

Abstract

This thesis aims at studying in details the behavior of complex molecular clusters and focuses on two main aspects. First, the description of low-energy isomers of ammonium/ammonia water clusters and protonated uracil water clusters through an extensive exploration of potential energy surfaces (PES) using a combination of global and local optimization schemes. Structural, solvation and thermodynamics properties of the newly identified low-energy isomers were characterized. Second, the dynamical simulations of collision-induced dissociation of protonated uracil water clusters and pyrene dimer cation were carried out to explore collision trajectories, dissociation mechanism, energy partition, mass spectra, and collision cross-sections to complement experimental measurements conducted on these species.

Global optimization of $(\text{H}_2\text{O})_{1-10}\text{NH}_4^+$ and $(\text{H}_2\text{O})_{1-10}\text{NH}_3$ clusters is conducted at the self-consistent-charge density-functional based tight-binding (SCC-DFTB) level of theory, for which improved N-H parameters are proposed, in combination with the parallel-tempering molecular dynamics (PTMD) approach. Low-energy isomers of $(\text{H}_2\text{O})_{1-10}\text{NH}_4^+$ and $(\text{H}_2\text{O})_{1-10}\text{NH}_3$ are further optimized at MP2 level in order to evaluate the reliability of our modified N-H parameters. Both structures and binding energies obtained with SCC-DFTB are in line with the results at MP2/Def2TZVP level, which demonstrates the ability of SCC-DFTB to describe the PES of molecular species and represents a first step towards the modeling of complex aggregates of atmospheric interest.

Focus on protonated uracil water clusters aims at providing a detailed description of recent collision-induced dissociation (CID) experiments. First, stable isomers of $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ are calculated using the same methodology as described above. Then, dynamical simulations of the collisions between various $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ isomers and argon is conducted at a constant collision energy at the SCC-DFTB level. Simulated proportion of formed neutral vs. protonated

uracil containing clusters, fragmentation cross-section as well as mass spectra are consistent with the experimental data which highlights the accuracy of our simulations. They allow to probe which fragments are formed on the short time scale and rationalize the location of the excess proton on these fragments. This latter property is highly influenced by the nature of the aggregate undergoing the collision. Analyses of proportion of time-dependent fragments and mass spectra demonstrate that, up to 7 water molecules, a shattering mechanism occurs after collision whereas for $n=11,12$ a statistical mechanism is more likely to participate. These simulations appear as a useful tool to complement CID experiments of hydrated molecular species.

Dynamical simulation of CID experiments of pyrene dimer cation for different collision energies between 2.5 and 30 eV is also presented. The dynamical simulations allow to understand the dissociation processes. The agreement between the simulated and measured mass spectra suggests that the main processes are captured by this approach. It appears that most of the dissociation occurs on a short timescale (less than 3 ps). At low collision energies, the dissociation cross-section increases with collision energies whereas it remains almost constant for collision energies greater than 10 to 15 eV. Analysis of the kinetic energy partition is used to get insights into the collision/dissociation processes at the atomic scale. The simulated time of flight mass spectra of the parent and dissociated products are obtained from the combination of molecular dynamics simulations and phase space theory to address the short and long timescales dissociation, respectively.

Keywords: SCC-DFTB, CID, molecular dynamics, ammonium/ammonia water clusters, uracil water clusters,

Résumé de la thèse

Cette thèse vise à étudier en détails le comportement d'agrégats moléculaires complexes et se concentre sur deux aspects principaux. Tout d'abord, la description des isomères de faible énergie des clusters d'ammonium et ammoniac et des clusters d'uracile/eau protonés à travers l'exploration des surfaces d'énergie potentielle (PES) en utilisant une combinaison d'approches d'optimisation globales et locales. Les propriétés structurales, de solvation et thermodynamiques des isomères de basse énergie nouvellement identifiés ont été caractérisées. Par la suite, des simulations dynamiques de la dissociation induite par collision des agrégats d'uracile/eau protonés et du dimère de pyrène ont été réalisées et analysées en termes de : mécanisme de dissociation, répartition d'énergie, spectres de masse et sections efficaces de collision pour compléter des mesures expérimentales récentes menées sur ces espèces.

L'optimisation globale des clusters $(\text{H}_2\text{O})_{1-10}\text{NH}_4^+$ et $(\text{H}_2\text{O})_{1-10}\text{NH}_3$ a été réalisée au niveau de théorie SCC-DFTB (pour self-consistent-charge density-functional based tight-binding), pour laquelle des paramètres NH améliorés ont été proposés, en combinaison avec l'approche d'exploration PTMD (pour parallel-tempering molecular dynamics). Les isomères de basse énergie nouvellement déterminés ont été optimisés au niveau MP2 afin d'évaluer la fiabilité de nos paramètres N-H modifiés. Les structures et les énergies de liaison obtenues avec la méthode SCC-DFTB sont en très bon accord avec les résultats de niveau MP2/Def2TZVP, ce qui démontre la capacité de l'approche SCC-DFTB à décrire la PES de ces espèces moléculaires et représente ainsi une première étape vers la modélisation d'agrégats complexes d'intérêt atmosphérique.

L'intérêt porté aux agrégats uracile/eau protonés vise à fournir une description détaillée d'expériences récentes de dissociation induite par collision (CID).

Premièrement, les isomères stables des agrégats $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ sont calculés en utilisant la même méthodologie que celle décrite ci-dessus. Ensuite, des simulations dynamiques des collisions entre divers isomères $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ et un atome d'argon sont réalisées à énergie de collision constante au niveau SCC-DFTB. La proportion simulée de d'agrégats neutres contenant l'uracile par rapport à celle d'agrégats chargés contenant l'uracile, la section efficace de fragmentation

ainsi que les spectres de masse sont cohérents avec les données expérimentales ce qui met en évidence la précision de nos simulations. Ces dernières permettent de sonder en détails les fragments qui se forment aux temps courts et de rationaliser la localisation du proton en excès sur ces fragments. Cette dernière propriété est fortement influencée par la nature de l'agrégat soumis à la collision. L'analyse de la proportion des fragments en fonction du temps et des spectres de masse démontrent que, jusqu'à 7 molécules d'eau, un mécanisme de dissociation direct est mis en jeu après la collision alors que pour 11 et 12 molécules, un mécanisme statistique est plus susceptible d'intervenir. Ces simulations, uniques jusqu'à présent, apparaissent comme un outil indispensable pour comprendre et interpréter les expériences CID d'espèces moléculaires hydratées.

Enfin, des simulations d'expériences CID du dimère de pyrène à différentes énergies de collision, entre 2,5 et 30 eV, sont également présentées. Les simulations permettent de comprendre les processus de dissociation mis en jeu. L'accord entre les spectres de masse simulés et mesurés suggère que les principaux processus sont bien pris en compte par cette approche. Il semble que la majeure partie de la dissociation se produise sur une courte échelle de temps (moins de 3 ps). Aux faibles énergies de collision, la section efficace de dissociation augmente avec les énergies de collision alors qu'elle reste presque constante pour des énergies de collision comprises entre 10 et 15 eV. L'analyse de la répartition d'énergie cinétique est utilisée pour obtenir des informations sur les processus de collision/dissociation à l'échelle atomique. Les spectres de masse simulés des clusters parents et dissociés sont obtenus à partir en combinant simulations de dynamique moléculaire et théorie de l'espace des phases pour traiter respectivement la dissociation aux courtes et longues échelles de temps.

Mots clés : SCC-DFTB, CID, dynamique moléculaire, agrégats aqueux d'ammonium/ammoniac, agrégats protonés uracile-eau

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Glossary

BIRD	blackbody infrared radiative dissociation
BO	Born-Oppenheimer
BSSE	basis set superposition errors
CAD	collisionally activated dissociation
CC	coupled cluster
CI	configuration interaction
CID	collision-induced dissociation
CM3	class IV - charge model 3
CSF	configuration state function
DFT	density functional theory
DFTB	density-functional based tight-binding
DFTB3	third-order extension of DFTB
FF	force field
GGA	generalized gradient approximation
HF	Hartree-Fock
HK	Hohenberg–Kohn
KS	Kohn-Sham
LCAO	linear combination of atomic orbitals
LDA	local density approximation
LEP	location of excess proton
LOC	line of center model

GLOSSARY

MCPs	micro-channel plates
MCTDH	multi-configuration time-dependent Hartree
MD	molecular dynamics
MM	molecular mechanics
MP2	Møller-Plesset perturbation theory at second-order
NBO	natural bond order
NUL	neutral uracil loss
PAH	polycyclic aromatic hydrocarbons
PES	potential energy surface
PST	phase space theory
PTMD	parallel-tempering molecular dynamics
QM	quantum mechanics
RRKM	Rice-Ramsperger-Kassel-Marcus
SCC-DFTB	self-consistent-charge density-functional based tight-binding
SCF	self-consistent field
TCID	threshold collision-induced dissociation
TOF	time-of-flight
TOFMS	time-of-flight mass spectrometry
VV	velocity Verlet algorithm
WF	wavefunction
ZPVE	zero-point vibrational energy

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General Introduction

The term *cluster* was coined by F. A. Cotton in the early 1960s to refer to compounds containing metal-metal bonds such as $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Br}_8]^{2-}$. [1] He defined metal atom cluster compounds as "those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster". Subsequently, the study of clusters, also referred to as aggregates, has greatly diversified and the definition of the term *cluster* has evolved considerably from that given by Cotton. Indeed, in chemistry, the term cluster now refers to an ensemble of bound atoms or molecules which can be isolated or incorporated within larger chemical compounds, for instance within a solid-state compounds. A cluster is intermediate in size between a single molecule or atom and a nanoparticle. A hundred billion *particles* (here the term particle referred to the constituents of the cluster, which can be either atoms, ions, molecules or a mix) held together behave in most ways like bulk matter, whereas small clusters contain no more than a few hundred or a thousand particles and a large cluster designates something containing about a few thousands of particles. [2] Clusters are also intermediate in terms of properties between a single molecule or atom and the corresponding bulk compound.

Cluster chemistry developed contemporaneously along several independent research lines and several families of compounds can be referred to as clusters. Among them, one can mention **naked metal clusters**, [3, 4] metal cluster compounds such as **transition metal carbonyl clusters**, [5] **transition metal halide clusters**, [6] **transition metal organic carbon clusters** (organometallic), [7] **metalloid clusters**, [8] **intermetalloid clusters**, [9, 10] as well as **atomic clusters** composed of non-metal atoms [11, 12, 13, 14] and **molecular clusters**. [15, 16]

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Naked metal clusters encompass only metal atoms that are held together by metallic bond for instance Rh_{13} and Au_{13} .^[3] **Transition metal carbonyl clusters** are compounds containing a core that consists of two or more metal atoms linked in part by metal-metal bonds and embraced by carbon monoxide (CO) ligand groups exclusively or predominantly. Similarly, **transition metal halide clusters** are compounds that contains two or more metal atoms (prevalent for heavy metals) linked in part by metal-metal bonds and embraced by halide ligands. Some representative species for transition metal carbonyl and halide clusters are $\text{Mn}_2(\text{CO})_{10}$,^[5] $\text{Fe}_2(\text{CO})_9$,^[17] $[\text{Rh}_6(\text{CO})_{15}]^{2-}$,^[17] $\text{Re}_3\text{Cl}_{12}^{3-}$,^[18] $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$,^[6] Nb_3Cl_8 ,^[19] **Organometallic clusters** contain metal-metal bonds as well as at least one organic ligand directly bonded to a metal atom. It can be neutral or ionic. One example of organometallic cluster is $[\text{Co}_3(\text{CCH}_3)(\text{CO})_9]$.^[7] **Metalloid clusters** are ligand-stabilized clusters that metal atoms possess more direct element-element contacts than element-ligand contacts such as $[\text{Al}_{69}(\text{N}(\text{SiMe}_3)_2)_{18}]^{3-}$ and $[\text{Ga}_{84}(\text{N}(\text{SiMe}_3)_2)_{20}]^{4-}$.^[8] The suffix “oid” highlights that such clusters possess atom arrangements that appear in bulk intermetallic compounds with high coordination numbers of the atoms at a molecular scale. **Intermetalloid** clusters consist in at least two different (semi) metallic elements, and possesses more direct metal-metal contacts than metal-ligand contacts. This kind of cluster often appears as discrete units in intermetallic compounds separated from each other by electropositive atoms for instance $[\text{Sn}@\text{Cu}_{12}@\text{Sn}_{20}]^{12-}$.^[9] ^[10] Finally, **clusters composed of non-metal atoms or molecules** are usually found in gas-phase for instance **fullerenes**,^[12] **rare-gas clusters**,^[11, 14] **water clusters**,^[20, 21] and **PAHs (Polycyclic aromatic hydrocarbons) clusters**.^[15, 16]

These listed various kinds of clusters, which has no mean to be exhaustive, can be differentiated by the bounding mode, *i.e.* the nature of the interaction, between the cluster particles. They can be of different natures:

- **Van der Waals interactions**, which is the main interaction in the rare-gas clusters such as argon clusters.^[22]
- **Hydrogen-bond interaction**, which is of paramount importance in a variety of molecular clusters, in particular those containing water molecules.
- **Covalent bond**, as found in fullerenes,^[12] or more generally pure carbonaceous aggregates, and other atomic aggregates made of non-metallic atoms.
- **Metallic bond**, as found in Cu, Ag, and Au clusters.^[4]

of gas-phase molecules and ions. [53, 54, 55, 56, 57]

Although it is possible to experimentally probe a large range of properties of clusters, one difficulty is to extract all the chemical and physical information provided by these experiments. Indeed, in the "simplest case", a property determined experimentally can result from a unique isomer of the probed species. The first major task is then to determine the nature of this lowest energy isomer which is not straightforward. This is where theoretical calculations come in. Indeed, a vast majority of experiments require the contribution of theoretical calculations in order to determine the lowest energy isomer of a given cluster. For instance, a vast amount of theoretical calculations have been conducted to determine the low energy structures of $(\text{H}_2\text{O})_n$ and $(\text{H}_2\text{O})_n\text{H}^+$ aggregates. Among them, we can mention the studies performed by D. Wales and co-workers using the basin-hopping algorithm. [58, 59, 60, 61] In more difficult cases, the proper properties result from the contribution of several isomers which has to be taken into account. When considering finite-temperature properties, an ergodic exploration of the PES also needs to be performed. For instance, J. Boulon *et al.* reported heat capacity curves as a function of temperature of mass selected protonated water clusters and highlighted a stronger steepness of the curve of $(\text{H}_2\text{O})_{21}\text{H}^+$ as compared to adjacent sizes. [29] Theoretical simulations latter provided explanations for this peculiar behavior. [62] When considering dissociation of clusters, which can be a non-equilibrium process, theoretical calculations allow to understand dissociation mechanisms and energy partition that are not accessible from the experiment. [63, 64, 65, 66] It is worth noting that theoretical calculations can also be useful to make predictions when the experiments are restricted by cost or other conditions. [67]

Among these variety of systems and properties, the present thesis has focused on the study of two kinds of molecular clusters: **water clusters containing an impurity** and **polycyclic aromatic hydrocarbon clusters** with a focus on the **exploration of PES** and the modelling of **collision induced dissociation** processes. In the following, I briefly introduce these different aspects.

