Ion interaction with biomolecular systems and the effect of the environment

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Abstract. To fully understand the mechanisms of radiation damage in living tissues, a detailed knowledge of the processes occurring at the molecular level is needed. In the gas phase, most of the investigations concerning the ionization and fragmentation of biologically relevant molecular systems are performed with isolated molecules. The importance of such studies is limited to the intrinsic properties of these molecules because of the lack of a chemical environment. To probe the effect of such an environment on the behavior of small biomolecules under irradiation, the molecules (α-amino acids, adenine) were embedded into clusters. The present results, obtained with multiply charged ions, clearly indicate the protective role of the clusters since the total fragmentation yield is reduced for all systems. The surrounding molecules allow for a redistribution of the excess energy and of the charge within the cluster. In the case of adenine clusters, a new fragmentation channel is identified. Moreover, for hydrated adenine clusters, low-energy ion induced chemical reactions are observed, namely the proton transfer from the water cluster to the adenine molecule.

1. Introduction

To explore the molecular mechanisms underlying radiation damage, intensive studies concerning ionization and fragmentation of biomolecular systems have been performed in recent years. Such detailed knowledge is required in the context of cancer therapies (e.g. hadron-therapy) to investigate possible undesirable side effects and to possibly optimize the therapy strategies. A large fraction of radiation damage has been associated with effects of secondary particles (electrons, radicals, ions) which are created along the ion track.

It has been shown that slow electrons (with energy below the ionization threshold of the molecules) may lead to single or double DNA strand breaks [1,2]. Furthermore, small fragment ions originating from the break-up of nucleobases following collisions with highly charged ions were found to have a sufficient amount of kinetic energy (up to 100 eV) [3] to cause further harmful reactions within the DNA [4,5]. Therefore, ions with kinetic energies in the eV as well as in the keV range, are relevant for heavy ion induced biological radiation damage close to the region of the Bragg peak.

The interactions of different ionizing projectiles with isolated biomolecules have been addressed by means of gas-phase collision studies. This technique is excellent to obtain information about the fragmentation dynamics via mass spectrometric analysis. Unfortunately,
it neglects any effect of the chemical environment (presence of other biomolecules and surrounding water molecules) such as modified ionization energies [6, 7] and/or the dissipation of the excitation energy via solvent molecule evaporation (e.g., water). It has been shown that even a single water molecule can act as a catalyst in chemical reactions [8]. Therefore, in real biological systems the influence of the molecular environment has to be taken into account.

Embedding the molecule into a cluster of identical molecules or other molecules present in a realistic biological environment may lead one step further towards a more realistic case. Such an approach allows to keep the system under study simple enough to explore the underlying fundamental processes. For example, Liu et al. [9] have observed the protective effect of water molecules attached to the anion of RNA nucleotide adenosine 5'-monophosphate (AMP−) when a such system undergoes Collision Induced Dissociation (CID). The energy transferred during the collision to the solvated molecule is used primarily to liberate the loosely bound water molecules, leading to a cooling of the residual system (the fragmentation yield of the AMP molecule was strongly reduced). Very surprisingly, this protective behavior was not at all observed in the case of Electron Capture Induced Dissociation (ECID) [10]. The AMP dianion is always fragmented (H-loss) regardless of the number of attached water molecules. This damaging effect becomes even more important as the number of initially attached water molecules increases [10].

The results for neutral clusters of nucleobases show that the presence of other molecules strongly influences the slow multiply charged ion induced fragmentation pathways. For example, in the case of thymine clusters two new dissociation channels were observed (loss of OH and NH2CH) compared with the isolated thymine molecule. Such a behavior is interpreted as being caused by the weakening of intramolecular bonds due to the presence of an additional intermolecular interaction between the molecules in the cluster (hydrogen bonds) [11]. Therefore, by looking at these types of clusters environmental effects can be studied and the influence of different surroundings on molecular fragmentation can be clarified.

In this paper, we summarize environmental effects observed in collisions of different biomolecular clusters (glycine, α-alanine, valine, adenine) with slow multiply charged ions. Moreover, results for mixed adenine - water clusters will be compared with those obtained for pure adenine clusters as well as for the isolated molecule.

2. Experimental method

Experiments were performed at the low-energy ion beam facility ARIBE of GANIL (Caen, France). A brief overview of the experimental set-up is given here, for more details see reference [12].

