Ion induced radiation damage on the molecular level
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The experimental results presented in the course of this thesis require understanding of electron removal, molecular fragmentation and molecular structure. The first two are associated with the collision process and its consequences. The third ingredient is used to understand the results of the collision process. In this chapter the basic concepts of ion–molecule collisions will be described for ions at keV energies. Possible fragmentation mechanisms will be discussed. At the end of the chapter some of the quantum chemical models used to explore the geometry, stability and internal energy of the biomolecules under study will be introduced.
3.1. Scenario for ion-molecule interaction

For projectile velocities of 0.1–1 a.u., the ion–molecule interaction time is around $10^{-16}$ to $10^{-15}$ s which is much shorter than typical vibrational time scales in molecules ($10^{-13}$ to $10^{-12}$ s). During the collision, electronic and vibrational wave-functions can thus be decoupled, i.e. the Born-Oppenheimer approximation is applicable. For very slow projectiles, this approximation is not valid. The scenario for the interactions under study can thus be divided in two steps:

1) The collision itself, involving the excitation of the molecular target or the creation of one or more vacancies in the molecular target by charge transfer, transfer ionization or direct ionization.

2) Fragmentation of the excited/ionized target. The excited and/or ionized transient molecular complex follows its reaction path on a multidimensional potential energy landscape. Here, the Coulombic repulsion and the energy deposited by the projectile play an important role.

Much work has been devoted to the study of collisions between highly charged ions (HCl) and small diatomic or triatomic molecules (for example H$_2$, D$_2$, CO and CO$_2$). The process of fragmentation for these small systems can be explored in great detail and is better understood than collisions involving larger systems, where it is virtually impossible to map the multidimensional potential energy surfaces. For a review see for example references [42, 43].

3.1.1. Charge exchange

The first step in fast collisions involves mainly the projectile and the electrons of the molecule. The positions of the nuclei remain fixed. All electronic transitions therefore, follow the Franck–Condon principle: the electronic transition occurs without changes in the positions of the nuclei. Because of the large mass difference between the electrons and the nuclei, the electronic motions are much faster than the nuclear ones. Then, in potential energy diagrams as the ones in fig. 3.1, the transition will be vertical. In a quantum mechanical picture, the highest transition probability is found for the particular level whose wave function maximum lies just above the maximum of the ground state [44].

In the velocity range used in this thesis (0.1–1 a.u.), the three main processes involved in the collision are: charge transfer, direct ionization and excitation of the molecular target. The collision process depends on the impact parameter: for small impact parameters (close collisions) multiple ionization is expected but for large impact parameters (distant collisions) it is more likely that electron capture is the dominant process. Both processes are usually accompanied by excitation of the molecular target. The collision of a projectile $A$ with charge $q$ with a molecule $BC$ can thus leave the molecule in different states, depending on the kind of collision. The collision can lead to an excited molecule:

$$A^{q+} + BC \rightarrow A^{q+} + BC^* \text{ (excitation)} \quad (3.1)$$

a charged molecule accompanied by release of electrons:

$$A^{q+} + BC \rightarrow A^{q+} + BC^{s+} + se^- \text{ (multiple – ionization)} \quad (3.2)$$
3.1 Scenario for ion-molecule interaction

or a combination of both. In particular distant collisions are characterized by gentle charge transfer from the target to the projectile in a process called electron capture:

\[ A^{q+} + BC \rightarrow A^{(q-r)+} + BC^{r+} \quad \text{(electron capture)} \]  

(3.3)

Single and multiple electron capture processes have been extensively studied in ion-atom collisions but barely for molecular systems. Some of the models used for charge transfer from atoms and some molecules are the classical over the barrier model [45] and more sophisticated classical trajectory Monte Carlo approaches [46]. In the case of our systems, there are usually many electrons involved and it is difficult to apply any of the previous models.

