [7] of neutral weakly bound molecular clusters from a liquid nitrogen cooled cluster aggregation source. The positively charged collision products are analyzed with the aid of a linear time-of-flight mass spectrometer (cf. figure 2) [8] promptly after the beam pulses have left the interaction region. The collision products hit a gold coated steel plate at the end of the spectrometer, where secondary electrons emitted from the plate are guided to a microchannel (MCP) detector by a weak magnetic field. This arrangement give high detection efficiency, which is crucial for coincidence measurements of charged fragment from the same collision events.

3. Collisions with monomer targets

In the present collision energy regime, the projectiles are slower than the typical target valence electrons and electron capture is the dominant target ionization process. By varying the projectile charge, velocity, and mass, it is then possible to systematically investigate the effects of charging and heating molecular systems. In the present Section we summarize results for collisions with monomer targets - i.e. for targets in which the individual molecules are isolated from each other in vacuum.

3.1. High charge state projectiles

Collisions with highly charged projectiles are dominated by large impact parameter ionization...
through electron capture, where small amounts of energy is deposited directly in the collisions. Still, the molecules may be internally heated as the so formed multiply charged systems are born in their neutral geometry on the subfemtosecond timescale of the collision (vertical ionization), but later relax to minima on the potential energy surfaces from which they may statistically decay. For rigid molecular structures such as e.g. PAHs and fullerenes this heating processes is negligible and highly charged metastable systems may therefore survive on the experimental microsecond timescales. This is illustrated in figure 3, which shows the mass spectrum from collisions between 300 keV Xe^{20+} projectiles and coronene molecules (C_{24}H_{12}) [9]. The dominant peaks correspond to intact C_{24}H_{12}^{7+} in charge states up to q=4, which are due to sequential electron capture processes at large impact parameters. A small fraction of the multiply charged systems (q=2-4) decay through statistical fragmentation processes, mainly through C_{2}H_{2} and H-loss - the lowest dissociation energy channels at about 5 eV [10]. Thus, the relative intact peak intensities (including H-loss channels) reflect the sequence of ionization energies, i.e. the relative ionization cross sections. These are in good agreement with the results from a novel classical over-the-barrier model where PAHs are modeled as infinitely thin metal discs [11]. In this model, the energy barriers experienced by the active electrons are calculated along straight line ion trajectories. When these barriers become lower than the Stark shifted ionization energies the so called over-the-barrier criterion is fulfilled, and electrons are captured by the projectiles. The favorable comparison with experimental results show that the model catches the essentials of the collision dependent target-polarization effects, and that PAHs may be successfully described as small metallic objects when perturbed by an external electrostatic field [11]. Interestingly, fullerene molecules also display metallic behaviors in such interactions, as was recently demonstrated through comparisons between the electrostatic interaction energy for a metal sphere in the presence of a point charge and the corresponding results from molecular structure calculations [12, 13].

Smaller impact parameter collisions yield more highly charged coronene molecules (q>4), which promptly Coulomb explode into the small hydrocarbons with m/q<70 as can be seen in figure 3. This is commonly referred to as charge driven fragmentation. For smaller and less rigid systems such as e.g. biomolecules, internal heating through relaxation processes (cf. above) and Coulomb explosions become important already for moderately charged systems. This gives rise to a much richer fragmentation mass spectrum as illustrated by the example in figure 4 for collisions between 387.5 keV Xe^{25+} projectiles and the amino acid glycine (m/q=75) [14].
Two of the most intense peaks in this spectrum have m/q=30 and m/q=45, which correspond to NH$_2$CH$_2$+ and COOH$,^+$. From the coincidence analysis it becomes evident that these fragments stem from the doubly charged parent molecule, i.e. from Coulomb exploding doubly charged glycine (NH$_2$CH$_2$COOH$^{2+}$). This is consistent with results from molecular structure calculations and ab-initio Molecular Dynamics simulations, which give information about the fragmentation dynamics leading to the formation of the doubly charged fragments (cf. the peaks at mass-to-charge ratios 14.5, 27.5 and 28.5 amu in the insets in figure 4). Interestingly, these calculations show that Coulomb explosions compete with neutral fragment emission following ultrafast intramolecular hydrogen migrations (~ 30 fs). Such ultrafast hydrogen transfers are expected to be important for other biomolecular systems [14]. This example and the recent study of γ-Aminobutyric Acid (NH$_2$-(CH$_2$)$_3$COOH) at ARIBE [15] clearly illustrate the synergy effects and power of combining coincidence time-of-flight mass spectrometry with ab-initio calculations and simulations.