Water clusters. Water is ubiquitous in our environment. In view of the importance of water to life and its complex properties, a significant amount of experimental [68, 69, 70, 71, 72, 73, 74, 75] and theoretical [76, 77, 78, 79] studies have been devoted to this fundamental substance since the first realistic interaction potential of water was proposed in 1933. [80, 81] Water clusters are intermediate species between gas and condensed phases, their study is therefore of fundamental importance to understand properties of liquid water and ice. They also offer the opportunity to understand how the properties of liquid water and ice emerge from

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the assembling of an increasing number of water molecules.^[82] They also allow to study at the molecular scale proton transfer processes,^[83, 84] finite-temperature effects as well as nuclear quantum effects. Molecular clusters with a controlled number of solvent molecules are also ideal model systems for providing a fundamental understanding of solute-solvent and solvent-solvent interactions at the molecular level.^[85] From a more applicative point of view, they play a significant role in atmospheric sciences where the physical and chemical properties of aerosols are strongly impacted by the properties of the water clusters they are made of.^[86, 87, 88, 89, 90, 91, 92] In particular, water clusters can absorb a significant amounts of radiative energy,^[93] and therefore they have to be included in climate models.^[94] This is not actually the case due to the lack of data regarding their formation. They can also play a role in astrochemistry where water ice can act as a catalyst for the formation of a large range of chemical species. ^[95, 96, 97, 98]

From a theoretical point of view, the study of water clusters is not straightforward as water clusters display **two major difficulties**:

- As stated above, the PES of aggregates can display a large number of local minima, *i.e.* stable configurations, and energy barriers. Determination of low-energy structures or ergodic exploration of PES is thus not straightforward. This is all the more true that, for molecular aggregates, the range of considered temperatures often results in a low diffusion of molecules which makes it possible for a given aggregate to be trapped in a local minimum of the PES. One textbook case for the complexity of water clusters is $(\text{H}_2\text{O})_6$. Despite the apparent simplicity of $(\text{H}_2\text{O})_6$, which is the smallest neutral water cluster displaying a tridimensional structure, the nature of its lowest energy isomer has been a subject of debate for several years. It is only in 2012 that C. Pérez *et al.* published an experimental paper in Science in which the authors unambiguously identified three of its isomers: cage, prism and book and concluded that the most stable isomer is the cage.^[99] The theoretical description of water clusters thus requires simulation tools specifically devoted to the exploration of complex PES such as **molecular dynamics** or **Monte-Carlo simulations** in combination with efficient **enhanced sampling methods**.
- Molecular scale modelling of water is also made difficult as there is no potential, *ab initio* or empirical, that makes it possible to reproduce all the properties of the different phases of water, that are applicable to large systems and are easily transferable. It is

therefore often necessary to make a choice between computational efficiency, transferability, and accuracy. This balance determines the nature of the questions that can be addressed. Furthermore, the aforementioned **enhanced sampling methods** generally require to repeat a large amount of calculations. Therefore, they need to be combined with computationally efficient approaches to compute the PES. As presented in chapter 2, the method I use within this thesis is the **self-consistent-charge density-functional based tight-binding** (SCC-DFTB) method.

Water clusters are usually combined with other inorganic/organic ions or molecules that make them relevant to astrochemistry, atmospheric chemistry and biological sciences. Therefore, it is of paramount importance to investigate **water clusters containing an impurity**, whether it is experimentally or theoretically. And indeed, in parallel to the study of pure water clusters, such studies have drastically grown over the last years. For instance, one can mention studies devoted to $\text{Cl}^-(\text{H}_2\text{O})_n$, [100] $\text{Na}^+(\text{H}_2\text{O})_n$, $\text{H}_2\text{PO}_4^-(\text{H}_2\text{O})_n$, [101] $\text{NH}_4^+(\text{H}_2\text{O})_n$, $\text{NH}_3(\text{H}_2\text{O})_n$, $\text{C}_6\text{H}_6\text{O}(\text{H}_2\text{O})_n$, [20] $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$, [102, 103] $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$, [103] $(\text{CO})_m(\text{H}_2\text{O})_n$, $((\text{CH}_3)_2\text{NH}_2^+)_m(\text{HSO}_4^-)_m(\text{H}_2\text{O})_n$, [35] $\text{C}_4\text{H}_5\text{N}_2\text{O}_2^+(\text{H}_2\text{O})_n$, [104] and $(\text{C}_5\text{H}_5\text{N})_m\text{H}^+(\text{H}_2\text{O})_n$. [105] In the domain of astrochemistry, the growth of atmospheric particles can initiate the process of acid cloud formation and participates in reactions leading to the destruction of the ozone layers in polar regions. [106, 107] More detailed studies of atmospheric particles demonstrated the existence of charged molecular aggregates in the stratosphere, [108, 109] in particular sulfate containing aggregates, [103] and ammonium/ammonia containing aggregates. [20, 110] In the latter case, **ammonia has been highlighted as an important component of atmospheric nucleation** together with water and sulphuric acid. [111, 112, 113] This important role of ammonia and ammonium water clusters, and the lack of theoretical studies devoted to these species, motivated a thorough benchmark of the SCC-DFTB approach to model these systems which is presented in chapter 3. In parallel, understanding the **properties of the proton** and how it can impact the solvation properties of molecules of biological interest is of paramount importance for understanding fundamental processes in biology and chemistry. In particular, uracil, one of the nucleobases, plays a key role in the encoding and expression of genetic information in living organisms. The study of **water clusters containing uracil** is therefore a good playground to probe how uracil properties vary from isolated gas-phase to hydrated species and how this is impacted by protonation. Chapters 3 and 4 try to address these questions.

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Polycyclic aromatic hydrocarbon clusters. Polycyclic aromatic hydrocarbons (PAHs) are a family of organic molecules made up of two or more aromatic carbon rings containing peripheral hydrogen atoms. These hydrocarbon molecules have aromatic behavior resulting from the presence of sp^2 carbon atoms. Several examples of PAHs molecules are presented in Figure 1.2.

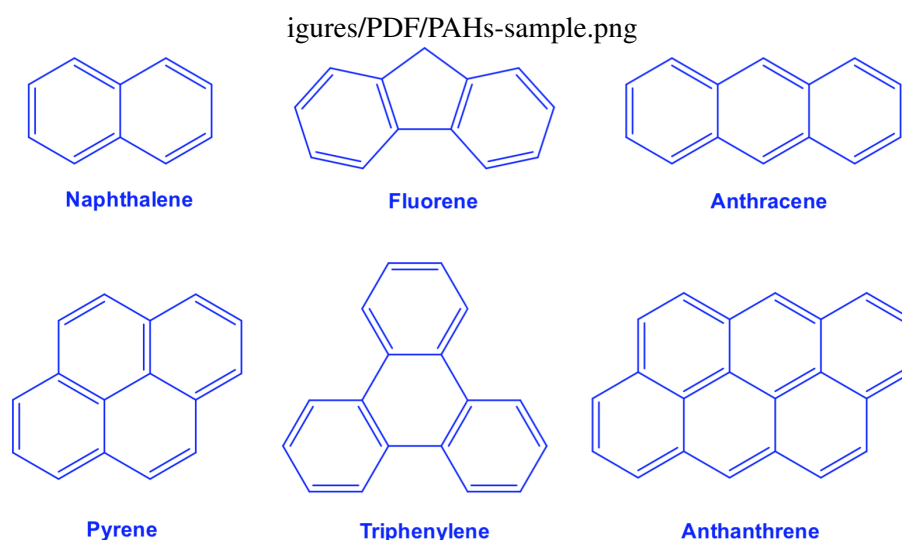


Figure 1.2: Examples of several PAH molecules.

PAHs have been investigated in various scientific fields, both experimentally and theoretically, for instance in astrophysics and astrochemistry, environmental science, combustion science, or the search for new organic solar cell devices.

The presence of PAHs in the interstellar medium was proposed in the middle of the 80s, [114, 115] and they have since played an important role in the astrophysical context. In particular, the so-called unidentified infrared bands in the gas phase of the interstellar medium are thought to be partially attributable to emission by PAHs. [114, 116, 117] They have been proposed to be present in the form of a mixture of neutral, ionised, and partly dehydrogenated molecules and to account for $\sim 10 - 20\%$ of the total carbon in the interstellar medium. [117, 118] In addition, cationic PAH clusters are expected to be abundant in photo-dissociation regions [119, 120] since the ionization energy of the clusters is lower than that of neutral PAHs and decreases with the cluster size, [121, 122] leading to the efficient formation of cationic clusters. These charged species are expected to survive longer than their neutral counterparts due to higher dissociation energies, as predicted by calculations. [121] PAHs are also found in the atmosphere as

highly toxic molecules. Their significant abundance arises from their efficient formation as by-products of natural processes, biomass burning, or human activities such as combustion of fossil fuels.^[123] In the atmosphere, PAHs with more than three rings can be adsorbed by various particles, for instance carbonaceous aerosols, ferric oxides, and icy particles.^[124] The role of **PAH clusters** in the process of soot nucleation is a major topic in the context of combustion and leads to consider the competition between clustering, evaporation, and oligomerization.^[125, 126] Finally, PAH stacks provide possible compounds to define new organic solar cell junctions.^[127, 128] Due to the importance of PAHs as mentioned above, the stability of PAH clusters have been extensively studied experimentally and theoretically.^[16, 65, 119, 129, 130, 131] IN particular, their evolution following absorption of photons, collision with high or low energetic particles as well as their behaviour in very high pressure environments has been thoroughly studied.^[122, 129, 132, 133, 134, 135] Chapter 4 provides thorough theoretical analysis of the **collision-induced dissociation** of the simplest pyrene cluster, *i.e.* the **pyrene dimer cation** in order to complement recent experiments.

Collision-induced dissociation of molecular clusters. The structure, energetics and reactivity of a variety of molecular clusters can be explored by collision-induced dissociation.^[136, 137, 138, 139, 140, 141] By colliding a molecule or a molecular cluster with a non-reactive noble gas atom or a small molecule such as N₂, it is possible to monitor the parent ions and collision products by means of mass spectrometry that can provide a wealth of structural information from which one can infer, for instance, dissociation mechanisms,^[142, 143] or bond and hydration enthalpies.^[144] Collision-induced dissociation has also been used to understand the impact of high-energy radiations on living cells and DNA or RNA,^[139, 145, 146] as well as the impact of low-energy collisions on biological molecules.^[147, 148]

Extracting energetics or collision process from collision-induced dissociation is not straightforward and it often needs to be **complemented by theoretical calculations**. Two main methodologies can be conducted. The first one is to make an exhaustive description of the PES connecting both parent ions and products. Energetic information on both minima and transition states can then be introduced in Rice-Ramsperger-Kassel-Marcus ^[149, 150] and/or Kinetic Monte Carlo simulations.^[151, 152] The second approach is to perform **molecular dynamics simulations to explicitly model the collision trajectory** of the target ion and the projectile, the energy redistribution, the subsequent reorganizations and fragmentations. A potential is needed to describe the PES of the system and its reactivity in both methodology. For the latter one, the potential needs to reach a very good balance between accuracy and computational

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efficiency as this methodology requires the propagation of tens, hundreds or even thousands of trajectories. With this in view, it appears that wave-function based methods do not allow to reach a sufficient amount of simulations to describe dynamical behavior at finite temperature. Unfortunately, the same is true for density-functional theory (DFT). Force-field approaches can easily handle molecular dynamics simulations of system with hundred of atoms for several hundred nanoseconds, but they can poorly describe formation or breaking of covalent bonds and they are poorly transferable. In between DFT and force-field methods, semi-empirical approaches provide interesting alternatives. In particular, the **SCC-DFTB** method allows to perform molecular dynamical simulations of systems containing several tens or hundreds of atoms for simulation time of several hundred picoseconds. This approach has therefore been used in the present thesis to model collision-induced dissociation experiments.

To summarize, the goal of this thesis is to go a step further into the theoretical description of the properties of molecular clusters with the view to complement complex experimental measurements. It has focused on two different types of molecular clusters. First, I focused on water clusters containing an impurity, *i.e.* an additional ion or molecule. I have first focused my studies on **ammonium and ammonia water clusters** in order to thoroughly explore their PES to characterize in details low-energy isomers for various cluster sizes. Then I tackled the study of **protonated uracil water clusters** through two aspects: characterize low-energy isomers and model collision-induced dissociation experiments to probe dissociation mechanism in relation with recent experimental measurements. Finally, I address the study of the **pyrene dimer cation** to explore collision trajectories, dissociation mechanism, energy partition, mass spectra, and cross-section.

To introduce, develop, and conclude on these different subjects, this manuscript is organised as follow:

- The **first chapter** introduces the objectives of this thesis. Generalities about clusters, in particular molecular clusters, and collision-induced dissociation are provided.
- The **second chapter** is devoted to the introduction of the fundamental concepts used in theoretical chemistry to solve the electronic structure problem and to explore the PES. It describes the main approaches used along this thesis and their foundations. The **SCC-DFTB** approach, which is the main method used along this thesis, is described in details as well as the **parallel-tempering molecular dynamics** approach to explore PES.

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- The **third chapter** focuses on the thorough exploration of the PES of ammonium and ammonia water clusters, as well as protonated uracil water clusters, in the view to discuss their structural and energetic properties. Along this chapter, the results obtained at the SCC-DFTB level are compared to MP2 results and discuss in the light of the actual literature.
 - The **fourth chapter** presents molecular dynamics simulations of collision-induced dissociation of protonated uracil water clusters and pyrene dimer cation. In the former case, the theoretical proportion of formed neutral uracil aggregates *vs.* protonated water cluster as well as total fragmentation cross sections are compared to the experimental results by S. Zamith and J.-M. L'Hermite. The molecular dynamics simulations allow to probe the nature of the formed fragments one the short time scale and to rationalize the location of the excess proton on these fragments. The simulation of the collision-induced dissociation of the pyrene dimer cation at different collision energies is then addressed in this chapter.
 - Finally, the conclusions of this thesis, as well as a number of perspectives, are presented in the **fifth chapter**.

scribe the main methods to compute PES, *i.e.* the electronic energy, through the solving of the Schrödinger equation. Second, I present the main computational tools that I have used to explore PES.