Usually during our experiments excitation, capture and ionization occur at the same time, leading to multiple electron dynamics described by the following general equation:

\[ A^{q+} + BC \rightarrow A^{(q-r)+} + BC^{(r+s)+} + se^{-} \]  

(3.4)

Here, \( r \) is the number of electrons captured from the target to the projectile and \( s \) is the number of electrons released in the collision.

3.1.2. Fragmentation process

After the collision, the projectile has left an excited ionic molecular complex behind. Excitation alone will not be treated here since neutral molecules are difficult to access experimentally. If the vibrational excitation energy is small and the molecular ion is not in a repulsive state, an intact parent ion is finally observed. In all other cases however, the excited molecular ion will dissociate, either promptly or delayed. Typical dissociation timescales of this process range from \( 10^{-12} \) s to several \( 10^{-6} \) s.

The dissociation and fragmentation process is accompanied by release of kinetic energy \( (U_{KER}) \), the process for a molecule BC in an ionic/excited state can be described as follows:

\[ BC^{(r+s)+} \rightarrow B^{u+} + C^{(r+s-u)+} + U_{KER} \]  

(3.5)

here \( r + s \) are the electrons removed during the collision, \( u \) is the charge of one of the fragments and \( r + s - u \) is the charge of the other fragment. \( U_{KER} \) is the kinetic energy released in the dissociation. A molecular ion such as \( BC^{(r+s)+} \) can decay with release of fragments with different charge states and kinetic energies. The energy released in the dissociation is distributed over the fragments in accordance with the conservation of momentum. In this thesis, \( U_r \) is used for the energy of each fragment and \( U_{KER} \) is used for the total kinetic energy released.

The dissociation path that the molecular ion follows depends on its potential energy, in particular on the shape of its potential energy surface (PES). A potential energy surface of a molecular system is defined as the electronic potential energy including nuclear repulsion, at a given nuclear configuration. More details will be given in the next section.

A simple case of a molecular system is the homonuclear diatomic molecule \( \text{H}_2 \). Here, the potential energy surface of the neutral and ionic states is only one–dimensional since the only nuclear coordinate is the internuclear distance. In fig. 3.1, different potential energy curves for \( \text{H}_2 \) and \( \text{H}_2^+ \) together with the Coulombic potential of \( \text{H}_2^+ \) are plotted. The values are taken from a compilation of theoretical and experimental data by Sharp [47].
Figure 3.1: Potential energy curves for the ground state and one excited state of $H_2$ (—), two electronic states of $H_2^+$ (— —) and the Coulomb potential of $H_2^{2+}$ (···). The tabulated data from [47] was used to draw the potential energy curves.
3.2 Molecular structure

The ground state $X^1\Sigma_g^+(1s\sigma)^2$ of $H_2$ is stable. This means that the potential energy curve has a minimum at $R_e=1.4$ a.u. such that the energy $E$ at this point satisfies $E(R_e) < E(H) + E(H)$, where $2E(H)$ is the sum of the energies of the individual H atoms, the dissociation limit. In this case, the H products are in the ground state H(1s). If the potential-energy curve does not possess any minimum then the molecule is unstable. This means the potential is repulsive, for example the triplet state of the neutral $H_2$ molecule: $b^3\Sigma_u^+(1s\sigma 2p\sigma)$, the $2p\sigma_u$ state of $H_2^+$ and the Coulomb potential of $H_2^{3+}$. In fig. 3.1, it can be seen that if a Franck-Condon transition occurs from the ground state of the neutral molecule to one of the repulsive potentials, the molecule will unavoidably dissociate. For example, if the transition involves removing two electrons from the $H_2$ ground state then $H_2^{2+}$ will dissociate in the products $H^+ + H^+$ with an associated $U_{KER} \approx 17$ eV.