The keV multiply charged ion beams, employed in our studies, were extracted from an electron cyclotron resonance (ECR) ion source. The mass selected, collimated and pulsed ion beam was guided to the collision zone where it crossed the neutral molecular beam.

Isolated molecular targets were produced by evaporation of a powder sample (Sigma-Aldrich, purity better than 98 %) in a heated oven. The temperature of the oven was chosen to assure sufficient vapor density and to avoid the thermal decomposition of the molecule. Alternatively, a modified gas phase aggregation source was used to produce amino acid and adenine clusters as well as hydrated adenine clusters. The biomolecules produced by an oven device entered a chamber filled with helium gas at the pressure of a few mbar. Molecules were then guided by the helium flow through a condensation channel (kept at liquid nitrogen temperature) where they aggregated. The neutral cluster beam was guided to the collision chamber by the helium flow through several differential pumping stages. To produce hydrated adenine clusters, water vapor was introduced to the helium gas injection line via a leak valve. To assure a sufficient water quantity a water tank was kept at 320 K and the injection line was heated to 340 K to avoid water condensation.

After the interaction, the cationic products were extracted into a modified Wiley-McLaren
Figure 1. a) Comparison of the molecular fragmentation of the glycine molecule after the interaction with 300 keV Xe$^{20+}$ ions: upper part – isolated molecule, lower part – cluster case. b) Cluster distribution shown in a wide-scale mass spectrum for collisions of 300 keV Xe$^{20+}$ with neutral glycine clusters.

time-of-flight spectrometer [13], and were post-accelerated before impacting a gold-coated plate. The secondary electrons, produced at the plate, were deviated by a magnetic field towards a microchannel plate detector. This Daly-type detector assured a constant detection efficiency for cluster-ions with different masses and charges.

3. Results and discussion

3.1. Protective role of the cluster environment

The studies to identify the influence of the environment were performed in two steps: i) dissociation of the isolated molecule, ii) dissociation of the molecule embedded in a cluster. Figure 1b) displays a spectrum of the cationic cluster distribution (containing up to four molecules: Gly$^+_n$, $n=1$–4) obtained after collisions of 300 keV Xe$^{20+}$ ions with neutral glycine clusters [14]. No multiply charged clusters or multiply charged fragments are observed. This finding will be discussed below. Furthermore, the absence of structures between cluster peaks indicates that there is no signal corresponding to clusters containing a fragment of the monomer. The observed production of small size fragments ($m<m_{monomer}$) probably occurs after the monomer has been emitted from the multiply charged cluster either in a fission or an evaporation process, similar to what has recently been reported for clusters of polycyclic aromatic hydrocarbons [15,16].

In figure 1a) we compare the mass spectrum for masses below 85 amu for Xe$^{20+}$ ion collisions with isolated glycine molecules and glycine clusters. In both cases we find the intact molecular glycine cation as well as small size fragments. In the cluster case, the width of the Gly$^+$ peak is larger compared to the molecular case (by a factor of 2), reflecting the kinetic energy acquired during the fragmentation process. The distribution of the small fragments is found to be different for the molecular and the cluster case. For example, the C-C$_\alpha$ bond cleavage, which leads to the formation of the (Gly-COOH)$^+$ cation (32 amu) and which is dominant in the molecular case (with a relative intensity of 18, see table 1), is strongly reduced for the cluster collision (relative intensity of 1.4 only). Also the complementary fragment COOH$^+$ is observed in the spectrum of the molecular target, but disappears totally in the cluster case. Thus, both observations suggest that the C-C$_\alpha$ bond of the glycine molecule is protected in the cluster case. The energy
transferred during the collision is redistributed among the cluster constituents leading to the rupture of the hydrogen bonds between molecules (typical binding energy about hundreds of meV [17]) cooling the total system at the same time.