2.1 Schrödinger Equation

The discovery of the Schrödinger equation by E. Schrödinger in 1925 is an extremely significant landmark in the development of the quantum mechanics. The behavior of a molecular system can be described by the Schrödinger equation (a linear partial differential equation), which describes the wavefunction or state function of a quantum-mechanical system. [155] In quantum mechanics, the concept of wavefunction Ψ is a fundamental postulate which defines the state of a system at each spatial position and time. The Schrödinger equation governs the evolution of the wavefunction Ψ of particles in an atomic or molecular system. In the case of a system composed of M nuclei and N electrons, the Schrödinger equation for the wavefunction in position space $\Psi(\mathbf{R}_\alpha, \mathbf{r}_j, t)$ can be written as:

$$i\hbar \frac{\partial \Psi(\mathbf{R}_\alpha, \mathbf{r}_j, t)}{\partial t} = \hat{H}(\mathbf{R}_\alpha, \mathbf{r}_j, t) \Psi(\mathbf{R}_\alpha, \mathbf{r}_j, t), \quad \alpha = 1, 2, \dots, M; j = 1, 2, \dots, N. \quad (2.1)$$

The vectorial variables are in bold in this manuscript. This equation describes the evolution of the wavefunction in space and time, where i is the imaginary unit. $\hbar = h/2\pi$ (1.054572×10^{-34} J·s) is the reduced Planck constant and t is the time. \mathbf{R}_α and \mathbf{r}_j refer to the coordinates of nucleus α and electron j , respectively. \hat{H} is the so called Hamiltonian operator corresponding to the total energy of the system. When the Hamiltonian itself is explicitly independent on time (the total wavefunction still has a time dependency), it is possible to decompose the space variables and the time variable to write the time-independent Schrödinger equation:

$$\hat{H}\Psi_k(\mathbf{R}_\alpha, \mathbf{r}_j) = E_k\Psi_k(\mathbf{R}_\alpha, \mathbf{r}_j) \quad (2.2)$$

where E_k is the total energy of the system associated with the eigenstate Ψ_k . According to this, the evolution of the wavefunction becomes:

$$\Psi(\mathbf{R}_\alpha, \mathbf{r}_j, t) = \sum_k c_k \Psi_k(\mathbf{R}_\alpha, \mathbf{r}_j) e^{-iE_k t/\hbar} \quad (2.3)$$

where c_k is a coefficient. The eigenstates obtained from equation [2.2] are the stationary states of the system and form a complete basis of orthonormal vectors. The lowest energy eigenstate is called the ground state usually denoted as Ψ_0 and E_0 is the corresponding energy.

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In a system made up of M nuclei and N electrons, the Hamiltonian operator (in a non-relativistic framework) is written as following:

$$\begin{aligned}
 \hat{H} &= \hat{T} + \hat{V} \\
 &= \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne} \\
 &= -\frac{1}{2} \sum_{\alpha=1}^M \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{1}{2} \sum_{j=1}^N \nabla_j^2 + \sum_{\alpha=1}^M \sum_{\beta>\alpha}^M \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \\
 &\quad + \sum_{j=1}^N \sum_{i>j}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} - \sum_{\alpha=1}^M \sum_{j=1}^N \frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}_j|}
 \end{aligned} \tag{2.4}$$

in which the atomic unit system is used. The energy is thus expressed in Hartree. The mass is in unit of the mass of electron and the length is in Bohr. M_α refers to the mass of nucleus α (in atomic unit) and Z_α is the atomic number. \hat{T}_n and \hat{T}_e are the kinetic energy operators of nuclei and electrons, respectively. \hat{V}_{nn} , \hat{V}_{ee} and \hat{V}_{ne} denote the potential energy operators of the repulsion between the nuclei, repulsion between the electrons and electrostatic attraction between nuclei and electrons, respectively. ∇^2 is the Laplace operator. For nucleus α in three dimensions using Cartesian coordinates, its position vector is $\mathbf{R}_\alpha=(X_\alpha, Y_\alpha, Z_\alpha)$ and ∇^2 is expressed as following:

$$\nabla^2 = \frac{\partial^2}{\partial X_\alpha^2} + \frac{\partial^2}{\partial Y_\alpha^2} + \frac{\partial^2}{\partial Z_\alpha^2} \tag{2.5}$$

2.2 Born-Oppenheimer Approximation

Electrons are very light particles which can not be described correctly even qualitatively through classical mechanics. If we want to describe the electron distribution in details, quantum mechanics must be applied, *i.e.* solving the Schrödinger equation. Usually in atomic and molecular systems, it is very hard, if not impossible, to obtain the exact solutions of Schrödinger equation. It is only possible in the system containing one nucleus and one electron, *i.e.*, the hydrogen atom or hydrogenic ions. For molecular species, the mathematical complexity to solve the Schrödinger equation will increase with the number of degrees of freedom of the system. Thus, it is necessary to resort to approximations in almost all cases. The **Born-Oppenheimer (BO) approximation** or adiabatic approximation is a cornerstone in real-life quantum analysis of atoms and molecules, which helps to solve the Schrödinger equation.

BO approximation is based on the large difference of mass between nuclei and electron and correspondingly the time scales of their motions. Indeed, the mass of proton is much higher

than that of electron ($m_p/m_e \approx 1836$). With the same amount of kinetic energy, the electrons move much faster than the nuclei.

Then, it is considered that the electrons move in the field of the fixed atomic nuclei, *i.e.*, the electrons adapt instantly to the displacement of the nuclei while remaining in their ground state. [156]

BO approximation consists of expressing the total wavefunction of a molecule as the product of a nuclear (vibrational, rotational) wavefunction and an electronic wavefunction, which enables a separation of the Hamiltonian operator into the fast electronic term and the usually much slower nuclear term, where the coupling between electrons and nuclei is neglected so that the two smaller and non-coupled systems can be solved more efficiently. In mathematical terms, the total wavefunction Ψ_{tot} of a molecule can be expressed as an expansion in the complete set of electronic wavefunctions ψ_k^e with the expansion coefficients being parametric functions of the nuclei coordinates \mathbf{R}_α :

$$\Psi_{\text{tot}}(\mathbf{R}_\alpha, \mathbf{r}_j) = \sum_{k=1}^{\infty} \psi_k^e(\mathbf{r}_j; \mathbf{R}_\alpha) \psi_k^n(\mathbf{R}_\alpha) \quad (2.6)$$

where the semicolon symbolizes the positions of the nuclei as parameters and not the variables of electronic wavefunction. This indicates that, although ψ_k^e is a real-valued function of \mathbf{r}_j , its functional form depends on \mathbf{R}_α .

Two smaller, consecutive steps can be used when using the BO approximation. In the first step, the nuclei is treated as stationary. The corresponding operator \hat{T}_n is subtracted from the total molecular Hamiltonian operator \hat{H} leading to the electronic Hamiltonian without considering nuclear kinetic energy:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne} \quad (2.7)$$

The major computational work is in solving the electronic Schrödinger equation for a given set of nuclear coordinates.

$$\hat{H}_e(\mathbf{R}_\alpha, \mathbf{r}_j) \psi_k^e(\mathbf{R}_\alpha, \mathbf{r}_j) = E_k^e \psi_k^e(\mathbf{R}_\alpha, \mathbf{r}_j) \quad (2.8)$$

where the eigenvalue E_k^e , electronic energy, depends on the chosen positions \mathbf{R}_α of the nuclei. By varying these positions \mathbf{R}_α in small steps and repeatedly to solve the electronic Schrödinger equation, so one can obtain E_k^e as a function of \mathbf{R}_α , which generates the PES.

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In the second step, the nuclear kinetic energy T_n is reintroduced, and the Schrödinger equation for the nuclear motion is:

$$(\hat{T}_n + E_k^e(\mathbf{R}_\alpha) + \langle \Psi_k | \nabla_n^2 | \Psi_k \rangle) \psi_k^n(\mathbf{R}_\alpha) = E_k^{\text{tot}} \psi_k^n(\mathbf{R}_\alpha) \quad (2.9)$$

The eigenvalue E_k^{tot} is the total energy of the molecule, which includes the overall rotation translation of the molecule, contributions from electrons, and nuclear vibrations. This second step involves a separation of vibrational, translational, and rotational motions. M. Born and R. Oppenheimer assumed that the integral $\langle \Psi_k | \nabla_n^2 | \Psi_k \rangle$ (diagonal correction) weakly depends on the nuclear coordinates, so that it can be ignored. [156] Therefore, the Born-Oppenheimer approximation allows to describe the movement of nuclei in the corresponding potential to an adiabatic electronic state by the following equation:

$$(\hat{T}_n + E_k^e(\mathbf{R}_\alpha)) \psi_k^n(\mathbf{R}_\alpha) = E_0^{\text{tot}} \psi_k^n(\mathbf{R}_\alpha) \quad (2.10)$$

In this thesis, I will assume electrons adapt fast to reach their electronic ground state. The potential energy E_0^e thus equals the ground state electronic energy E_0 and the total energy is then $E_0^{\text{tot}} = T_n + E_0$. The Schrödinger equation for $\psi_0^n(\mathbf{R}_\alpha)$ can therefore be written as:

$$(\hat{T}_n + E_0) \psi_0^n(\mathbf{R}_\alpha) = E_0^{\text{tot}} \psi_0^n(\mathbf{R}_\alpha) \quad (2.11)$$

The next step is usually to consider the nuclei can be described classically. One can then consider that they evolve classically *i.e.* following new Newton's equation, on a PES defined by the ground state electronic energy. The calculation of the ground state electronic energy is discussed in section 2.3. The BO approximation only introduces very small errors in most systems, which explains it is widely applied in quantum chemistry to speed up the computation of molecular wavefunctions of large molecules. However, the BO approximation is only valid when the electronic state is sufficiently separated from other electronic states. That is to say that, when two or more solutions of the electronic Schrödinger equation come close to each other energetically, the approximation loses validity (usually called "break down") but it can be used as a starting point for more refined methods. [157] [158]

2.3 Computation of Electronic Energy

Experimental spectroscopic investigations help in understanding the electronic structure of molecules, for instance measurements of absorption, emission and scattering. These measurements can often provide a detailed picture of molecular systems but sometimes they are

difficult to interpret. In the last few decades, molecular electronic-structure theory has developed to a stage where it can provide invaluable assistance in the interpretation of experimental measurements of a wide range of important properties of molecules in rotational and vibrational spectroscopies, magnetic-resonance spectroscopies, ultraviolet/visible spectroscopies, and others.[\[159\]](#) [\[160\]](#) [\[161\]](#) [\[162\]](#) [\[163\]](#) [\[164\]](#)

Electronic wavefunction of systems including three or more interacting particles can not be obtained analytically, so approximations must be applied. Many approximations have been proposed to obtain approximate solutions of the exact electronic wavefunction. Each one of them is usually the basis of one or more calculation approaches, which have their own advantages and disadvantages. When solutions of the Schrödinger equation are obtained without reference to experimental data, the methods are usually referred to as *ab initio* compared to semi-empirical models. The Hartree-Fock (HF) model takes all interactions between electrons into account except for the correlation between electrons that is neglected. Post-HF theory usually generates more accurate results by considering the electronic correlation.[\[165\]](#) DFT methods in the Kohn-Sham formulation can be regarded as an improvement over the HF theory as it considers approximated electronic correlation. Density-functional based tight-binding (DFTB) formalism is an approximated DFT method that involves additional approximations.[\[166\]](#) [\[167\]](#) [\[168\]](#) [\[169\]](#) Compared with quantum chemical (QM) methods that require considerable computer resources, molecular mechanics (MM) calculations are much cheaper but present severe limitations in the treatment of chemical reactivity. QM/MM techniques that combine QM for the reactive region and MM for the remainder are very promising, especially for large systems.[\[170\]](#) [\[171\]](#) [\[172\]](#)

The following section focuses on the description of wavefunction based methods, DFT method, and the DFTB methods used to solve Schrödinger equation and the electronic structure problem.

2.3.1 Wavefunction based Methods

Hartree-Fock theory. Hartree-Fock theory is one of the earliest wavefunction based approximation methods, which is the foundation for a large part of the computational work on the electronic structure of atoms and molecules.[\[173\]](#) [\[174\]](#) [\[175\]](#) The HF approximation transforms the many-body Schrödinger equation into many coupled single-particle equations, which often assumes the N -body electronic wavefunction of a system is approximated by a single Slater determinant and every electron is considered to be independent. Hartree proposed that the

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electronic wavefunction could be approximated by assuming that in addition to the nuclei, the individual electrons could be separated as well. Therefore, the many-electron wavefunction would be a product of one-electron wavefunctions ψ_j :

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_n(\mathbf{r}_n) \quad (2.12)$$

The HF theory assumes that every electron moves in an average field of all the other electrons and the nuclei in the molecule, which is an example of a mean-field approximation. The HF equations for an individual electron j moving in the mean field V_i^{HF} , can be expressed as:

$$\left(-\frac{1}{2}\nabla_j^2 + V_\sigma(\mathbf{r}_j) + V_H(\mathbf{r}_j) \right) \psi_\sigma^{HF}(\mathbf{r}_j) - \sum_{k=1}^{N_\sigma} \int d^3r' \frac{\psi_{k\sigma}^{HF*}(\mathbf{r}')\psi_{k\sigma}^{HF}(\mathbf{r}_j)}{|\mathbf{r}_j - \mathbf{r}'|} \psi_\sigma^{HF}(\mathbf{r}') = E_\sigma^{HF} \psi_\sigma^{HF}(\mathbf{r}_j) \quad (2.13)$$

where ∇_j^2 depends on the j th electron coordinates. $V_\sigma(\mathbf{r}_j)$ refers to the external potential. σ is the spin. The last term on the left-hand side is the HF exchange potential. Using the electronic density, we can obtain:

$$V_H(\mathbf{r}_j) = \int d^3r' \rho(\mathbf{r}') \frac{1}{|\mathbf{r}_j - \mathbf{r}'|} \quad (2.14)$$

$V_H(\mathbf{r}_j)$ is the Hartree potential:

$$\rho(\mathbf{r}_j) = \sum_{\sigma} \sum_j^{N_\sigma} \rho_{\sigma}(\mathbf{r}_j) = \sum_{\sigma} \sum_j^{N_\sigma} |\psi_{\sigma}^H(\mathbf{r}_j)|^2 \quad (2.15)$$

\mathbf{r}' refers to the positions of all other electrons except electron j .

HF or self-consistent field (SCF) theory can be derived by invoking the variational principle in a restricted space of wavefunctions, which was introduced in many books.[\[176\]](#) [\[177\]](#) [\[178\]](#) [\[179\]](#) C. Roothaan then put forward the approximation of molecular orbitals (MOs) as a linear combination of atomic orbitals (LCAO) in 1951, namely, a linear combination of atomic basis functions to solve the HF equations of molecules.[\[180\]](#) Thus was a significant improvement in the practical solution of the HF equations. Roothaan equations allow to transform the HF problem into a linear algebra problem, for which algebraic equations are particularly suitable for modern computers.[\[181\]](#) The vast majority of computational approaches, whether *ab initio*, semi-empirical, or even some sophisticated force-fields are based on the concept that the molecular orbitals of a given molecule can be built from the atomic orbitals of its constituent atoms.[\[182\]](#)

The HF theory showed some success. [183] However, it does not contain the electron correlation beyond the minimum required to satisfy the antisymmetry for electronic wavefunctions. The resulting approximated electronic energies are therefore not accurate enough for most practical applications in chemistry. Good HF results can account for over 99% of the true total energy of the system. Due to the variational principle, the HF wavefunction is always too high in energy. So, the remaining 1% error with respect to the true total energy, which is defined as the correlation energy ($E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$) is essential to account for the chemical properties of atoms and molecules. Electron correlation results from the correlated behavior of electrons, and the failure of HF theory to describe it originates from that the mean-field approximation can not treat electron-electron interactions properly. [184]

Post Hartree-Fock methods. Post Hartree-Fock methods provide improvements to HF theory by adding the electron correlation. [165, 185] The calculation of the correlation energy is then the objective of several post-HF methods (for instance, the configuration interaction (CI) method, [186, 187] Møller-Plesset perturbation theory (MP2, MP3 and MP4) methods, [188, 189, 190] coupled cluster (CC) method, [191, 192, 193, 194] quantum chemistry composite (G2, G3, and T1) methods, [195, 196, 197] and so on). Post-Hartree-Fock methods usually give more accurate results than Hartree-Fock calculations, [186, 198, 199] but the additional accuracy comes to the price of a higher computational cost. Among the aforementioned post-HF methods, the Møller-Plesset perturbation theory at second-order (MP2) method was used along this thesis.