3.2. Low charge state projectiles

For low charge state projectiles electrons are captured at small impact parameters, typically accompanied with substantial amounts of energy transfer to the molecule. Here the energy transfers may be localized to regions close to the projectile ion trajectories and are due to interactions with the electron clouds (electronic stopping) and with the individual atomic nuclei in the molecule (nuclear stopping). For light projectiles such as e.g. He$,^+$, the excess energy is mainly due to electronic stopping processes, as the results from model calculations illustrate in figure 5 [16]. The left panel shows the pure electronic stopping for face on 11.25 keV He collisions with anthracene. This was calculated using the friction coefficients from Puska and Nieminen[17] for He traversing a free electron gas, where the molecular valance electron densities were taken from Density Functional Theory calculations. The corresponding nuclear stopping energies for binary He+C/H interactions using a screened Bohr potential is shown in the middle panel of figure 5, while the total (electronic+nuclear) stopping is shown in the right panel. The total stopping is clearly dominated by electronic stopping with energies on the order of 40 eV, which is well above the activation energies of about 5 eV for fragmentation [10].

After this subfemtosecond excitation process, the stopping energy is typically converted into internal heating followed by statistical decay processes [19]. This is for instance seen in the mass spectrum recorded in He$,^+$ + C$_{14}$H$_{10}$ collisions [18], which is shown in the upper panel of figure 6. The most prominent peaks corresponds to intact singly and doubly charged anthracene. On the left hand side of these there are peaks due to fragmentation of moderately heated systems, yielding fragments corresponding to losses of H atoms and loss of C$_2$H$_x$ (x=2-4). High energy deposits lead to multifragmentation processes as manifested by a broad distribution of C$_n$H$_x^+$ fragments with n=1-11. In this case the total fragmentation yield is (63±1)% , i.e. significantly larger than the (39±1)% recorded using 360 keV Xe$^{20+}$ projectiles (cf. lower panel of figure 6). This clearly demonstrates that the target molecules on the average are much hotter when exposed to projectiles in low charge states compared to when they are exposed to high charge
state projectiles. In the latter case, the molecules are typically multiply charged (cf. above) leading to several small singly charged fragments in Coulomb explosions, which explains why the fragment mass distribution is shifted towards smaller fragments in the lower panel of figure 6 and in figure 3.

4. Collisions with cluster targets

As mentioned in the Introduction, it is possible to systematically investigate the role of a surrounding environment by embedding the molecules inside a cluster. Here, key findings from such studies are briefly summarized. The first part is devoted to charge and energy flow processes when clusters are exposed to keV-ions, while the second part deals with intracluster reactions induced in such interactions.

4.1. Charge and energy flow processes

In 2003, the first study of keV-ions interacting with weakly bound clusters of complex molecules was carried out at the ARIBE facility in Caen [20]. The total mass spectrum from this study is shown in figure 7, which is due to 400 keV Xe$^{20+}$ projectiles colliding with a broad distribution of neutral clusters of fullerenes (including monomers). In this spectrum, intact singly and multiply charged fullerenes are the most dominant products. A large fraction of these are due to collisions with neutral monomers in the target, as they appear in the single-stop spectrum (the spectrum for events where only one charged ion is detected) and has a charge-state intensity distribution ($C_{60}^{+}$, $C_{70}^{+}$, $C_{80}^{+}$ etc.) similar to those for a pure monomer target (cf. Ref. [20] for details). However, a substantial fraction of the singly charged intact monomers were shown to be detected in coincidence with each other or with smaller singly charged fragments. This means that they stem from fragmentation of multiply charged clusters, where the charges have been rapidly redistributed before the decay. Thus, in this study it was demonstrated that weakly bound clusters of fullerenes become highly conducting when charged, while being insulators as neutrals (i.e. like small pieces of bulk fullerite). This behavior is in strong contrast to weakly bound atomic Ar$_n$ clusters where the charge stays localized to a few atoms when ionized by highly
charged keV-projectiles [21]. To the right hand side of the singly charged monomer peak, there are distributions of intact singly and multiply charged clusters surviving on the experimental microsecond timescales, where the smallest cluster sizes for a given charge state (appearance sizes) were shown to be as small as n=5, 10, 21, and 33 for q=2, 3, 4, and 5, respectively.