**Table 1.** Relative intensities of the main and the complementary fragments observed after collisions of low-energy multiply charged ions with glycine, α-alanine, valine and adenine as isolated molecules and as clusters, respectively. The intensities were normalized with respect to the monomer cation signal intensity. Data for isolated molecules and clusters of glycine and valine are from reference [14]. Results for isolated α-alanine molecules (20 keV He\(^{2+}\)) were taken from reference [18].

| Target      | Projectile | Isolated molecule | Cluster            |
|-------------|------------|-------------------|--------------------|
| Glycine     | 300 keV Xe\(^{20+}\) | (Gly-COOH)\(^+\)  | (Gly-COOH)\(^+\)  |
|             |            | 18                | 1.4                |
|             |            | COOH\(^+\)       | COOH\(^+\)        |
|             |            | 6                 | 0                  |
| α-Alanine   | 32 keV He\(^{2+}\) | (Ala-COOH)\(^+\) | (Ala-COOH)\(^+\)  |
|             |            | ∞                 | 0.96               |
|             |            | COOH\(^+\)       | COOH\(^+\)        |
|             |            | ∞                 | 0.09               |
| Valine      | 300 keV Xe\(^{20+}\) | (Val-COOH)\(^+\) | (Val-COOH)\(^+\)  |
|             |            | ∞                 | 1                  |
|             |            | COOH\(^+\)       | COOH\(^+\)        |
|             |            | ∞                 | 0.05               |
| Adenine     | 37.2 keV O\(^{3+}\) | HNCH\(^+\)       | HNCH\(^+\)        |
|             |            | 0.62              | 0.04               |
|             |            | (Ade-HCNH)\(^+\) | (Ade-HCNH)\(^+\)  |
|             |            | 0.27              | 0.07               |

Furthermore, as to the fragments with masses below the monomer mass, the total fragmentation yield is also strongly reduced in the cluster case as shown in table 2. This decrease is not only due to the redistribution of the transferred energy, but also due to the charge repartitioning over the cluster volume. Recent ion-induced fragmentation studies of the amino acid molecules clearly show that the singly charged carboxyl group is mainly formed after multi-electron capture processes [19]. Thus, charge mobility explains why the COOH\(^+\) fragment disappears in the cluster case. Multi-fragmentation processes (increasing markedly with the charge state of the glycine molecule) lead to the production of small fragments like C\(^+\) or N\(^+\) (the peaks in the range of \(m/q\) = 16–18 amu are due to collisions with the residual gas). Therefore, the strong decrease of the C\(^+\) fragment intensity in the cluster case also indicates the high charge mobility within the cluster.

As indicated in tables 1 and 2, we have also performed experiments with other biomolecular systems: the α-amino acids (α-alanine (NH\(_2\)CH\(_2\)CH\(_3\)COOH) and valine (NH\(_2\)(CH\(_2\))\(_2\)(CH\(_3\))\(_2\)COOH)), and the nucleobase adenine (C\(_5\)H\(_5\)N\(_5\)). The findings are similar to those observed for glycine. It should be noted that for isolated α-alanine and valine molecules, the cationic intact molecule (M\(^+\)) is not observed [14,18]. Similar results have been obtained with
other ionizing methods [20–23]. The main dissociation channel occurs via C-Cα bond cleavage, where the loss of neutral COOH takes place (formation of the decarboxylated ion, (M-COOH)+). The COOH+ cation is also observed with lower intensity. As α-alanine and valine molecules do not survive the collision, the intensity ratios presented in the table 1 for (M-COOH)+ and COOH+ channels are equal to ∞ and total fragmentation yields are 1, respectively.

Table 2. Relative intensities of singly charged carbon ions (IC+/IT) and of the total fragmentation yield (IF/IT) for isolated biomolecules and molecules embedded in a cluster environment. IT is the integral intensity of the measured spectrum for masses above 10 amu. The projectiles correspond to those given in table 1.

| Target    | IC+/IT | IF/IT |
|-----------|--------|-------|
| Glycine   | 0.07   | 0.98  |
| α-Alanine | 0.04   | 1     |
| Valine    | 0.06   | 1     |
| Adenine   | 0.1    | 0.79  |

In summary, the present results clearly indicate the protective role of the cluster environment. The total fragmentation yield is significantly reduced (up to 50%). Moreover, embedding the α-alanine and valine molecule into clusters allows to protect the C-Cα bonds, and intact molecular cations are observed. In the same way as for glycine clusters, the (M-COOH)+ signal intensities are reduced and the quenching of the COOH+ fragments is observed.