HF theory variationally optimize the orbitals of a single configuration state function (CSF). In the case of a closed-shell singlet and some open-shell cases, this would be a single Slater determinant. To include the electron correlation in wavefunction theory, a superposition of CSFs should be considered. This superposition, referred to as a multiconfigurational wavefunction, is a linear combination of two or more CSFs. Standard multiconfigurational approaches are the CI, CC, and perturbation theory methods.

2.3.2 Density Functional Theory

For a long time, approximations based on the wavefunction were systematically applied to solve the Schrödinger equation. However, it is usually impractical to perform a wavefunction based calculation with chemical accuracy for complex or large systems. Density functional theory is based on the electron density rather than the electronic wavefunction. [200, 201] Because DFT displays a more favourable scaling of computational resources with respect to system

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size, DFT is nowadays the most widely used method available in computational chemistry, computational physics, and condensed-matter physics for ground state calculation of large and complex systems.

Although DFT has a history almost as old as the Schrödinger equation, the modern form dates back to the paper published by P. Hohenberg and W. Kohn [202] that introduced the two Hohenberg–Kohn (HK) theorems in 1964 and the extension by M. Levy in 1979.[203] The theory is usually applied in the form latter suggested by W. Kohn and L. J. Sham in 1965.[200] DFT makes it possible to transform the problem of electrons interacting and evolving in a nuclear potential to a problem of independent electrons evolving in an effective potential. The electron density $\rho(\mathbf{r})$ corresponds to the number of electrons per unit volume in a given state.

$$\rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (2.16)$$

The central idea of DFT is to promote $\rho(\mathbf{r})$ (function which only depends on three spatial coordinates) as the key variable in the determination of the electronic energy of a system.

This idea originates from the the model of the uniform electron gas in the phase space around an atom developed in 1927 by L. H. Thomas [204] and E. Fermi [205], which is the predecessor to density functional theory. Nevertheless, the Thomas-Fermi model is unable to correctly describe molecular bonds because it does not take into account the exchange and correlation energies.

The first HK theorem shows that, for a many-electron system in its ground state, the energy is uniquely determined by the electron density $\rho(\mathbf{r})$. In other words, the first HK theorem shows that it is not necessary to know the wavefunction of the system to obtain its energy and that the knowledge of the electron density alone is sufficient. It sets down the foundation for reducing the many-body problem of N electrons with $3N$ spatial coordinates to three spatial coordinates, through using functionals of the electron density. From this theorem, it follows that $\rho(\mathbf{r})$ determines the external potential $V_{\text{ext}}(\mathbf{r})$ and N can be obtained via the normalization of $\rho(\mathbf{r})$:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (2.17)$$

N and $V_{\text{ext}}(\mathbf{r})$ determine the electronic Hamiltonian. $\rho(\mathbf{r})$ determines the energy and all other ground state electronic properties of a system. This is clearly shown in Figure 2.2.

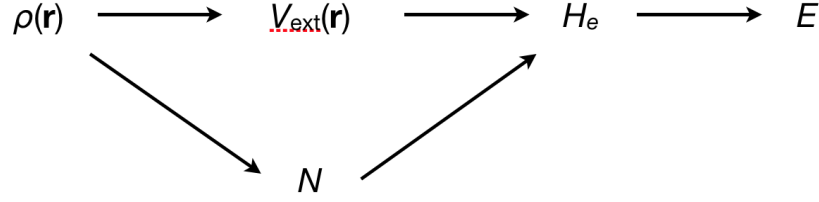


Figure 2.2: Interdependence of basic variables in the Hohenberg-Kohn theorem.

The second HK theorem is a variational electron density theorem which defines an energy functional of the electronic density for a system. For a given external potential $V_{\text{ext}}(\mathbf{r})$, the ground state energy E_0 of the system is obtained by minimizing this energy function with respect to the electronic density, the corresponding density is exactly the ground state electronic density $\rho(\mathbf{r})$. From the HK theorems, we can write the functional of the total energy of the system as a sum of the kinetic energy of the electrons $T_e[\rho(\mathbf{r})]$, and the electronic interaction energy $E_{\text{ee}}[\rho(\mathbf{r})]$:

$$E[\rho(\mathbf{r})] = T_e[\rho(\mathbf{r})] + V_{\text{ee}}[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) \quad (2.18)$$

the last term represents the interaction between the electron density and the external potential, *i.e.* the nuclei in the case of atoms and molecules. To obtain the energy of the ground state from this equation, the variation principle can be applied with respect to $\rho(\mathbf{r})$. To do this, the form of $T_e[\rho(\mathbf{r})]$ and $V_{\text{ee}}[\rho(\mathbf{r})]$ should be known.

The HK theorems do not provide mathematical expressions for $T_e[\rho(\mathbf{r})]$ and $V_{\text{ee}}[\rho]$ for a system of interacting particles. To solve this problem, Kohn and Sham first proposed to treat the electrons as non-interacting particles subject to the $V_{\text{ext}}(\mathbf{r})$ potential only. [200] The idea was to work with a fictitious system of N non-interacting electrons evolving in an effective potential and having the exact electronic density of the system. The resolution of equation 2.18 for a system of non-interacting electrons is known exactly, and if the correct electron density is reproduced, then the exact electronic energy of the system can be calculated. The total energy of the real system is composed as follows:

$$E_{\text{DFT}}[\rho(\mathbf{r})] = T_{\text{no}}[\rho(\mathbf{r})] + \underbrace{E_{\text{H}}[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d(\mathbf{r}) + E_{\text{xc}}[\rho(\mathbf{r})]}_{E_{\text{eff}}[\rho(\mathbf{r})]} \quad (2.19)$$

where the sum of last three terms on the right-hand side is the effective energy $E_{\text{eff}}[\rho(\mathbf{r})]$. $T_{\text{no}}[\rho(\mathbf{r})]$ is the kinetic energy of a system of non-interacting electrons:

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$$T_{\text{no}}[\rho(\mathbf{r})] = \sum_i^N \left\langle \Psi_i \left| -\frac{1}{2} \nabla^2 \right| \Psi_i \right\rangle \quad (2.20)$$

$E_H[\rho(\mathbf{r})]$ represents the Hartree energy which corresponds to the interaction energy of a classical charge distribution of density $\rho(\mathbf{r})$:

$$E_H[\rho(\mathbf{r})] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2.21)$$

$V_{\text{ext}}(\mathbf{r})$ is the external potential. The remaining energy components are assembled in the exchange-correlation energy $E_{\text{xc}}[\rho(\mathbf{r})]$ functional containing the difference between the kinetic energy of the real system $T[\rho(\mathbf{r})]$ and that of the non-interacting system $T_n[\rho(\mathbf{r})]$ and the non-classical part of $E_{\text{ee}}[\rho]$, adding the difference between $V_{\text{ee}}[\rho(\mathbf{r})]$ and $E_H[\rho(\mathbf{r})]$. The $E_{\text{xc}}[\rho(\mathbf{r})]$ functional can thus be expressed as:

$$E_{\text{xc}}[\rho(\mathbf{r})] = (T[\rho(\mathbf{r})] - T_{\text{no}}[\rho(\mathbf{r})]) + (V_{\text{ee}}[\rho(\mathbf{r})] - E_H[\rho(\mathbf{r})]) \quad (2.22)$$

In practice, to minimize the energy $E[\rho(\mathbf{r})]$ with respect to $\rho(\mathbf{r})$ applying by the variational principle while considering the constraints of orbital orthogonality, one performs an optimization under the constraints using Lagrange multipliers.

Combining eqs [2.19](#), [2.20](#), and [2.21](#), the effective potential $V_{\text{eff}}[\rho(\mathbf{r})]$ can be introduced as:

$$\begin{aligned} V_{\text{eff}}[\rho(\mathbf{r})] &= V_{\text{ext}}[\rho(\mathbf{r})] + V_H[\rho(\mathbf{r})] + V_{\text{xc}}[\rho(\mathbf{r})] \\ &= V_{\text{ext}}[\rho(\mathbf{r})] + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \end{aligned} \quad (2.23)$$

$$= \frac{\partial E_{\text{eff}}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (2.24)$$

where $V_H[\rho(\mathbf{r})]$ refers to the Hartree potential and $V_{\text{xc}}[\rho(\mathbf{r})]$ is the exchange-correlation potential.

In addition, the molecular orbitals $\phi_i(\mathbf{r})$ should satisfy the one-electron KS equations:

$$\underbrace{\left(-\frac{1}{2} \nabla_i^2 + V_{\text{eff}}[\rho(\mathbf{r})] \right)}_{\text{KS operator}} \phi_i(\mathbf{r}) = E_i \phi_i(\mathbf{r}) \quad (2.25)$$

This result can be reobtained within a variational context when looking for those orbitals minimizing the energy functional of equation 2.18, subject to orthonormality conditions:

$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij} \quad (2.26)$$

The one-electron KS equation of equation 2.25, just as the HF equations, needs to be solved iteratively. The computational cost for the incorporation of electron correlation is the one necessary to calculate $V_{xc}[\rho(\mathbf{r})]$.

DFT is in principle correct if one knows the “exact” exchange-correlation functional. However, despite a lot of work aimed at determining this exact functional, its form is still unknown and a systematic strategy for improvement is not available. Therefore, it is always necessary to use an approximate functional that is characterized by more or less important artefacts in effective calculations. Over the last decades, many exchange-correlation functionals have been proposed. Although they are different, it is possible to classify them into families according to some common characters. **Local Density Approximation (LDA)**, **Generalized Gradient Approximation (GGA)**, **meta-GGA**, and **hybrid functionals** (containing to some extent a contribution of HF exact-exchange) are some of the most widely used approximations. **LDA** is the first approximation of $E_{xc}[\rho(\mathbf{r})]$ proposed by W. Kohn and L. J. Sham, [200] which is based on the description of the homogeneous electron gas. For atomic or molecular systems, when densities vary rapidly in space, the assumption of a uniform electron density is not correct and the LDA approximation is not applicable any more. For example, binding energies in molecules are usually overestimated by the LDA approximation. To solve this problem, a new family of functionals, **GGA functional**, which includes a contribution of the electron density gradient was developed. [200, 206, 207] **Hybrid functionals** were first proposed by Becke in 1993. [208] The main idea is that for an uncorrelated system, the HF energy is exact while for a highly correlated system LDA or GGA energy is more appropriate. These two states are then connected by a continuum of partially correlated real systems of identical density. This connection is described by the adiabatic connection formula:

$$E_{xc}[\rho(\mathbf{r})] = \int_0^1 E_{xc}[\rho(\mathbf{r})]\lambda d\lambda \quad (2.27)$$

where $\lambda=0$ corresponds to the uncorrelated case and $\lambda=1$ corresponds to the highly correlated case. Hybrid functionals usually provide higher quality results than those provided by LDA and GGA functionals for the study of molecular properties. Hybrid functionals have been

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very successful for ground-state properties. B3LYP (Becke, 3-parameter, Lee-Yang-Parr), [208, 209, 210, 211] PBE with one empirical parameter (PBE0, also called PBE1PBE), [212] Heyd-Scuseria-Ernzerhof (HSE06), [213, 214], and M06-2X [215] are some of the most popularly hybrid functionals. Approximate functionals suffer from some generic problems, many of which can be traced to the so-called delocalization error [216] or the closely related problem of self-interaction error. Nevertheless, it should be emphasized that today DFT, cast in the Kohn-Sham formalism, provides a computational tool with a remarkable quality and computationally less expensive than wavefunction based methods.

2.3.3 Density Functional based Tight-Binding Theory

DFT is computationally too expensive for systems with more than hundreds of atoms especially when one needs to perform global optimization or to perform molecular dynamics (MD) simulations with sufficient statistical sampling of the initial conditions or to perform fairly long trajectories. It is therefore necessary to further simplify the method in order to reduce the computational cost. To do so, W. Foulkes and R. Haydock showed that tight-binding models can be derived from the DFT. [217] Later, DFTB was proposed by D. Porezag *et al.* [218]

Non-self-consistent DFTB scheme is suitable to study systems in which polyatomic electronic density is well described by a sum of atom-like densities. This is the case ighly ionic and homonuclear covalent systems. However, uncertainty rises in the non-self-consistent DFTB scheme when chemical bonds are controlled by a subtler charge balance between atoms especially for polar, semi-conductor and heteronuclear molecules. The self-consistent-charge extension of DFTB, SCC-DFTB, was born as an improvement of standard DFTB to provide a better description of electronic systems in which long-range Coulomb interactions are significant. [168, 168, 218, 219, 220, 221] I now describe in more details how SCC-DFTB can be derived from DFT.

General principles of DFTB. DFTB is derived from DFT based on the following approximations:

- Only valence electrons are treated explicitly.
- Molecular orbitals are developed on atomic valence orbitals.
- A Taylor expansion of the total energy around a reference density is realized.
- Integrals involving more than two centers are neglected.

First-order DFTB (historically referred to as zeroth-order DFTB) takes into account the first term of Taylor's expansion and which is equivalence with the other tight-binding model. **Second-order DFTB** (historically the SCC-DFTB) introduces a self-consistent procedure on atomic charges. There is also a more recent **third-order extension of DFTB** (referred to as DFTB3). [222] DFTB3 was not used in this thesis so the third-order expansion term will not be shown in the following equations.