As the charge is rapidly redistributed, the detection of two charged intact fullerene monomers in coincidence can be taken as a fingerprint for Coulomb explosion of a multiply charged dimer system. In Refs. [23] and [24] this was used to extract the relative ionization yields (by counting the number of such events) and the kinetic energy releases in the fragmentation processes (from the peak widths) as functions of the dimer charge state. Interestingly, the relative ionization yields display strong even-odd effects, which can only be explained if the charge communication
takes place during the collisions, i.e. on the sub-femtosecond timescales (cf. Ref. [23] for details). This was later supported by combined Density Functional Theory (DFT) molecular structure calculations and modeling work [22]. However, the kinetic energy releases predicted from theory were shown to be significantly smaller than the measured ones (cf. figure 8). The reason for this discrepancy was attributed to internal heating by Coulomb explosions, i.e. that a substantial fraction (about 50%) of the potential energy is converted into internal energy of the separating monomers. The theoretical values are for internally cold systems and thus serve as upper limits for the kinetic energy release values.

![Mass-to-charge spectra](image)

**Figure 9.** Left panels: Mass-to-charge spectra below m/q=190 for 11.25 keV He\(^+\) + [C\(_{14}\)H\(_{10}\)]\(_k\) (upper panel) and 360 keV Xe\(^{20+}\) + [C\(_{14}\)H\(_{10}\)]\(_k\) collisions (lower panel). (Reproduced with permission from [18] © 2011 APS). Insets show relative C\(_n\)H\(_j\)\(^+\) intensity distributions as functions of n for the cluster (filled symbols) and monomer target (open symbols) scaled by the ratio between the cluster and monomer fragmentation efficiencies. Right panels: Size-to-charge spectra for fragment clusters, [C\(_{14}\)H\(_{10}\)]\(_j<k\), produced in He\(^+\)/Xe\(^{20+}\) + [C\(_{14}\)H\(_{10}\)]\(_k\) collisions. Insets: zoom-ins for j>4 with logarithmic intensity scales.

Interestingly, rapid charge and energy redistribution appear to be a general feature in collisions with weakly bound molecular systems, as it has also been demonstrated for biomolecular clusters [26, 27, 15, 28] as well as for PAH clusters [18, 29]. The latter is illustrated in figure 9, which shows the mass spectra recorded in collisions between He\(^+\)/Xe\(^{20+}\) projectiles and anthracene (C\(_{14}\)H\(_{10}\)) clusters [18]. The monomer- and cluster-fragment regions of the mass spectra are shown in the left and right panels, respectively. The cluster distributions are rather similar for both projectiles, with a rapidly decreasing trend as a function of size, but the collision scenarios are different. In the He\(^+\) case (upper panel), energy is mainly deposited in electronic stopping processes along the ion trajectories (cf. Sec. 3.2). This energy is redistributed and the clusters cool down by long sequences of neutral emissions of intact anthracene molecules, in most cases all the way down to the singly charged anthracene. Indeed, in this case monomer fragments stemming from clusters are significantly colder than when the anthracene monomer target is ionized by the same projectile at the same velocity (cf. figure 6). The fragmentation yield is about a factor of ten smaller, only (6±1)% in the cluster case. Thus, the monomers are
protected from damage by the cluster environment. In the Xe$^{20+}$ case (lower panel), only small amounts of energy is deposited directly in collisions (cf. Sec. 3.1). Surprisingly, the monomers are not protected from damage in collisions with Xe$^{20+}$ as the fragmentation yield is similar to that for the pure monomer target (cf. figure 6). The reason for this is most likely heating by Coulomb explosions of multiply charged clusters, which was shown to be important for multiply charged fullerene dimers (cf. Fig 8).

![Figure 10](image_url)

**Figure 10.** Left: Zoom-in of the mass spectrum recorded in collisions between 50 keV O$^{5+}$ projectiles and thymine clusters. The corresponding data for the monomer target is shown in grey. Right: Thymine dimer structure. (Reproduced with permission from [26] © 2006 John Wiley & Sons)

Another intriguing result is that the cluster environment may open up decay pathways which are closed in interactions with the isolated molecules. This was demonstrated in collisions between 60 keV C$^{5+}$ and nucleobase monomers and clusters [26]. Figure 10 shows that the mass spectra for collisions with thymine targets display similar features, but there are important differences. The most striking effect is the appearance of new channels in the cluster case corresponding to O- and OH-loss. Using coincidence data, it was shown that this channel appears already in collisions with the smallest clusters (dimers) [26]. The most likely explanation for this new channel is that the intermolecular O-H bonds weakens the intramolecular bonds in the clusters, which favor the loss of a single O and a single H atom involved in the hydrogen bonds (cf. figure 10). This illustrates another type of effect due to the cluster environment which so far has not been observed with PAH and fullerene targets.