Figure 2 shows the mass spectra of the cations produced in the interaction of O3+ ions with isolated adenine (upper part) and neutral adenine clusters (lower part). The choice of the region of interest (from m/q = 10 to 140 amu) facilitates the comparison of the fragmentation patterns. In both cases, fragments are divided into series containing a fixed number of heavy atoms (carbon and/or nitrogen - the number is indicated on the top of figure 2) and a varying number of hydrogen atoms. The fragmentation of isolated adenine molecules is mainly driven by the successive loss of neutral HCN fragments [24–27]. The fragmentation of adenine within the cluster follows the same pattern. However, from a global point of view, the fragmentation is considerably reduced by a factor of 2 (table 2 and figure 2), showing the protective effect already presented for amino acids. For example, the main fragmentation channel – formation of HCNH+ (28 amu) – has been lowered by a factor of 15 (table 1). As mentioned before, the cluster dissipates the excess energy by evaporation of monomers and/or by cluster fission where the hydrogen bonds break preferably. The intensity ratios of carbon ions to the total yield of ionic products (IC+/IT), like in the case of amino acid clusters, are substantially reduced indicating that a rapid charge redistribution takes place within the clusters. This statement is also supported by the fact that doubly charged adenine ions (Ade2+) are not observed any more for the cluster case.

3.2. New fragmentation channels due to cluster environment

Nevertheless, protection is not the only environmental effect that appears in the case of adenine clusters. The intensity of the fragment signals containing 9 and 7 heavy atoms are indeed stronger in the cluster case (see figure 2). Such a behavior for nucleobase clusters has already
Figure 2. Cationic products of the interaction between 37.2 keV O\(^{3+}\) ions and isolated adenine molecules (upper part) and adenine clusters (lower part). The numbers given on the top of the graph correspond to the number of heavy atoms in a fragment. The insert displays a neutral adenine dimer which has been observed experimentally [28]. Regions in red indicate new fragmentation channels observed for adenine molecules embedded in the cluster.

been mentioned by Schlathölter et al. [11]. The opening of additional fragmentation channels for the adenine molecule is related to the interplay between intra- and intermolecular interactions. It is shown that in hydrogen bonded regions, the electronic structure of the molecule is strongly modified [29]. The IR-UV spectrum of the adenine dimer indicates a molecular structure where molecules are bound by a N\(\cdots\)HN and a C-NH\(_2\)\(\cdots\)N bond [28]. Such an interaction weakens the neighbored C-NH\(_2\) bond and gives rise to the fragment ions (Ade-NH\(_n\))\(^+\) with masses of 118 \((n = 3)\) and 119 amu \((n = 2)\). In a second step, this fragment may lose an HCN unit leading to C\(_4\)H\(_2\)N\(_3\) where an additional H atom might be lost or added (91 and 93 amu). Similar results have been obtained for uracil and thymine molecules [11].

3.3. Proton transfer within hydrated adenine clusters

In general, biological reactions occur in aqueous solutions. Therefore, hydration plays a very important role in the chemistry of biological systems. A better understanding of radiation damage depends on the knowledge of the physical and chemical behavior of the hydrated complexes consisting for example of nucleobases and water molecules. Over the last years, intensive efforts were made to study the water binding sites and energies, the effect of water molecules on conformation of biomolecules, as well as the effect on their stability (e.g. [9, 10, 30–33]).

Here, we present preliminary results for low-energy ion interaction (37.2 keV O\(^{3+}\)) with neutral mixed adenine-water clusters. To our knowledge, these are the first results on nucleobase-water complexe dissociation in the gas phase induced by low-energy ions. Figure 3 displays a part of the observed mass spectrum, showing the mass range between the adenine monomer and the
Figure 3. Cationic products of the interaction between 37.2 keV O$^{3+}$ ions and neutral hydrated adenine clusters shown in the range between the adenine monomer (Ade) and dimer (Ade$_2$). For more details see text.

adenine dimer. In addition to these two peaks, we observe two series of peaks which correspond to protonated water clusters (H$^+$(H$_2$O)$_m$) with $m=7$ to 14 and the adenine monomer to which up to $n=8$ water molecules are attached (Ade(H$_2$O)$_n$). In general, these clusters are fragments from larger clusters which evaporate or fragment due to the energy and charge transferred in the collision. This is partly indicated by the increased peakwidth of the adenine peak compared to ion collisions with an isolated molecule. The fact that during these fragmentation processes water molecules remain linked to the adenine, at a microsecond time scale, is not surprising. Indeed, binding energies between water molecules, adenine molecules and between water and adenine molecules within clusters have similar values [34, 35]. Compared to the non-hydrated cluster case, the fragmentation yield (fragments with masses below the adenine monomer, not shown in figure 3) is lower and these low-mass fragments are not observed with a water molecule attached. This suggest that the fragmentation of the adenine molecule occurs after liberation of all loosely bound water molecules. Moreover, this evaporation chain leads to a cooling of the system. Therefore, the fragmentation probability of the adenine molecule itself is lowered.