According to equation [2.19], $E_{\text{DFT}}[\rho(\mathbf{r})]$ can be written as:

$$E_{\text{DFT}}[\rho(\mathbf{r})] = \langle \psi_i | \hat{T}_{\text{no}}[\rho(\mathbf{r})] | \psi_i \rangle + E_{\text{eff}}[\rho(\mathbf{r})] \quad (2.28)$$

The SCC-DFTB scheme is built on the second-order Taylor series development around a reference electronic density $\rho_0(\mathbf{r})$, so $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})$. In practice, $\rho_0(\mathbf{r})$ is taken as the superimposition of the densities of isolated atoms. Then $E_{\text{DFTB}}[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})]$ can be written as follows:

$$E_{\text{DFTB}}[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] = \langle \psi_i | \hat{T}_{\text{no}}[\rho(\mathbf{r})] | \psi_i \rangle + E_{\text{eff}}[\rho_0(\mathbf{r})] + \int \frac{\delta E_{\text{eff}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{\rho_0} \delta\rho(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \iint \frac{\delta^2 E_{\text{eff}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \Big|_{\rho_0, \rho'_0} \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (2.29)$$

with $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0(\mathbf{r})$. Equation [2.29] can be rewritten as:

$$E_{\text{DFTB}}[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] = \overbrace{E_{\text{eff}}[\rho_0(\mathbf{r})] - \int \frac{\delta E_{\text{eff}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{\rho_0} \rho_0(\mathbf{r}) d\mathbf{r}}^{E_{\text{rep}}} \\ + \underbrace{\langle \psi_i | \hat{T}_{\text{no}}[\rho(\mathbf{r})] | \psi_i \rangle + \int \frac{\delta E_{\text{eff}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \Big|_{\rho_0} \rho_0(\mathbf{r}) d\mathbf{r}}_{E_{\text{band}}} \\ + \underbrace{\frac{1}{2} \iint \frac{\delta^2 E_{\text{eff}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \Big|_{\rho_0, \rho'_0} \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}'}_{E_{2\text{nd}}} \quad (2.30)$$

The right-hand side terms in the first line of equation [2.30] only depends on with $\rho_0(\mathbf{r})$, and correspond to a repulsive contribution E_{rep} . The sum of the terms in the second line is the so-called band energy E_{band} . We can define that a reference Hamiltonian \hat{H}^0 , which only depends

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on the reference electron density ρ_0 :

$$\hat{H}^0 = -\frac{1}{2}\nabla^2 + \underbrace{V_{\text{ext}}[\rho(\mathbf{r})] + \int \frac{\rho'_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}[\rho_0(\mathbf{r})]}_{V_{\text{eff}}([\rho_0(\mathbf{r})])} \quad (2.31)$$

where we combined the last three terms in the operator as $V_{\text{eff}}([\rho_0(\mathbf{r})])$. The third line is the second-order energy $E_{2\text{nd}}$. Equation 2.30 can be rewritten as follows:

$$E_{\text{DFTB}}[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] = E_{\text{rep}}[\rho_0(\mathbf{r})] + \overbrace{\sum_i^{\text{occ}} n_i \langle \psi_i | \hat{H}^0 | \psi_i \rangle}^{E_{\text{band}}} + E_{2\text{nd}}[\rho_0(\mathbf{r}), (\delta\rho(\mathbf{r}))^2] \quad (2.32)$$

Band energy term. In DFTB, it relies on the use of LCAO for the description of the KS molecular orbitals $\psi_i(\mathbf{r})$. Here the atomic orbitals are limited to the valence orbitals of atoms:

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{v}} C_{i\mathbf{v}} \varphi_{\mathbf{v}}(\mathbf{r} - \mathbf{R}_{\alpha}) \quad (2.33)$$

where φ_{μ} is the orbital of atom α . E_{band} can be rewritten with equations 2.24 and 2.33:

$$\sum_i^{\text{occ}} n_i \langle \psi_i | \hat{H}^0 | \psi_i \rangle = \sum_i^{\text{occ}} n_i \sum_{\mu}^{\text{occ}} \sum_{\mathbf{v}}^{\text{occ}} C_{i\mu} C_{i\mathbf{v}} \underbrace{\langle \varphi_{\mu} | \hat{T}_e[\rho(\mathbf{r})] + V_{\text{eff}}[\rho_0(\mathbf{r})] | \varphi_{\mathbf{v}} \rangle}_{H_{\mu\mathbf{v}}^0}, \text{ with } \mu \in \alpha, \mathbf{v} \in \beta \quad (2.34)$$

The Hamiltonian matrix element $H_{\mu\mathbf{v}}^0$ is defined as:

$$H_{\mu\mathbf{v}}^0 = \langle \varphi_{\mu} | \hat{H}^0 | \varphi_{\mathbf{v}} \rangle, \quad (2.35)$$

The effective potential $V_{\text{eff}}[\rho_0(\mathbf{r})]$ is defined as the sum of potentials $V_{\alpha}(\mathbf{r})$ centered on the atoms:

$$V_{\text{eff}}[\rho_0(\mathbf{r})] = \sum_{\alpha} V_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}) \quad (2.36)$$

The Hamiltonian matrix elements can be written as follows:

$$H_{\mu\mathbf{v}}^0 = \left\langle \varphi_{\mu} \left| -\frac{1}{2}\nabla_i^2 + V_{\alpha} + V_{\beta} \right| \varphi_{\mathbf{v}} \right\rangle \quad (2.37)$$

For diagonal elements, the energy level in the free atom is chosen, which ensures the correct dissociation limits. The interatomic blocks are computed as given in equation [2.37](#), depending on the choice of potential generation. Because of the orthogonality of the basis functions, the off-diagonal elements of the intraatomic blocks are exactly zero. To summarize, within the electronic density superposition approach, the $H_{\mu\nu}^0$ elements can be unfolded as:

$$H_{\mu\nu}^0 = \begin{cases} \varepsilon_{\mu}^{\text{free atom}}, & \mu = \nu \\ \langle \varphi_{\mu} | -\frac{1}{2}\nabla_i^2 + V_{\alpha} + V_{\beta} | \varphi_{\nu} \rangle, & \mu \in \alpha, \nu \in \beta, \alpha \neq \beta \\ 0, & \text{otherwise} \end{cases} \quad (2.38)$$

It should be noted that the $H_{\mu\nu}^0$ elements only depend on atoms α and β . Therefore only the two-center matrix elements and the two-center elements of the overlap matrix can be explicitly calculated, in other words, interactions at three or more centers are neglected as stated above.

Second-order term. In SCC-DFTB, the electronic density is corrected by including the second-order contribution $E_{2\text{nd}}$ in equation [2.32](#), which is ignored in first-order DFTB.

To include the density fluctuations in a simple but efficient way according to tight-binding method, $\delta\rho$ can be written as a superposition of atom-like contributions $\delta\rho_{\alpha}$, which has a fast decrease with the increase of the distance from the corresponding atomic center:

$$\delta\rho(\mathbf{r}) = \sum_{\alpha}^N \delta\rho_{\alpha}(\mathbf{r}) \quad (2.39)$$

where $\delta\rho_{\alpha}$ can be simplified with the monopole approximation as follows:

$$\delta\rho_{\alpha}(\mathbf{r}) = \Delta q_{\alpha} F_0(\mathbf{r} - \mathbf{R}_{\alpha}) \quad (2.40)$$

where the atomic charge fluctuation Δq_{α} (difference between the Mulliken population q_{α} [\[223\]](#) of atomic α and the number of valence electrons of the atom at infinity) is estimated by the Mulliken expression. F_0 represents the normalized radial dependence of the electronic density fluctuation in atom α . This means the effects of charge transfer are included, however, the changes in the shape of the electronic density are ignored. $E_{2\text{nd}}$ can be rewritten with equations [2.30](#) and [2.32](#) as follows:

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$$\begin{aligned}
 E_{2\text{nd}} &\approx \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N \Delta q_{\alpha} \Delta q_{\beta} \overbrace{\iint \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}[\rho_0(\mathbf{r})]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \Big|_{\rho_0, \rho'_0} \right) F(\alpha, \beta) d\mathbf{r} d\mathbf{r}'}^{\gamma_{\alpha\beta}} \\
 &= \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N \Delta q_{\alpha} \Delta q_{\beta} \gamma_{\alpha\beta}
 \end{aligned} \tag{2.41}$$

where $F(\alpha, \beta) = F_0(\mathbf{r} - \mathbf{R}_{\alpha}) \times F_0(\mathbf{r}' - \mathbf{R}_{\beta})$ the two-electron integrals $\gamma_{\alpha\beta}$ is introduced for convenience.

To calculate equation [2.41](#), $\gamma_{\alpha\beta}$ must be analyzed. In the limit case, the interatomic distance is very large, $|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}| = |\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ with GGA-DFT, the exchange-correlation term tends to zero. $\gamma_{\alpha\beta}$ that describes the interaction of two normalized spherical electronic densities reduces to $1/|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|$, so $E_{2\text{nd}}$ can be expressed as follows:

$$E_{2\text{nd}} = \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N \frac{\Delta q_{\alpha} \Delta q_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} + f(U_{\alpha}, U_{\beta}, (\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})) \tag{2.42}$$

where U_{α} , U_{β} are the Hubbard parameters: $\gamma_{\alpha\alpha} \approx I_{\alpha} - A_{\alpha} \approx 2\eta_{\alpha} \approx U_{\alpha}$. I is the ionisation potential and A is the electronic affinity of atom α . η_{α} refers to the chemical hardness of atom α . [\[168\]](#)

It is worth noting that the electronic density $\rho(\mathbf{r})$ influences explicitly the calculation of the electrostatic energy in DFT. In the context of DFTB, point charges are used and the electronic density around the atom is condensed at a point. In practice, Mulliken's definition of charge is often used, [\[223\]](#) which is defined as:

$$q_{\alpha}^{\text{Mull}} = \frac{1}{2} \sum_{\alpha}^{\text{occ}} n_i \sum_{\mu \in \alpha} \sum_{\nu} (C_{i\mu}^* C_{i\nu} S_{\mu\nu} + C_{i\nu}^* C_{i\mu} S_{\nu\mu}) \tag{2.43}$$

Repulsive energy term. E_{rep} is a repulsive contribution obtained from the sum of atomic-pair terms, which only depend on the reference electronic density $\rho_0(\mathbf{r})$. It is assumed to make E_{rep} only rely on the two-center contributions:

$$E_{\text{rep}}[\rho_0(\mathbf{r})] \approx \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N V(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}) \tag{2.44}$$

In practice, it is possible to calculate E_{rep} with known values of $\rho_0(\mathbf{r})$, but it's more convenient to adjust the expression of E_{rep} to *ab initio* calculations. Therefore, E_{rep} is determined

by comparing the difference between the DFT energy E_{DFT} and $E_{\text{band}}+E_{2\text{nd}}$ as a function of the interatomic distance $R_{\alpha\beta}$:

$$E_{\text{rep}}[\rho_0(\mathbf{r})] \equiv E_{\text{rep}}(R_{\alpha\beta}) = E_{\text{DFT}}(R_{\alpha\beta}) - E_{\text{band}}(R_{\alpha\beta}) - E_{2\text{nd}}(R_{\alpha\beta}) \quad (2.45)$$

Total energy. The total energy in SCC-DFTB can be written from the previous different contributions as follows:

$$\begin{aligned} E_{\text{SCC}} = & \sum_i^{\text{occ}} n_i \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{occ}} C_{i\mu} C_{i\nu} \langle \psi_i | \hat{H}^0 | \psi_i \rangle + \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N V(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}) \\ & + \frac{1}{2} \sum_{\alpha}^N \sum_{\beta}^N \Delta q_{\alpha} \Delta q_{\beta} \gamma_{\alpha\beta} \end{aligned} \quad (2.46)$$

Secular equations. From this energy expression model, we can get the secular equations:

$$\sum_{\nu} C_{i\nu} (H_{\mu\nu}^0 - \varepsilon_i S_{\mu\nu}) = 0, \quad \forall \mu, \nu \quad (2.47)$$

where $H_{\mu\nu}^0$ is the DFTB operator matrix element and $S_{\mu\nu}$ are the overlap matrix elements.

The secular equations can be rewritten using the matrix, $H_{\mu\nu}$, defined by:

$$H_{\mu\nu} = H_{\mu\nu}^0 + \underbrace{\frac{1}{2} S_{\mu\nu} \sum_{\zeta} (\gamma_{\alpha\zeta} + \gamma_{\beta\zeta}) \Delta q_{\zeta}}_{H'_{\mu\nu}} \quad (2.48)$$

$H_{\mu\nu}^0$ comes from the band energy and $H'_{\mu\nu}$ is from the second order term. The $H_{\mu\nu}$ elements rely on the atomic charges explicitly, and the atomic charges depend on the molecular orbitals (see equation [2.43](#)). Then the resolution can be achieved in a self-consistent way. First, from an initial set of charges the $H_{\mu\nu}$ elements which depend on these charges can be computed. The KS equations (equations [2.47](#)) are then solved which gives the energy of the KS orbitals and the corresponding eigenvectors. The corresponding coefficients allow to compute a new set of charges which will be used in the calculation of new $H_{\mu\nu}$ elements. This procedure is repeated until the atomic charges are converged.

DFTB is derived from DFT, it therefore inherits the specific problems of DFT. For instance, the traditional DFT functionals can not describe properly dispersion interaction and charge resonance phenomena in charged aggregates. DFTB also display some specific problems because of its own approximations such as the use of Mulliken atomic charges, the absence of atomic polarization, the absence of coupling between atomic orbitals located on the same atom. This differs from DFT that explicitly considers atomic polarization.

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Atomic charges. As presented above, DFTB was initially developed with Mulliken charges; However, other definitions of atomic charges are possible such as Natural Bond Order (NBO) [224, 225, 226, 227] and Electrostatic Potential Fitting (EPF) charges. [228, 229] EPF has a fairly good representation of the electrostatic term of a molecule dominated by the Van der Waals interactions. CM3 (Class IV / Charge Model 3) charges were proposed by J. Li *et al.* in 1998 and they have been considered in DFTB. They give good results for the description of the electric dipole and the electrostatic potential, partial atomic charges in molecules, and Coulombic intermolecular potential of polycyclic aromatic hydrocarbon clusters. [230, 231, 232, 233] The CM3 charges are defined as:

$$q_{\alpha}^{\text{CM3}} = q_{\alpha}^{\text{Mull}} + \sum_{\beta \neq \alpha} (D_{t_{\alpha\beta}} K_{\alpha\beta} + D_{t_{\alpha\beta}} K_{\alpha\beta}^2) \quad (2.49)$$

where $K_{\alpha\beta}$ is the Mayer bond order, [234, 235, 236] between atoms α and β . $C_{t_{\alpha\beta}}$ and $D_{t_{\alpha\beta}}$ are empirical parameters which are related to the nature of atoms α and β .

In this thesis, in practice for the calculation of electronic energy, the definition of CM3 charges is simplified as:

$$q_{\alpha}^{\text{CM3}} = q_{\alpha}^{\text{Mull}} + \sum_{\beta \neq \alpha} D_{t_{\alpha\beta}} K_{\alpha\beta} \quad (2.50)$$

Dispersion energy. In order to correctly describe the energies of molecular systems, it is necessary to take into account the Van der Waals interactions. London dispersion interaction acts between atoms and molecules and represents a large part of the Van der Waals interactions. London dispersion interaction arises from the interactions between fluctuating dipoles. One of the major drawbacks within DFTB is that it does not take dispersion interactions into account. This is also true for DFT, when using LDA or GGA functionals. To overcome this limitation, semi-empirical energy corrections can be applied in DFT and DFTB calculations, which usually gives good results. [237, 238, 239, 240, 241, 242, 243, 244] Moreover, a semi-empirical correction to the dispersion in the DFTB energy leaves the freedom to use the already existing DFTB parameters without any need of re-parametrization. For the studies presented in this thesis, the dispersion energy plays a fairly important role. The correction we apply for the dispersion energy is of the following form:

$$E_{\text{disp}}(\mathbf{R}_{\alpha\beta}) = - \sum_{\alpha} \sum_{\beta \neq \alpha} f(\mathbf{R}_{\alpha\beta}) \frac{C_{\alpha\beta}^6}{R_{\alpha\beta}^6} \quad (2.51)$$

where $f(\mathbf{R}_{\alpha\beta})$ is a cutoff function, which allows to avoid the divergence of this term at a short distance. $C_{\alpha\beta}^6$ is an empirical coefficient calculated for each pair of atoms.

2.3.4 Force Field Methods

Force field is a computational method utilized to estimate the forces between particles, in other words it is the functional form and parameter sets applied to calculate the potential energy of a system. FF is interatomic potential and use the same concept with force field in classical physics, a vector field which describes a non-contact force acting on a particle at different positions in space. The acting force on each particle is derived as a gradient of the potential energy with respect to the particle positions. [245] In such case, the interactions in a system are determined from parameterized potentials in which the electronic structure can not be described explicitly because each particle is treated as a material point. The particles interact with each other through the FF and the integration algorithm is applied to the particles. In most cases, this leads to a big decrease of the precision level in the description of the system but it can reduce the calculation cost drastically, which allows to model systems containing several thousands of particles.