Diatomic potential-energy curves can also be like the one for $H_2^+ 1s\sigma_g$ state (fig. 3.1) where the potential energy shows a relative shallow minimum. They can also be a mixture of states and have a relative minimum and a potential maximum, such as the E,F singlet state of $H_2$. Molecules described by such a curve are considered to be metastable. Molecules trapped within the potential well, which can be very shallow as for the first case, will ultimately fragment due to either tunnelling or predissociation. Predissociation occurs if there exists a coupling between the metastable state and an unstable (repulsive) state. If the transition between the states is possible, then the molecule will dissociate. The lifetime of a metastable species depends on the barrier height and width, and on the probability of predissociation.

3.2. Molecular structure

Computational chemistry models are used to describe the geometrical and electronic characteristics of a molecule, compute energies and vibrational frequencies of a given structure. Within computational chemistry there are two broad areas: molecular mechanics and electronic structure theory. Molecular mechanics use the laws of Newtonian physics to model molecular systems. The potential energy is calculated using force fields. It can model very large systems of thousands or millions of atoms but its limitation is that electrons are not included explicitly. Electronic structure methods use the laws of quantum mechanics to predict the properties of molecular systems. They are more accurate for predicting properties which depend on subtle electronic details [48]. In this section an overview of electronic structure methods used by the GAUSSIAN software [49] will be given. This program was used to estimate geometrical structures at stationary points, orbital shape and ionization potentials of some of the systems under study.

3.2.1. Theoretical background

Electronic structure methods are based on solving the time independent, non relativistic Schrödinger equation for the electronic states of the molecule:

$$H_{elec}\Psi_{elec}(\vec{r},\vec{R}) = E_{elec}(\vec{R})\Psi_{elec}(\vec{r},\vec{R})$$  (3.6)

Here, $\Psi$ is a function of the position of the electrons ($\vec{r}$) and the nuclei ($\vec{R}$) within the molecule. These symbols are a shorthand for a set of component vectors describing the position of each
particle. This form of the Schrödinger equation is the result of using the Born-Oppenheimer approximation (electronic adiabatic approximation). This approximation allows the electronic and nuclear part of the problem to be solved independently. As mentioned before, it is valid for molecular systems since the nuclei are much heavier than the electrons and their motions can be separated. In other words, the nuclei are stationary on the timescale of electron movement. The electronic motion can be described as occurring in a field of fixed nuclei. The Hamiltonian operator ($H_{\text{elec}}$), using atomic units, is constructed in the following way:

\[
H_{\text{elec}} = -\frac{1}{2}\sum_{i}^{\text{elec}} \nabla^{2}_{i} - \sum_{i}^{\text{elec}} \sum_{I}^{\text{nuclei}} \frac{Z_{I}}{|\vec{R}_{I} - \vec{r}_{i}|} + \sum_{i}^{\text{elec}} \sum_{j \leq i}^{\text{elec}} \frac{1}{|\vec{r}_{i} - \vec{r}_{j}|} + \sum_{I}^{\text{nuclei}} \sum_{J < I}^{\text{nuclei}} \frac{Z_{I}Z_{J}}{|\vec{R}_{I} - \vec{R}_{J}|}
\] (3.7)

Here, the first term corresponds to the kinetic energy of all electrons in the molecule, the second term corresponds to the electron–nuclear attraction, the third one is the electron–electron repulsion, and the last one is the nuclear–nuclear repulsion.

Solving eq. 3.6 for the electronic wave function will produce the effective nuclear potential function $E_{\text{elec}}$. The solution depends on the nuclear coordinates and describes the potential energy surface (PES) for the system. For a given set of nuclear coordinates ($\vec{R}$), $E_{\text{elec}}$ corresponds to the total energy predicted by a single point energy calculation. Such calculations, of course, do not solve this equation exactly. An exact solution to the Schrödinger equation is not possible for any but the smallest molecular systems, for example $\text{H}^{+}_{2}$. However, a number of simplifying assumptions and procedures make an approximate solution possible for a wide range of molecules. The methods using rigorous mathematical approximations are called ab initio since their computations are based solely on the laws of quantum mechanics and the values of a small number of physical constants: the speed of light, the masses and charges of electrons and nuclei and Plank’s constant.