4.2. *Intracluster reactions*

It is well established that heated fullerenes emit C$_2$-molecules rather than single carbon atoms in statistical fragmentation processes [31]. This simply reflects the large differences in dissociation energies, about 10 eV [32] and 15 eV [33], respectively. However, despite intense research the actual fullerene formation mechanism is still debated, as it is not fully understood why C$_{60}$ are formed so much more abundantly than other fullerenes in nature (e.g. in a fire flame). Possible explanations involve e.g. bottom-up mechanisms in which individual C-atoms or C$_2$-molecules are ingested by smaller fullerenes [34], top-down mechanisms from decay of hot giant fullerenes [35], or emission of electromagnetic radiation [36]. These rely on the lower reactivity [34], more stable structure [35], and more effective radiative cooling of C$_{60}$ [36] with respect to neighboring fullerene sizes.

It has been demonstrated that larger fullerenes may be formed from smaller ones when fullerene films and fullerene clusters are exposed to various kind of photon fluxes [37, 38, 39]. This typically leads to broad distributions of fullerene sizes with an even number of carbon atoms,
quires 80–85 eV collision energies. We operate the cluster source in two modes with low fullerene monomer densities in the cluster source, i.e. with small and large neutral clusters, respectively. Fullerene dimers, trimers, and pentamers are indicated with \([C_{60}]_2^+, [C_{60}]_3^+, [C_{60}]_5^{2+}\) and fullerene monomers with \(C_n^+.\)

Figure 11. Zoom-in of the mass spectra due to 400 keV Xe\(^{20+}\) + \([C_{60}]_n\) collisions. (Reproduced with permission from [30] © 2010 AIP). The spectra were recorded with low (\(\rho_{low}\)) and high (\(\rho_{high}\)) fullerene monomer densities in the cluster source, i.e. with small and large neutral clusters, respectively. Fullerene dimers, trimers, and pentamers are indicated with \([C_{60}]_2^+, [C_{60}]_3^+, [C_{60}]_5^{2+}\) and fullerene monomers with \(C_n^+.\)

reflecting the higher stabilities of those with respect to the odd-numbered ones. Similar mass distributions were observed in collisions between Xe\(^{20+}\) projectiles and weakly bound clusters of fullerenes [30]. As shown in figure 11 these molecular fusion reactions are only seen with large cluster targets. The scenario here is that the individual molecules are destroyed along cluster-penetrating ion trajectories and that the surrounding environment (i.e. large clusters) allows the fragments to react with neighboring intact fullerenes or with other fragments before the clusters completely disintegrate. The measured kinetic energies of the fusion products in Ref. [30] suggest that both size-up and size-down processes are responsible for the mass broad distribution in figure 11. A large fraction of these fusion products corresponds to the most stable closed caged fullerenes, as concluded from the strong correlation between the measured relative peak intensities and the calculated relative stabilities as a function of fullerene size.

More recently, a novel type of molecular fusion reaction has been observed in collisions between He\(^{2+}\) projectiles and clusters of fullerenes [33]. This is illustrated in figure 12, where the left part shows the mass spectra for all collision events (upper panel) and events correlated with one or several intact \(C_{60}^{2+}\) ions (lower panel). The total mass spectrum is rather similar to the one recorded in Xe\(^{20+}\) + \([C_{60}]_n\) collisions (cf. figure 7), but there is significantly more intensity in the dimer region. A large fraction of this intensity appears in the coincidence spectrum and is due to three peaks at the positions for 120, 119, and 118 carbon masses per atomic unit of charge. Surprisingly, the most prominent peak corresponds to an odd number of carbon atoms. These are produced in prompt, nonstatistical, knockouts in Rutherford-like binary He+C scattering processes. The so formed \(C_{59}^+\) ions rapidly react with neighboring \(C_{60}\) molecules in the clusters efficiently forming dumbbell shaped molecular fusion products while the clusters explode (cf. the right part of figure 12). This scenario was supported by molecular dynamics simulations, which show that \(C_{59}^+\) are highly reactive and thus easily form thermodynamically stable dumbbell \(C_{119}^{2+}\) systems [33].