Different potentials have been proposed, [246, 247, 248, 249, 250, 251] which can be classified two main groups: pair potentials and multi-body potentials. For pair potentials, harmonic interaction is the most basic form: [252]

$$V(R_{\alpha\beta}) = k(R_{\alpha\beta} - R_{eq})^2 \quad (2.52)$$

where $R_{\alpha\beta}$ is the distance between two interacting particles α and β . k is the harmonic force constant. R_{eq} is the equilibrium distance where the force of repulsion equals to the one of attraction. This potential is sufficient for systems only deviating very slightly from the bond distance at equilibrium and interactions reasonably limited to adjacent pairs of particles. However, for systems with large deviations, other potential forms must be used, for instance, the Morse potential which describes the potential energy of a diatomic molecule: [248, 253]

$$V(R_{\alpha\beta}) = D_{eq} \left(1 - e^{-a(R_{\alpha\beta} - R_{eq})} \right)^2 \quad (2.53)$$

where D_{eq} is the depth of the Morse potential well. Parameter a determines the width of the potential, the smaller a the larger the well. The force constant of the bond can be found via the Taylor expansion of $V(R_{\alpha\beta})$ around $R_{\alpha\beta} = R_{eq}$ to the second derivative of the potential energy function, from which it can obtain $a = (k_{eq}/2D_{eq})^{\frac{1}{2}}$ in which k_{eq} is the force constant of the minimum well.

Lennard-Jones potential as known as LJ potential or 12-6 potential is a pair potential, which is proposed by J. Lennard-Jones in 1924. [246, 247] It models soft repulsive and attractive

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interactions, therefore, the LJ potential describes electronically neutral atoms or molecules. Because of its simple mathematical form, it is one of the most widely used intermolecular potentials especially to describe the interaction within noble gas molecules. The total energy can be written as the sum of the interaction energy of all atomic pairs, which is defined as follows: [254]

$$V_{\text{LJ}}(R_{\alpha\beta}) = 4\epsilon_0 \left[\left(\frac{\sigma}{R_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{R_{\alpha\beta}} \right)^6 \right] = \epsilon_0 \left[\left(\frac{R_{eq}}{R_{\alpha\beta}} \right)^{2n} - 2 \left(\frac{R_{eq}}{R_{\alpha\beta}} \right)^n \right] \quad (2.54)$$

ϵ_0 denotes the depth of the potential well that usually refers to the dispersion energy. σ is the interparticle distance at which the potential energy is zero. $n = 6$ and ϵ_0 denotes the bonding energy, the energy required to separate the atoms. And the LJ potential has its minimum ($-\epsilon_0$) at a distance of $R_{\alpha\beta} = R_{eq} = 2^{\frac{1}{6}}\sigma$.

It becomes more complicated for molecular systems in which the modes of intermolecular and intramolecular interactions are very different. So it requires to develop force fields including several kinds of potentials. The expression of the potential energy for a molecular system which is the most frequently used for simple organic molecules and biological macromolecules is written as follows: [255]

$$\begin{aligned} V_{\text{total}}(R) &= \overbrace{V_{\text{bond}} + V_{\text{angle}} + V_{\text{dihedral}}}^{V_{\text{bonded}}} + \overbrace{V_{\text{VW}} + V_{\text{Coulomb}}}^{V_{\text{nonbonded}}} \\ &= \sum_{\text{bond}} \frac{k_{\alpha\beta}}{2} (R_{\alpha\beta} - R_{eq})^2 + \sum_{\text{angle}} \frac{k_{\theta}}{2} (\theta - \theta_{eq})^2 + \sum_{\text{dihedral}} \frac{k_{\phi}}{2} (1 + \cos(n\phi - \phi_{eq}))^2 \\ &\quad + \sum_{\text{VW}} 4\epsilon_0 \left[\left(\frac{\sigma}{R_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{R_{\alpha\beta}} \right)^6 \right] + \sum_{\text{Coulomb}} \frac{1}{4\pi\epsilon_0} \frac{q_{\alpha}q_{\beta}}{R_{\alpha\beta}} \end{aligned} \quad (2.55)$$

Molecular interactions can determine the macroscopic properties of matter. Van der Waals interaction is an important force between atoms and molecules but it is extremely short ranged. Van der Waals interaction energy is also termed London dispersion energy. This repulsive distance dependence is usually modeled as a term that scales with $1/R_{\alpha\beta}^{12}$ although there is no absolute physical reason for it. The van der Waals interaction energy is usually approximated by a Lennard-Jones potential.

Now we know how to calculate the potential energy of nuclei (electronic energy). Many thermal dynamical, chemical, and physical properties require the association of PES. Different methods will be shown for the exploration of the PES in the next section.

Such integral can be evaluated more efficiently using conventional numerical means than using Monte Carlo methods. However, the extension to higher dimensions (number of degrees of freedom greater than 3) is always difficult in practice with conventional numerical integration. It is then possible to use stochastic approaches that one explores the configuration space randomly and the computation of the integral is estimated in the form of an average value:

$$I_N = \frac{V}{N} \sum_i^N f(\mathbf{x}_i) \quad (2.57)$$

where V is the volume of the integration space and N is the number of points drawn randomly. Within the limit of numbers ($N \rightarrow \infty$), the computation of the integral is exact as follows:

$$I = \lim_{N \rightarrow \infty} I_N \quad (2.58)$$

In addition, according to the central limit theorem, we can obtain a Gaussian distribution of the integral result and the statistical error is independent of the dimension of the problem to be solved.

In practice, a completely random exploration is inefficient if $f(\mathbf{x})$ is located in a specific space region. It is then interesting to constrain the exploration of space by introducing a distribution $\rho(\mathbf{x})$ to preferentially visit the regions where the function has the maximum influence in the integral. The integral can be rewritten as:

$$I = \int_{\Omega} \frac{f(\mathbf{x})}{\rho(\mathbf{x})} \rho(\mathbf{x}) d\mathbf{x} \quad (2.59)$$

then the integral is estimated with the mean value of f/p of the points explored:

$$I_N = \frac{V_p}{N} \sum_i^N \frac{f(\mathbf{x}_i)}{\rho(\mathbf{x}_i)} \quad (2.60)$$

where V_p is the volume of the integration space weighted by the distribution $\rho(\mathbf{x})$. In order to explore the surface as efficiently as possible in calculating the mean value, the best choice for the points distribution is $\rho(\mathbf{x}) = f(\mathbf{x})$.

In physical system, it usually needs to consider the weighting of different possible configurations to calculate the mean values. By definition, the computation of an average value of an observable A is the integral of A over the whole phase space weighted by $\rho(\mathbf{x})$ divided by the volume of this weighted space and is written as follows:

$$\langle A \rangle = \frac{\int A(\mathbf{x}) \rho(\mathbf{x}) d\mathbf{x}}{\int \rho(\mathbf{x}) d\mathbf{x}} \quad (2.61)$$

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Then the problem is to generate a distribution of configurations according to the law $\rho(\mathbf{x})$. The solution used by the Monte Carlo methods is to generate these points using a Markov chain, in other words, a sequential series of configurations where each configuration belongs to the state space and only depends on the previous point. The properties of Markov processes have the following consequences:

$$\sum_{\mathbf{x}_{i+1}} p(\mathbf{x}_i \rightarrow \mathbf{x}_{i+1}) = 1 \quad (2.62)$$

$$\sum_{\mathbf{x}_i} \rho(\mathbf{x}_i) p(\mathbf{x}_i \rightarrow \mathbf{x}_{i+1}) = \rho(\mathbf{x}_{i+1}) \quad (2.63)$$

the transition probability from configuration i to configuration j is $p(\mathbf{x}_i \rightarrow \mathbf{x}_j)$. To ensure the validity of equation 2.63, the condition of microreversibility is sufficient that the movements in one direction are exactly compensated by the reverse movements. This condition is verified by the detailed balance sheet equation:

$$\rho(\mathbf{x}_i) p(\mathbf{x}_i \rightarrow \mathbf{x}_j) = \rho(\mathbf{x}_j) p(\mathbf{x}_j \rightarrow \mathbf{x}_i) \quad (2.64)$$

The transition probability $p(\mathbf{x}_i \rightarrow \mathbf{x}_j)$ can be defined as the product of the probability of attempting a transition $\eta(\mathbf{x}_i \rightarrow \mathbf{x}_j)$ with the probability of accepting this same transition $\sigma(\mathbf{x}_i \rightarrow \mathbf{x}_j)$. In the case of symmetrical movements, $\eta(\mathbf{x}_i \rightarrow \mathbf{x}_j) = \eta(\mathbf{x}_j \rightarrow \mathbf{x}_i)$ and the probability of accepting a relocation must satisfy the condition of the detailed assessment:

$$\frac{\sigma(\mathbf{x}_i \rightarrow \mathbf{x}_{i+1})}{\sigma(\mathbf{x}_{i+1} \rightarrow \mathbf{x}_i)} = \frac{\rho(\mathbf{x}_{i+1})}{\rho(\mathbf{x}_i)} \quad (2.65)$$

In physics related problems, Monte Carlo methods are applied to simulate systems displaying many coupled degrees of freedom, such as fluids, strongly coupled solids, disordered materials, and cellular structures. In statistical physics not related to thermodynamics, Monte Carlo molecular simulation is an alternative to MD simulations. Monte Carlo methods can be used to compute statistical field theories of simple particles and polymer systems.[\[258\]](#) [\[259\]](#) [\[260\]](#) When solving practical problems using a Monte Carlo methods, it includes two main parts. First, random variables with various probability distributions need to be generated to simulate a certain process. Second, statistical methods need to be used to estimate the numerical characteristics of the model to obtain a numerical solutions to the actual problem. Monte Carlo methods make it possible for the sampling of a PES by performing random shifts in order to correctly reproduce the probability distribution of the configurations.

General principles. Monte Carlo calculations that lead to quantitative results may be regarded as attempts to estimate the value of a multiple integral. This is particularly true for the applications in equilibrium statistical thermodynamics, where one hopes to calculate the thermal average $\langle A \rangle_T$ of an observable $A(\mathbf{X})$ as an integral over phase space Ω , where \mathbf{X} is a point in Ω :

$$\langle A \rangle_T = \frac{1}{Z} \int_{\Omega} d\mathbf{X} A(\mathbf{X}) e^{-H(\mathbf{X})/k_B T} \quad (2.66)$$

in which Z is the partition function, and k_B is the Boltzmann constant. T refers to the temperature, and $H(\mathbf{X})$ denotes the Hamiltonian of the system.

5 One example for the calculation procedure of a molecular simulation is as follows:

1. A random molecular configuration is generated using a random number generator.
2. Random changes are made to the particle coordinates of this molecular configuration, resulting in a new molecular configuration.
3. Calculate the energy of the new molecular configuration.
4. Compare the energy change between the new molecular configuration and the former one to determine whether to accept the configuration change or not.
 - If the energy of the new molecular configuration is lower than that of the original one, the new configuration change is accepted, and the new configuration is used for the next iteration.
 - If not, the Boltzmann factor is calculated and a random number is generated. If this random number is greater than the calculated Boltzmann factor, then the new configuration is discarded. If not, the new configuration is conserved and is used for the next iteration.
5. If a new iteration is required, the process is repeated from step 2.

2.4.2 Classical Molecular Dynamics

MD is a powerful tool for analyzing the physical movements of atoms and molecules of many-body systems. MD was originally developed following the earlier successes of Monte Carlo

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simulations. The first work about MD was published in 1957 by B. Alder *et al.* which focused on the integration of classical equations of motion for a system of hard spheres.[261] Before long, radiation damage at low and moderate energies were studied using MD in 1960 and MD was also applied to simulate liquid argon in 1964.[262, 263] MD experienced an extremely rapid development in the years that followed. MD simulations have been applied in chemistry, biochemistry, physics, biophysics, materials science, and branches of engineering, which is often coupled with experimental measurements to facilitate interpretation. MD has a strong predictive potential thus making it possible to motivate the implementation of new experiments. The diversity, broadness, and sophistication level of MD techniques have been continuously reported.[245, 264, 265, 266, 267, 268, 269, 270, 271, 272] The range of applications of MD simulations is extremely wide, for instance, the study of structure,[269, 273, 274, 275] thermodynamic,[276, 277, 278, 279, 280] diffusion,[281, 282, 283, 284] viscosity,[282, 285, 286, 287] and spectroscopies.[288, 289, 290, 291] Moreover, MD simulations are not only limited to the study of homogeneous systems but also allow for the description of phase equilibria, the relaxation of metastable states and the dynamics of processes at interfaces. In addition, MD can also model chemical reactions in complex environments.

As MD simulations allow to model real time evolution of particles, one can then access time-dependent properties. If the time evolution is obtained by **integrating Newton's equations of motion** for a system of interacting particles, it is referred to as **classical MD**. A classical MD simulation needs the definition of a potential describing the interaction between particles in order to calculate the PES. Potentials can be of different levels of accuracy as described in the previous section. The most commonly used potentials in chemistry are **force fields**. In that case, one refers to **molecular mechanics**, which embodies a classical mechanics treatment of the interactions between particles. In classical molecular dynamics, electrons and nuclei are not distinguished and one refers only to particles. As already mentioned, the main drawback of force fields is that they usually can not model chemical reactions. If the potential comes from a quantum chemical treatment of the electrons only, the nuclei being treated as interacting point charge particles, one refers to **ab initio molecular dynamics**. **Quantum dynamics** differs from classical molecular dynamics as the temporal evolution of a system is described by the time-dependent Schrödinger equation. For instance, the MCTDH approach[292, 293] and discrete-variable representations,[294, 295] are particularly accurate but are limited in terms of number of degrees of freedom. The reduction from a full quantum description of all particles, electrons and nuclei, to a classical treatment involves two main approximations. The first one

is the BO approximation as described in section 2.2 which allows to treat separately electrons and nuclei. The second one treats the nuclei (much heavier than electrons) as point charge particles that follow classical Newtonian dynamics. In this thesis, **classical molecular dynamics was used** to perform simulations and use the term MD to denote classical molecular dynamics only.

Principles. In the classical formulation of MD, each particle or nucleus in the system is represented by a material point which interacts with all other particles via a potential defined by their positions. The principle of the dynamics of N atoms is to determine the forces \mathbf{F}_α acting on each of the particles in a given geometry and then calculate the accelerations and the velocities of the particles from these forces using Newton's second law:

$$\mathbf{F}_\alpha = m_\alpha \mathbf{a}_\alpha, \quad \alpha = 1, 2, \dots, N \quad (2.67)$$

where m_α is the mass of the atom α , \mathbf{a}_α being its acceleration and \mathbf{F}_α is the total force exerted on α . \mathbf{F}_α is defined as the derivative of the potential energy V of the system with respect to the corresponding position (\mathbf{R}_α) of α :

$$\mathbf{F}_\alpha = -\frac{\partial V}{\partial \mathbf{R}_\alpha} = m_\alpha \frac{d^2 \mathbf{R}_\alpha}{dt^2} \quad (2.68)$$

where V depends on the positions of all atoms or particles. This leads to a system of $f \times N$ second-order differential equations where f is the dimension of space. In our case, the number of degrees of freedom f is equal to 3. According to the known initial positions of particles, the potential energy can be obtained. Then, a numerical resolution of the partial derivative equations provided in equation 2.68 can be obtained using a suitable **integration algorithm**. The integration algorithm gives access to the positions and velocities of atoms or particles and to the forces acting on these atoms or particles over time. Here, the time is discretized in regular intervals and calculations are repeated at each time interval referred to as **time step**. Many high order integration algorithms have been proposed depending on the desired accuracy: Euler algorithm, [296, 297] Verlet algorithms, predictor-corrector algorithm, [298, 299] and Runge-Kutta algorithm. [300, 301, 302, 303] The Verlet algorithms include the Simple Verlet (SV), [304] the Leapfrog Verlet (LFV), [305] and the Velocity Verlet (VV). [306] The VV

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algorithm is the most widely used in many MD codes owing to its numerical stability and simplicity implementation. Furthermore, movement constants are very well preserved over time. We briefly describe the basis of the VV algorithm below.