Other electronic structure methods are the semi-empirical and the density functional ones. Semi-empirical methods use parameters derived from experimental data to simplify the computation. They are largely characterized by their differing parameter sets. Semi-empirical calculations are relatively inexpensive and provide reasonable qualitative descriptions of molecular systems. They can predict accurately energies and structures for systems for which good parameter sets exist. Among the best known are AM1 (Austin Model 1) [50], PM3 and MNDO (Modified Neglect of Diatomic Overlap) [51]. For our purposes we used mainly ab initio and density functional methods. These will be discussed in somewhat more detail in the following section.

### 3.2.2. Model chemistries

Ab initio calculations provide high quality quantitative predictions for a broad variety of systems. The calculations are not limited to any specific class of systems. A program like GAUSSIAN [49] which implements ab initio methods can be run on a typical workstation and can compute systems containing up to hundreds of atoms. GAUSSIAN’s calculations are based on theoretical model chemistries which have been tested for consistency and can be recommended for general use. Model chemistries are characterized by a combination of a theoretical procedure and a basis set. Additionally one can specify how the electron spin is handled: with a closed shell model (restricted) or with an open shell model (unrestricted).
1) Levels of theory

Hartree–Fock SCF

Hartree–Fock Self-Consistent Field (HF-SCF) is the simplest approximation for the solution of eq. 3.6. The basic idea is that the motion of each electron is described by a molecular orbital (MO). Then, the wave function can be approximated by a product of functions describing these orbitals, which is known as the Hartree product:

$$\Psi(\vec{r}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_1)...\phi_n(\vec{r}_n)$$  \hspace{1cm} (3.8)

However, the Hartree product is not antisymmetric. A first step is to include the intrinsic spin coordinate as a function $\sigma(\omega) = \alpha(\uparrow)\beta(\downarrow)$ where $\alpha$ and $\beta$ are functions for spin up and spin down. Each molecular orbital can thus be described by the product $\chi_i(\vec{x}_i) = \phi_i(\vec{r}_i)\sigma_i(\omega)$, usually called spin orbital. In order to make the product of the spin orbitals antisymmetric a determinant of spin orbitals known as the Slater determinant is formed. This determinant mixes all possible orbitals of all possible electrons in a molecular system to form an antisymmetric wavefunction.

$$\Psi(\vec{x}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \ldots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \ldots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \ldots & \chi_N(\vec{x}_N) \end{vmatrix}$$ \hspace{1cm} (3.9)

In order to solve the Schrödinger equation using this approximation, each unknown spatial MO is expressed as a linear combination of a set of known basis functions $\varphi$:

$$\phi_i(\vec{r}_i) = \sum_{\mu=1}^{N} c_{\mu i} \varphi_\mu$$ \hspace{1cm} (3.10)

These basis functions are usually centered on the atomic nuclei and they can be of any type. GAUSSIAN uses gaussian–type atomic functions as basis functions, i.e. $\varphi \propto e^{-\xi r^2}$. The Hartree-Fock procedure solves for the linear expansion coefficients $c_{\mu i}$ using the variational principle. So the problem becomes finding the set of coefficients that minimize the energy of the resultant wave function. The variables in the Hartree-Fock equations depend on themselves, so they must be solved in an iterative manner. The procedure which does that is the self-consistent field method. The name of the method comes from the fact that when convergence is reached (usually in 10 iterations) the energy is a minimum and the orbitals generate a field which produces the same orbitals. The Hartree–Fock theory does not include the instantaneous electron–electron interaction, i.e each electron sees all the other electrons as an average distribution. Higher level methods attempt to remedy this lack of electron correlation in order to improve the accuracy in the results.