Direct evidence for prompt knock-outs have recently been reported in PAH\(^+\) + He collisions [40, 41, 42], at significantly lower center of mass collision energies (110 eV) where nuclear stopping is the dominant energy loss process. Thus, the molecules are only slightly heated internally (by about 4 eV) in electronic stopping processes and the fragments, which are as highly reactive as \(C_{59}\), may therefore survive on the experimental microsecond timescales. This clearly illustrates that it is a general mechanism, and one would therefore expect to also see such non-statistical driven molecular fusion reactions for complex molecular cluster systems other than fullerenes. However, this has not yet been reported in the literature for collisions with pure PAH or mixed
fullerene/PAH cluster targets. According to pilot molecular structure calculations and molecular dynamics simulations, the kinetic energy required to fuse defect PAH structures with intact PAHs/fullerenes is too high, but it should be possible with molecular systems which are less rigid and more easily bond to the defects [16]. This calls for future studies of mixed clusters.

**Figure 12.** Left: The measured mass-to-charge distributions following 22.5 keV He$^{2+} + [C_{60}]_n$ collisions. (Reproduced with permission from [33] © 2013 APS). The top and bottom panels show the distributions including all events (total spectrum) and for events correlated with one or several intact C$_{60}^+$ ions, respectively. Note the different scales for the left and right panels. The inset in the lower right panel shows a zoom-in on the mass region from 100 to 125 carbon masses per atomic unit of charge. Right: Snapshot from molecular dynamics simulations where a covalently bound dumbbell C$_{119}^+$ system has been formed in a C$_{59}^+$+C$_{60}$ collision when a cluster of thirteen fullerenes explodes.

**Figure 13.** Left: The singly charged adenine monomer peaks recorded in collisions between 37.2 keV O$^{3+}$ ions and adenine monomers (grey area), pure adenine clusters (hatched area), and hydrated adenine clusters (white area). Right: A fit to the monomer peak from collisions with hydrated clusters show contributions from singly charged (m/q=135) and protonated adenine (m/q=136). (Reproduced with permission from [28] © 2012 IOP)
Other types of intracluster reactions have been observed for biomolecules embedded in water clusters [28]. The left panel of figure 13 shows the singly charged adenine monomer peaks following collisions between 37.2 keV O$^{3+}$ ions and adenine monomers, pure adenine clusters, and hydrated adenine clusters. The latter is significantly broader and centered around a higher mass to charge ratio compared to the other ones. This is due to formation of protonated adenine, as revealed from the fit shown in the right panel of figure 13. Here, the formation mechanism is most likely similar to that observed in 12 MeV/u Ni$^{25+}$ impact on pure water clusters [43], where it was demonstrated that water may capture protons from nearby ionized water molecules. The proton affinity is larger for adenine than for water, which readily explains the efficient formation of protonated adenine inside the water cluster.

5. Summary and outlook
To summarize, the first ever studies of ion impact on various kinds of clusters, such as e.g. pure clusters of fullerenes, PAHs, nucleobases, amino acids and hydrated nucleobases, have been performed at the ARIBE facility in Caen, France. One common conclusion from these studies is that charge and energy are rapidly redistributed among the clusters constituents. In addition, different types of intracluster reactions may be induced depending on the actual collision conditions. The cluster environment plays an important role here, proton transfer reactions have for instance been observed for nucleobases in water but not for pure clusters of nucleobases. Intracluster reactions also depend on the size of the clusters and the projectile type, as e.g. certain fullerene fusion reactions are only seen when large clusters are exposed to Xe$^{20+}$ projectiles, while He$^{3+}$ ions ignite different fusion processes.

In the near future it will be possible to study collisions between keV-ions and mass-selected cluster ions with the aid of the novel PIBALE (Plateforme d’Irradiation de Biomolécules et d’Agrégats Libres et Environnés) setup at ARIBE. This will be a tremendous advantage when interpreting the experimental results, as the collision system will be well-defined in contrast to the previous studies of broad distributions of neutral cluster sizes. Another important aspect is to determine the energy being deposited in the interactions, which is an unknown parameter and hampers the interpretations of the results. This is truly challenging from both an experimental and a theoretical point of view. To realize this, common efforts will be essential, for instance within the COST Action XLIC and the European Associated Laboratory (DYNAMO) consisting of research groups from ARIBE, Stockholm University (Sweden), and Universidad Autónoma de Madrid (Spain).

In a somewhat longer perspective, the unique expertise and experience gained from studies of complex molecular systems at ARIBE could serve as an excellent platform for even more advanced experiments, possibly including electrostatic storage devices - traps and/or rings. There ions could be monitored and manipulated on longer timescales. New such facilities, including cryogenically cooled ones, are now being built and commissioned in e.g. Japan [44], Germany [45], and Sweden [46, 47]. The cooling option is a way of controlling the experimental conditions as the ions are in more well-defined quantum states than in room temperature environments. Having such a storage device would further broaden the range of unique studies at ARIBE, and drive the relevant technology and science forward in this new emerging community.

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