The local error is quantified by inserting the exact values $\mathbf{R}_\alpha(t_{n-1})$, $\mathbf{R}_\alpha(t_n)$, and $\mathbf{R}_\alpha(t_{n+1})$ into the iteration and calculating the Taylor expansions at time $t = t_n$ of the position vector $\mathbf{R}_\alpha(t \pm \delta t)$

$$\mathbf{R}_\alpha(t + \delta t) = \mathbf{R}_\alpha(t) + \mathbf{v}_\alpha(t)\delta t + \frac{\mathbf{a}_\alpha(t)\delta t^2}{2} + \frac{\mathbf{b}_\alpha(t)\delta t^3}{6} + O(\delta t^4) \quad (2.69)$$

$$\mathbf{R}_\alpha(t - \delta t) = \mathbf{R}_\alpha(t) - \mathbf{v}_\alpha(t)\delta t + \frac{\mathbf{a}_\alpha(t)\delta t^2}{2} - \frac{\mathbf{b}_\alpha(t)\delta t^3}{6} + O(\delta t^4) \quad (2.70)$$

where $\mathbf{v}_\alpha(t)$ is the velocity of α and $\mathbf{b}_\alpha(t)$ is the derivative of $\mathbf{a}_\alpha(t)$ with respect to the time. Through summing equations [2.69](#) and [2.70](#), we can get the Verlet integrator:

$$\mathbf{R}_\alpha(t + \delta t) = 2\mathbf{R}_\alpha(t) - \mathbf{R}_\alpha(t - \delta t) + \mathbf{a}_\alpha(t)\delta t^2 + O(\delta t^4) \quad (2.71)$$

We can notice that the first-order and third-order terms cancel out from the Taylor expansion, which makes the Verlet integrator more accurate than the integration by a Taylor expansion only.

We can see in equation [2.71](#) that the position propagation equation does not involve the velocities. They can be computed by the following finite difference:

$$\mathbf{v}_\alpha(t) = \frac{\mathbf{R}_\alpha(t + \delta t) - \mathbf{R}_\alpha(t - \delta t)}{2\delta t} + O(\delta t^2) \quad (2.72)$$

This provides velocities at time t and not at time $t + \delta t$, which means the velocity term is a step behind the position term. The use of equation [2.72](#) has the advantage of low data storage, *i.e.* less memory is required, but a problem emerges in the calculation of the kinetic energy at time $t + \delta t$.

The VV algorithm is often applied to solve this problem as it allows velocities and positions to be computed simultaneously:

$$\mathbf{R}_\alpha(t + \delta t) = \mathbf{R}_\alpha(t) + \mathbf{v}_\alpha(t)\delta t + \frac{\mathbf{a}_\alpha(t)\delta t^2}{2} \quad (2.73)$$

$$\mathbf{v}_\alpha(t + \delta t) = \mathbf{v}_\alpha(t) + \frac{\mathbf{a}_\alpha(t) + \mathbf{a}_\alpha(t + \delta t)}{2}\delta t \quad (2.74)$$

The standard implementation of the VV algorithm is a four steps scheme: firstly to calculate the following equation,

$$\mathbf{v}_\alpha(t + \frac{1}{2}\delta t) = \mathbf{v}_\alpha(t) + \frac{1}{2}\mathbf{a}_\alpha(t)\delta t \quad (2.75)$$

Secondly to calculate equation as follows:

$$\mathbf{R}_\alpha(t + \delta t) = \mathbf{R}_\alpha(t) + \mathbf{v}_\alpha(t + \frac{1}{2}\delta t)\delta t \quad (2.76)$$

Thirdly to derive $\mathbf{a}_\alpha(t + \delta t)$ from the interaction potential at $\mathbf{R}_\alpha(t + \delta t)$, finally to compute the following equation.

$$\mathbf{v}_\alpha(t + \delta t) = \mathbf{v}_\alpha(t + \frac{1}{2}\delta t) + \frac{1}{2}\mathbf{a}_\alpha(t + \delta t)\delta t \quad (2.77)$$

Temperature is not a state variable in the simulations, an average kinetic temperature can be calculated from the average value of the kinetic energy.

At the end of each integration step, the VV algorithm gives directly access to $\mathbf{R}_\alpha(t + \delta t)$, $\mathbf{v}_\alpha(t + \delta t)$, and $\mathbf{F}_\alpha(t + \delta t)$. The VV algorithm ensures two intrinsic properties of the classical equations of motion. One is temporal reversibility, the invariance of the trajectories at t and $-t$. This symmetry leads to the independence of the dynamics from the direction of time. The other property is the conservation of the total energy over time. Because of the discretization of trajectories, this conservation can not be insured. A stable integration algorithm must impose this conservation for long enough time steps (δt) to allow for sufficiently long simulation time. The VV algorithm is able to do this due to its sufficient numerical stability. According to the conservation of energy, the natural ensemble corresponding to such dynamics is the microcanonical ensemble (N, V, E) . [307, 308] N is the number of particles. V denotes the volume and E is the energy of the system which is conserved. It is possible to extend the MD to other statistical ensembles by modifying the Hamiltonian of the system. For instance, in the canonical ensemble (N, V, T) , a thermostat is added to the system allowing for the control of the temperature T . [309, 310, 311, 312] The temperature is not a state variable in the simulations, an average kinetic temperature can be calculated from the average value of the kinetic energy.

The force, *i.e.* acceleration, calculation in the MD simulations is an extremely important part as it determines both the accuracy of the potential energy and the computational cost. Different methods were presented in section 2.3 to calculate the forces. **In this thesis, the SCC-DFTB method has been applied to compute the forces in all the MD simulations.**

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2.4.3 Parallel-Tempering Molecular Dynamics

In a number of cases, it is necessary to explore the PES as thoroughly as possible for the study of dynamical, thermodynamical, and structural properties of a given system. For atomic and molecular clusters, PES usually presents a large number of stable configurations linked together by energy barriers. Unfortunately, MD simulations cannot overcome these energy barriers in a reasonable simulation time even within the canonical ensemble (N, V, T) . This leads to non-ergodic simulations that cannot be used to extract meaningful statistical averages. Actually, when a simulation explores the well of a PES, it may often be blocked in this well at low temperature because the energy barriers are too high to be crossed. In this case, if E_b refers to the energy barrier and T is the temperature of the simulation, one can consider that $E_b \gg k_B T$ where k_B is the Boltzmann constant. At intermediate temperature, the possibility of crossing the energy barriers during a simulation increases, but this can not guarantee the PES to be explored exhaustively. For high temperatures, one has a high probability to cross the energy barriers whereas the bottoms of the wells can not be explored comprehensively. Therefore, it is very difficult to both cross the energy barriers and thoroughly explore the bottom of the wells using a unique MD simulation at a given temperature. Many methods have been proposed to solve this question and are referred to as **enhanced sampling methods**. They are classified into two groups: **biased methods** and **non-biased methods**. In **biased methods**, the dynamics of the system is influenced by an external factor, usually a non-physical force, which makes it possible to push the system outside of the wells even at low T .[\[313\]](#) [\[314\]](#) [\[315\]](#) [\[316\]](#) [\[317\]](#) For instance, Metadynamics is a biased method.[\[318\]](#) [\[319\]](#) [\[320\]](#) In **non-biased methods**, the dynamics of the system is not modified directly. Examples are simulated annealing,[\[321\]](#) [\[322\]](#) and multi-replica approaches such as the **parallel-tempering molecular dynamics** approach, which has been used in this thesis.

The replica exchange approach also termed parallel-tempering was originally devised by R. H. Swendsen *et al.* in 1986 [\[323\]](#) then extended by Geyer and coauthor in 1991 [\[324\]](#) and was further developed by Hukushima and Nemoto,[\[325\]](#) M. Falcioni and M. W. Deem,[\[326\]](#) D. J. Earl and coworker,[\[327\]](#) Y. Sugita and Y. Okamoto formulated a MD version of parallel tempering to enhance conformational sampling.[\[328\]](#) PTMD is a method which aims at enhancing the ergodicity of MD simulations. The principle of PTMD is shown in Figure [2.4](#).

N replicas $(C_i, i = 1, 2, \dots, N)$ of the same system are simulated in parallel each one at a given temperature T_i , ($i = 1, 2, \dots, N$) in the canonical ensemble. The time evolution of each

optimizations is a good choice to search for low-energy structures in this kind of system. Local optimizations are performed many times from initial conditions structures which are extracted from all PTMD trajectories, whether it be low or high temperature, in order to maximize sampling. **This approach, in combination with SCC-DFTB, has been conducted along this thesis to perform global optimization.**

3

Investigation of Structural and Energetic Properties

This **third chapter** of my thesis merges two independent studies dealing with the determination of the low-energy isomers of ammonium/ammonia water clusters, $(\text{H}_2\text{O})_n\text{NH}_4^+$ and $(\text{H}_2\text{O})_n\text{NH}_3$, and protonated uracil water clusters, $(\text{H}_2\text{O})_n\text{UH}^+$. As highlighted in the general introduction of this thesis and in chapter [2](#), performing global optimization of molecular clusters is not straightforward. The two studies presented in this chapter thus share a main common methodology which is the combination of the **SCC-DFTB** method for the efficient calculation of the PES and the **PTMD** approach for their exploration. All low-energy isomers reported in this chapter are discussed in terms of structure, relative energy and binding energy which are compared to the literature when available. Calculations at higher level of theory are also performed to refine the results obtained at the SCC-DFTB level or to validate the results it provides. In particular, in this chapter, an improved set of parameters is proposed to describe sp^3 nitrogen containing compounds at the SCC-DFTB level. Our results are also used to complement collision-induced dissociation experiments performed by S. Zamith and J.-M. L'Hermite at the *Laboratoire Collisions Agrégats Réactivité* (LCAR).

3.1 Computational Details

3.1.1 SCC-DFTB Potential

SCC-DFTB electronic structure calculations presented in this chapter were all performed with the deMonNano code.[\[333\]](#) The details of the method are presented in section [2.3.3](#) of chap-

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ter [2]. The mio-set for the Slater-Koster tables of integrals was used. [168] However, it has been shown that these integrals do not properly describe sp^3 hybridized nitrogen, in particular, proton affinity. [334] Consequently, in order to avoid spurious deprotonation of the sp^3 hybridized nitrogen in NH_4^+ and to correctly reproduce binding energies calculated at the MP2/Def2TZVP level, I propose to modify the original mio-set for Slater-Koster tables of N-H integrals by applying them a multiplying factor. Several of them were tested and I present here the results obtained for two of them: 1.16 and 1.28. For the sp^2 nitrogen of uracil, the original integrals of the mio-set were used. To improve description of the intermolecular interactions, the original Mulliken charges were replaced by the CM3 charges, [230, 233, 335] (see equation 2.49 in section 2.3.3) and an empirical correction term (see equation 2.51 in section 2.3.3) was used to describe dispersion interactions. [233, 239, 336] A. Simon *et al.* developed a SCC-DFTB potential that leads to geometries, frequencies, and relative energies close to the corresponding experimental and CCSD(T)/aug-cc-pVTZ results. [337, 338] The corresponding D_{OH} parameter, *i.e.* 0.129, is retained in the studies presented in this chapter. D_{NH} is tested in the study of ammonium/ammonia water clusters and two values were retained and thoroughly tested: 0.12 and 0.14. D_{NO} is set to zero.

3.1.2 SCC-DFTB Exploration of PES

To determine the lowest-energy isomers of $(H_2O)_{1-10,20}NH_4^+$, $(H_2O)_{1-10}NH_3$ and $(H_2O)_{1-7,11,12}UH^+$ clusters, their PES were thoroughly explored using PTMD [327, 328, 339] simulations combined with a SCC-DFTB [168] description of the energies and gradients. I describe below the **detailed parameters used for all the simulations conducted within this chapter.**

Detailed parameters for PTMD simulations of $(H_2O)_{1-10,20}NH_4^+$ and $(H_2O)_{1-10}NH_3$ clusters are as follows. For $(H_2O)_{1-3}NH_4^+$ and $(H_2O)_{1-3}NH_3$ clusters, 16 replicas were used with a linear distribution of temperatures with a 15 K step ranging from 10 to 250 K. 40 replicas with a 6 K step ranging from 10 to 250 K were considered for $(H_2O)_{4-10,20}NH_4^+$ and $(H_2O)_{4-10}NH_3$ species. All trajectories were 5 ns long and a time step of 0.5 fs was used to integrate the equations of motion. A Nosé-Hoover chain of 5 thermostats was employed for all the simulations to achieve simulations in the canonical ensemble. [310, 311] Thermostat frequencies were fixed at 400 cm^{-1} . To identify low-energy isomers of $(H_2O)_{1-3}NH_4^+$ and $(H_2O)_{1-3}NH_3$ clusters, 303 geometries were periodically selected from each replica and further optimized at the SCC-DFTB level, which produced 4848 optimized geometries per cluster.

3.2 Structural and Energetic Properties of Ammonium/Ammonia including Water Clusters

in ascending energy order, *i.e.* a designates the lowest-energy isomer. For comparison, “ $n-x$ ” and “ $n'-x$ ” isomers are also optimized at the MP2/Def2TZVP level. In that case, the resulting structures are referred to as “ $n-x^*$ ” and “ $n'-x^*$ ” to distinguish them more easily although they display the same general topology as “ $n-x$ ” and “ $n'-x$ ” isomers.