Many–Body Perturbation theory

Many-body perturbation theory (MBPT) is a way to account for electron correlation by treating it as a perturbation to the Hartree-Fock wave function. For this method to be valid, the
perturbation has to be small so that the perturbed wavefunction and energy can be expressed as a power series. Usually, the computations are made using second-order perturbation theory. A typical implementation is the second-order Møller-Plesset perturbation theory (MP2). It is possible to do higher orders of perturbation theory (MP3, MP4, etc), but the computing times become excessively longer and the results do not necessarily get better. MBPT is always an improvement on Hartree-Fock.

Density Functional theory

Density functional theory (DFT) approach is based on modelling electron correlation via general functionals of the electron density. It has its origin in the Hohenberg–Kohn theorem (1964) which demonstrates the existence of a unique density functional which determines the ground state energy exactly. The theorem does not provide the form of the functional. Kohn and Sham (1965) provided an approach to find approximate functionals. The method is based on partitioning the electronic energy into several terms:

\[ E_{\text{elec}} = E_T + E_V + E_J + E_{\text{XC}} \]  

(3.11)

where \( E_T \) is the kinetic energy term from the motion of the electrons, \( E_V \) includes terms describing the potential energy of the nuclear–electron attraction and of the repulsion between pairs of nuclei, \( E_J \) is the electron–electron repulsion term and \( E_{\text{XC}} \) is the exchange-correlation term and includes the remaining part of the electron–electron interactions. This last term is the functional which contains everything that is unknown. If the exact form of this term was known, the problem could be solved exactly because the method does not include, so far, any approximation. The quest is then to find good exchange-correlation functionals. But, this is also the main drawback of DFT, functionals cannot be systematically improved as they can be improved for \textit{ab initio} approximations. The \( E_{\text{XC}} \) functional is usually divided into an exchange \( E_X \) and a correlation \( E_C \) term. The initial letters of the corresponding author for some functional give it the name. If the same author has developed more than one functional, the letters are augmented by a year. Some of the typical exchange-correlations functionals used by GAUSSIAN are based on the exchange functional by Becke (1988) whilst different correlation functionals are used, \textit{e.g.} Perdew and Wang, 1991 (PW91) or Lee, Yang, and Parr, 1988 (LYP). They already provide fairly accurate results. Hartree-Fock theories also include an exchange term. Becke formulated functionals which include a mixture of HF and DFT exchange along with DFT correlation. These are called hybrid functionals. The most common hybrid exchange term is Becke-style 3 parameter functional (B3). DFT methods are attractive because they include the effects of electron correlation at the cost of HF calculations [52]. For excited states, time dependent density functional theory (TD-DFT) methods are used.

2) Basis set

The basis sets are mathematical representations of the molecular orbitals within a molecule. They restrict each electron to a particular region of space, larger basis sets impose less constraints to electrons and approximate more accurately the exact molecular orbitals.
As mentioned before, standard basis sets for electronic structure calculations often use linear combinations of gaussian functions to form the orbitals. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals (see eq. 3.10). GAUSSIAN offers a wide range of pre-defined basis sets, which are classified by the number and types of basis functions they contain. Some of the types of basis sets are: minimal, split valence and polarized basis sets. The minimal basis sets contain the minimum number of basis functions needed for each atom. These basis sets use fixed-sized atomic-type orbitals. One example is the STO-3G basis set. STO stands for \textit{Slater-type orbitals} and 3G indicates that it uses three gaussian primitives per basis function. The split valence basis sets use a single \textit{Slater-type} orbital to describe the inner shell electrons and two or more sizes of basis functions for each valence orbital. Some common examples are 3-21G and 6-31G, where the first digit represents the number of gaussian functions summed to describe the inner shell orbital and the second and third digit give the number of functions for a double split basis set. A triple split basis set like 6-311G uses three sizes of functions for each orbital type.