We should mention that similar mass spectra have been obtained by electron [36,37] and by photon impact [34,37]. In the latter case it was shown that the intensity of the hydrated adenine monomer depends strongly on the laser wavelength.

In figure 4, we compare the peak width of the adenine monomer for spectra obtained with isolated molecules, pure adenine clusters and hydrated adenine clusters. As already mentioned above, for the isolated molecule the peak is rather narrow showing its isotopic contributions and the loss of a hydrogen atom. For pure adenine clusters the monomer peak is widened due to evaporation/fragmentation processes preventing the observation of any fine structure. In the case of hydrated adenine clusters the peak is further widened and its center is shifted by about half a mass unit. This finding is interpreted in the following way: the monomer adenine peak of the hydrated cluster spectrum is in fact the result of two different contributions – the adenine molecule (Ade$^+$) as well as the protonated adenine ion (AdeH$^+$). As we do not observe proto-
Figure 4. Zoom into the $m/q = 130–140$ amu mass range, showing the adenine monomer after the collision with 37.2 keV $O^{3+}$ ions. a) Grey area - isolated molecule, hatched area - adenine clusters, and white area - hydrated adenine clusters. b) Large blue dots correspond to experimental points of the adenine monomer for hydrated adenine clusters. Full blue line represents the sum of fitting obtained for the contribution of adenine ion ($Ade^+$, $m/q = 135$ amu) and protonated adenine ion ($AdeH^+$, 136 amu).

nation in the pure cluster case (see figure 4a)), we assume that protonation of adenine (b) is due to the presence of water molecules. The protonated adenine monomer peak was also observed in the case of electron impact and multiphoton ionization [34,37,38]. The electron impact studies of hydrated nucleobases suggest that the protonated nucleobase monomer is only observed when the electron energy is above the ionization potential of water [36]. Therefore, to explain such a formation, we propose the following mechanism in the case of single electron capture for a water molecule within an hydrated adenine cluster:

\[
O^{3+} + [Ade + (H_2O)_n] \rightarrow O^{2+} + [Ade + (H_2O)_n]^+ \quad (1)
\]

\[
[Ade + (H_2O)_n]^+ \rightarrow [Ade + H'(H_2O)_{n-1}]^+ + OH^* \quad (2)
\]

\[
[AdeH^+ + (H_2O)_{n-1}]^+ + OH^* \quad (3)
\]

\[
[AdeH^+ + (H_2O)_{n-1}]^+ \rightarrow [AdeH^+]^+ + [(H_2O)_{n-1}]^* \quad (4)
\]

First, the $O^{3+}$ ion interacts with an hydrated cluster of adenine, removing an electron from one of the water molecules (equation (1)). Then, a protonated cluster is fastly formed by evaporation of a neutral OH fragment at the picosecond time scale (such a behavior was observed in water clusters [39]). As the proton affinity of the adenine molecule is higher than that of water [40, 41], a proton transfer to the adenine molecule may occur (see equation (2) and (3)). The protonated adenine monomer ($AdeH^+$) is observed after losing all the surrounding water molecules (4). Experiments performed with 300 keV $Xe^{20+}$ ions have shown similar results. The contribution of protonated adenine compared to $Ade^+$ was increased. It indicates that the number of electrons captured from the water molecules strongly influences this process.
4. Conclusions
We have studied the fragmentation of \(\alpha\)-amino acids and adenine molecules in the collision with low-energy multiply charged ions. We evidenced that the presence of an environment strongly influences the fragmentation dynamics of the molecules. On the one hand, the energy transferred during collisions is dissipated by evaporation and/or cluster fission leading to a protection of the C-C\(\alpha\) bond in the molecule. The hydrogen bonds in the cluster are preferentially broken. On the second hand, the fast charge redistribution within the cluster leads to a protection of the molecule as well (for example the COOH\(^+\) channel is quenched for amino acids).

For clusters of adenine molecules we have observed new fragmentation channels related to the weakening of the intermolecular bond due to hydrogen bonding of the clusters. Furthermore, we have observed ion-induced chemical reactions within hydrated adenine clusters, leading to a protonation of the adenine monomer.

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