Split valence basis sets allow orbitals to change size but not shape. Polarized basis sets add orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example 6-31G(d) adds polarization functions to heavy atoms whilst 6-31G(d,f) adds polarization functions to the hydrogens as well. Diffuse functions allow orbitals to occupy a larger region of space. They are small exponents which describe weakly bound electrons, for example molecules with lone pairs or systems with low ionization potentials. The sign $+$ adds diffuse functions to heavy atoms and $++$ adds them also to the hydrogen atoms. For example a basis set 6-311++G(3df,2pd) puts 3 d functions and 1 f function on heavy atoms, and 2p functions and 1 d function on hydrogens, and puts diffuse functions on both. Some basis sets as cc-pV6Z include already polarization functions in the definition but the diffuse functions are added with the prefix aug.

3) Restricted vs. unrestricted

There is a third component to every GAUSSIAN calculation involving how electron–spin is handled: with an open shell model (unrestricted) or with a closed shell model (restricted). For closed shell molecules, the default is to use doubly occupied orbitals, each containing two electrons of opposite spin. Open shell systems, for example most singly charged molecules, are usually modelled by an unrestricted model spin. Restricted, closed shell calculations force each electron pair into a single spatial orbital, while open shell calculations use separate spatial orbitals for the spin up and spin down electrons.

3.2.3. GAUSSIAN calculations

In practice, defining a chemistry model implies choosing a level of theory and a basis set which can be handled by the workstation but depends a lot on what is the goal of the calculation. Two different kind of calculations were performed for this thesis: i) geometry optimizations and ii) total energy calculations. While DFT has proven to be efficient in optimizing molecular structures, MP2 is more accurate for single point energy calculations. A mixed model combining different theory levels was used when the knowledge of the energy was crucial.
i) Geometry optimizations

A potential energy surface (PES) is a mathematical relationship between the molecular structure and the according energy. For a diatomic molecule, the PES is a one dimensional plot with the internuclear separation on the X-axis and the energy on the Y-axis. For larger systems, the surface has as many dimensions as degrees of freedom within the molecule. A surface can have valleys and mountains, i.e., minima and maxima. The minima can be local or global. Local minima are limited to certain regions of the potential surface. A global minimum is the lowest energy point anywhere on the potential surface. Minima correspond to equilibrium structures, different minima can be different conformations or structural isomers. Peaks and ridges are maxima. A peak is a point which is a maximum in all directions. A point which is a minimum in one direction but a maximum in other direction is called a saddle point, it usually corresponds to a transition structure connecting two equilibrium structures.

Geometry optimizations attempt to locate minima on the potential energy surface, and in this way predict equilibrium structures of molecular systems. A geometry optimization begins at the molecular structure specified as input, and evolves along the PES. It computes the energy and the gradient at that point and determines how far and in which direction it makes the next step. An optimization is complete when it has converged. The convergence criteria used by GAUSSIAN are: the forces must be zero, the root-mean-square of the forces must be essentially zero (below a certain tolerance), the calculated displacement for the next step must be smaller than the defined cutoff value and its root-mean-square as well. The presence of four criteria prevents premature identification of the minimum. In our cases, the input is a known geometry from a database. When the structure was very complex, for example for the clusters, the optimization was made following several steps in levels of theory: first a semiempirical approximation and then the results were used as input for DFT optimizations.

ii) Energy calculations

In order to estimate ionization potentials or molecular orbital shapes, single point energy calculations are performed. A single point energy calculation is a prediction of the energy and related properties for a molecule with a specified structure (geometry optimized structures were used). The energy calculated is the sum of the electronic energy and nuclear repulsion energy of the molecule at the specified nuclear configuration. The calculation is performed at a fixed point (single point) on the PES for the molecule. Single point energy calculations can be performed at any level of theory and with small or large basis sets. In order to obtain accurate total energies of the systems under study, zero-point vibration and thermal energy corrections must be computed.

Vertical ionization potentials are calculated based on the Franck–Condon principle. The molecular structure remains unchanged and there is only an electronic transition between the ground state(s) of the neutral molecule and the singly or doubly ionized molecule. Adiabatic ionization potentials are more difficult to compute, since the geometries in the excited/ionized state should be relaxed.