3.2 Structural and Energetic Properties of Ammonium/Ammonia including Water Clusters

3.2.1 General Introduction

Water clusters play an important role in various areas such as atmospheric and astrochemical science, chemistry and biology.[\[118\]](#), [\[347\]](#), [\[348\]](#), [\[349\]](#), [\[350\]](#), [\[351\]](#), [\[352\]](#), [\[353\]](#), [\[354\]](#), [\[355\]](#), [\[356\]](#), [\[357\]](#), [\[358\]](#), [\[359\]](#) They are involved into the critical stages of nucleation and growth of water-containing droplets in the atmosphere thus contributing to the physical and chemical properties of this medium.[\[360\]](#) In many cases, the presence of chemical impurities interacting with water aggregates strongly affect their properties. For instance, ammonia is an important compound commonly found in the atmosphere and which displays a key role in aerosol chemistry.[\[361\]](#) Its high basicity makes it a potential proton sink that can form a ionic center for nucleation.[\[362\]](#), [\[363\]](#) E. Dunne and co-workers also reported that most nucleation occurring in the atmosphere involves ammonia or biogenic organic compounds, in addition to sulfuric acid.[\[113\]](#) J. Kirkby *et al.* also found that even a small amount of atmospherically relevant ammonia can increase the nucleation rate of sulphuric acid particles by several orders of magnitude.[\[112\]](#) The significance of ammonium and ammonia water clusters have thus motivated a large amount of experimental and theoretical studies during the past decades.[\[340\]](#), [\[362\]](#), [\[364\]](#), [\[365\]](#), [\[366\]](#), [\[367\]](#), [\[368\]](#), [\[369\]](#), [\[370\]](#), [\[371\]](#), [\[372\]](#), [\[373\]](#), [\[374\]](#)

As a few examples, in 1984, $(\text{H}_2\text{O})_2\text{NH}_4^+$ was identified using mass spectrometry by M. D. Perkin *et al.*[\[362\]](#) In 1997, Stenhagen and co-workers studied the $(\text{H}_2\text{O})_{20}\text{H}_3\text{O}^+$ and $(\text{H}_2\text{O})_{20}\text{NH}_4^+$ clusters and found that both species display similar structures.[\[366\]](#) P. Hvelplund *et al.* later reported a combined experimental and theoretical study devoted to protonated mixed ammonia/water which highlighted the idea that small protonated mixed clusters of water and ammonia contain a central NH_4^+ core.[\[370\]](#) Theoretical calculations devoted to ammonium and ammonia water clusters have also been extensively conducted.[\[368\]](#), [\[369\]](#), [\[370\]](#), [\[373\]](#), [\[374\]](#), [\[375\]](#), [\[376\]](#), [\[377\]](#), [\[378\]](#) Among them, J. Novoa *et al.* studied the $(\text{H}_2\text{O})_4\text{NH}_3$ aggregate and found the existence of a minimum in its potential energy surface corresponding to

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a $(\text{H}_2\text{O})_3\cdots\text{NH}_4^+\cdots\text{OH}^-$ structure, resulting from one proton transfer from a water molecule to the ammonia molecule.^[375] D. Babelo later reported a number of low-energy minima for $(\text{H}_2\text{O})_{3-4}\text{NH}_3$ clusters obtained from *ab initio* calculation and a Monte Carlo exploration of the PES.^[373] More recently, J. Douady *et al.* performed a global optimization of $(\text{H}_2\text{O})_n\text{NH}_4^+$ ($n = 1-24$) clusters again using a Monte Carlo procedure in combination with a Kozack and Jordan empirical force field.^[371, 379] In this study, the finite temperature properties as well as vibrational signature of several clusters thus highlighting the key contribution of simulations in understanding such species. Morrell and Shields also studied the $(\text{H}_2\text{O})_n\text{NH}_4^+$ ($n = 1-10$) aggregates *via* a mixed molecular dynamics and quantum mechanics methodology to calculate energies and free energies of formations which were in good agreement with previous experimental and theoretical results.^[372] More recently, S. Pei *et al.* determined that $(\text{H}_2\text{O})_n\text{NH}_4^+$ clusters start to adopt a closed-cage geometry at $n=8$.^[380] Finally, W. Walters and collaborators determined the geometry of $(\text{H}_2\text{O})_{16}\text{NH}_3$ and $(\text{H}_2\text{O})_{16}\text{NH}_4^+$ at the HF/6-31G(d) level, and observed strong hydrogen bonding between water and the lone pair of NH_3 and between NH_4^+ and the four adjacent water molecules.^[381]

As for the study of other molecular clusters, the range of applicability of theoretical simulations to describe ammonium and ammonia water clusters is dictated by the balance between accuracy, transferability and computational efficiency. While *ab-initio* methods can accurately model small aggregates, their application to large species is more difficult, in particular when an exhaustive exploration of the PES is required. In contrast, force-field potentials are computationally extremely efficient and can be coupled to global optimization methods but their transferability is limited. The SCC-DFTB approach can be seen as an intermediate approach which combines the strengths of both *ab-initio* and force-field methods. Indeed, it can be as accurate as DFT while computationally more efficient and is more transferable than force fields (see chapter 2). In recent years, SCC-DFTB has been successfully applied to the study of various molecular clusters: pure, protonated, and de-protonated water clusters,^[62, 382, 383, 384] water clusters on PAHs,^[337, 385] sulfate-containing water clusters,^[103] water clusters in an argon matrix,^[130] whether it is for global optimization or for the study of finite-temperature properties. However, in its original formulation, SCC-DFTB does not provide good results for the description of ammonia and ammonium as nitrogen hybridization seems to be a problem for minimal basis-set methods like SCC-DFTB.^[386] M. Elstner and coworkers found consistent errors (about $14.0 \text{ kcal.mol}^{-1}$) for deprotonation energies of sp^3 hybridized nitrogen containing systems, whereas sp^1 and sp^2 systems display much smaller errors.^[334]

3.2 Structural and Energetic Properties of Ammonium/Ammonia including Water Clusters

Table 3.1: Relative binding energies ΔE_{bind}^{whole} and $\Delta E_{bind}^{sep.}$ of the low-energy isomers of $(H_2O)_{1-3}NH_4^+$ and $(H_2O)_{1-3}NH_3$ clusters. Values are given in $kcal.mol^{-1}$.

$(H_2O)_nNH_4^+$	ΔE_{bind}^{whole}	$\Delta E_{bind}^{sep.}$	$(H_2O)_nNH_3$	ΔE_{bind}^{whole}	$\Delta E_{bind}^{sep.}$
1-a	1.21	1.21	1'-a	-1.17	-1.17
2-a	0.82	0.91	2'-a	0.57	0.28
3-a	-0.25	0.11	3'-a	0.91	0.01
3-b	1.21	-0.15	-	-	-

3.2.2.3 Properties of $(H_2O)_{4-10}NH_4^+$ Clusters

Cluster $(H_2O)_4NH_4^+$. The five lowest-energy isomers of $(H_2O)_4NH_4^+$ are depicted in Figure 3.8. 4-a is the lowest-energy isomer obtained from the global SCC-DFTB optimization and also the lowest-energy configuration after optimization at MP2/Def2TZVP level with ZPVE corrections. This result is consistent with previous computational studies [367, 369, 371, 387, 388] and the experimental studies by H. Chang and co-workers. [367, 368] Isomer 4-a displays four hydrogen bonds around the ionic center which lead to no dangling N-H bonds. Other isomers of comparable stability are displayed in Figure 3.8. The energy ordering of 4-a to 4-e at SCC-DFTB level is consistent with that at MP2/Def2TZVP level with ZPVE correction, although they are slightly higher by $\sim 2.0 kcal.mol^{-1}$. Isomer 4-c was not reported in H. Chang's study, [369] and the corresponding energy ordering of the five lowest-energy isomers was the same as ours which certainly results from the use of a different basis set.

The relative binding energy of SCC-DFTB method to MP2/Def2TZVP method with BSSE correction for isomers 4-a to 4-e are listed in Table 3.2. When the four water molecules are considered as a whole part to calculate the binding energy, the relative binding energy of isomers 4-a to 4-e are -1.67, 0.00, 0.77, 0.77 and -4.04 $kcal.mol^{-1}$. As shown in Table 3.2, for isomers 4-a to 4-e, when the four water molecules are separately considered using the geometry in the cluster to calculate the binding energy, the biggest absolute value of the relative binding energy is 0.87 $kcal.mol^{-1}$. This shows the results of SCC-DFTB are in good agreement with those of MP2/Def2TZVP with BSSE correction for $(H_2O)_4NH_4^+$. From the relative binding energy of $(H_2O)_4NH_4^+$, it indicates that all the water molecules considered as a whole part or separately has an effect on the relative binding energy for the cluster $(H_2O)_4NH_4^+$ and the overall ΔE_{bind}^{whole} are bigger than $\Delta E_{bind}^{sep.}$.

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Table 3.2: Relative binding energies $\Delta E_{bind.}^{whole}$ and $\Delta E_{bind.}^{sep.}$ of the five lowest-energy isomers of $(H_2O)_{4-10}NH_4^+$ and $(H_2O)_{4-10}NH_3$. Binding energies are given in kcal·mol⁻¹.

$(H_2O)_nNH_4^+$	$\Delta E_{bind.}^{whole}$	$\Delta E_{bind.}^{sep.}$	$(H_2O)_nNH_3$	$\Delta E_{bind.}^{whole}$	$\Delta E_{bind.}^{sep.}$
4-a	-1.67	-0.87	4'-a	-1.11	-1.76
4-b	0.00	0.61	4'-b	-0.29	-1.62
4-c	0.77	0.44	4'-c	-0.29	-1.38
4-d	0.77	0.42	4'-d	1.08	-0.49
4-e	-4.04	0.69	4'-e	1.02	-1.07
5-a	-1.62	0.56	5'-a	0.82	-1.78
5-b	0.72	0.48	5'-b	-0.23	-2.26
5-c	0.69	0.55	5'-c	-0.34	-2.50
5-d	-1.08	-0.78	5'-d	-0.59	-1.84
5-e	-2.08	0.88	5'-e	-0.38	-2.60
6-a	-1.71	-0.38	6'-a	-0.27	-3.05
6-b	-1.14	-0.76	6'-b	-0.31	-3.55
6-c	-2.06	0.27	6'-c	-1.11	-4.67
6-d	-2.90	-1.06	6'-d	-0.05	-4.44
6-e	-1.18	-0.60	6'-e	0.55	-1.96
7-a	-2.95	-0.39	7'-a	1.09	-2.02
7-b	-2.92	-0.38	7'-b	-0.02	-4.07
7-c	-2.17	0.09	7'-c	-0.40	-4.15
7-d	-1.28	-1.35	7'-d	-0.14	-3.10
7-e	-3.22	-2.27	7'-e	-1.11	-4.32
8-a	-2.20	-1.63	8'-a	-1.12	-4.41
8-b	-1.61	-2.01	8'-b	-0.10	-3.04
8-c	-3.71	-1.17	8'-c	-0.41	-4.46
8-d	-2.43	-0.36	8'-d	0.20	-3.68
8-e	-0.55	0.35	8'-e	-1.28	-4.75
9-a	-2.02	-1.39	9'-a	-0.15	-4.47
9-b	0.51	-0.84	9'-b	-1.01	-4.45
9-c	-3.31	-0.85	9'-c	-1.04	-4.42
9-d	-1.58	-1.78	9'-d	-1.09	-5.14
9-e	-2.39	-0.91	9'-e	0.41	-2.57
10-a	-2.64	-1.94	10'-a	-0.03	-4.80
10-b	-5.79	-4.35	10'-b	0.13	-5.61
10-c	-1.26	-2.36	10'-c	-0.62	-6.50
10-d	-1.98	-1.42	10'-d	-1.10	-6.30
10-e	-7.17	-1.54	10'-e	0.23	-8.36

3.2 Structural and Energetic Properties of Ammonium/Ammonia including Water Clusters

9-b is the first low-energy isomer at MP2/Def2TZVP with ZPVE correction level in our calculation and it is also the first low-energy isomer at B3LYP/6-31++G(d,p) level in F. Spiegelman's study.[371] 9-c, 9-d and 9-e have a complete solvation shell. All the water molecules are connected together in the structure of 9-c. The structures of 9-a and 9-e are very similar and their energy difference is only 0.11 kcal·mol⁻¹ at MP2/Def2TZVP with ZPVE correction level. The energy difference of isomers 9-a to 9-e is less than 0.51 kcal·mol⁻¹ at SCC-DFTB and less than 0.86 kcal·mol⁻¹ at MP2/Def2TZVP with ZPVE correction, so it's easy for them to transform to each other making it possible for the variation of the energy order. The results certificate the SCC-DFTB is good enough to find the low-energy isomers for cluster (H₂O)₉NH₄⁺.

As shown in Table 3.2, for isomers 9-a to 9-e, the relative binding energy ΔE_{bind}^{whole} are -2.20, -1.61, -3.71, -2.43 and -0.55 kcal·mol⁻¹ and the relative binding energy $\Delta E_{bind}^{sep.}$ are -1.39, -0.84, -0.85, -1.78, and -0.91 kcal·mol⁻¹, respectively. It is obvious that the absolute values of ΔE_{bind}^{whole} are bigger than the corresponding $\Delta E_{bind}^{sep.}$. It shows the binding energies at SCC-DFTB level agree well with those at MP2/Def2TZVP with BSSE correction level when water molecules are calculated separately. According to the results, when all the water molecules are considered as a whole part, the results of SCC-DFTB didn't agree well with those of the MP2 with BSSE correction method.

Cluster (H₂O)₁₀NH₄⁺. For cluster (H₂O)₁₀NH₄⁺, 10-a to 10-e are the five low-energy isomers in which the ion core NH₄⁺ has a complete solvation shell shown in Figure 3.9. 10-a with eight three-coordinated H₂O molecules in its big cage structure is the first low-energy isomer calculated using the SCC-DFTB approach. 10-a is also the first low-energy structure at B3LYP/6-31++G(d,p) level including the harmonic ZPVE contribution in F. Spiegelman's study.[371] In 10-b and 10-e, there is a four-coordinated H₂O molecule in their cage structures. 10-d is the first low-energy structure in our calculation results using MP2/Def2TZVP with ZPVE correction, which is also the first low-energy isomer at B3LYP/6-31++G(d,p) level in F. Spiegelman's study.[371] The energy of 10-b is only 0.17 kcal·mol⁻¹ higher than that of 10-a at SCC-DFTB level, and it is only 0.31 kcal·mol⁻¹ lower than that of 10-a at MP2/Def2TZVP with ZPVE correction level. The energy of isomers 10-a to 10-e are very close at both SCC-DFTB and MP2/Def2TZVP levels, which indicates the results with SCC-DFTB agree well with those using MP2/Def2TZVP method for cluster (H₂O)₁₀NH₄⁺.

As shown in Table 3.2, for isomers 10-a to 10-e, the relative binding energies ΔE_{bind}^{whole} and $\Delta E_{bind}^{sep.}$ are not as small as the corresponding ones of clusters (H₂O)₁₋₉NH₄⁺, which implies the error of the relative binding energy increases with the number of water molecules in the

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cluster. The whole results of ΔE_{bind}^{whole} are still bigger than those of $\Delta E_{bind}^{sep.}$ for isomers 10-a to 10-e.

3.2.2.4 Properties of $(\text{H}_2\text{O})_{4-10}\text{NH}_3$ Clusters

Cluster $(\text{H}_2\text{O})_4\text{NH}_3$. For cluster $(\text{H}_2\text{O})_4\text{NH}_3$, the five low-energy structures 4'-a to 4'-e are displayed in Figure 3.10. 4'-a with three N-H bonds exposed is the first low-energy isomer at SCC-DFTB level. 4'-b with two N-H bonds exposed is the second low-energy isomer at SCC-DFTB level but it is the first low-energy isomer at MP2/Def2TZVP with ZPVE correction level. The energy differences between 4'-a to 4'-b are only 0.07 and 0.2 kcal·mol⁻¹ at MP2/Def2TZVP with ZPVE correction level and SCC-DFTB level, respectively. The energy difference of isomers 4'-a to 4'-e is less than 0.75 kcal·mol⁻¹ at MP2/Def2TZVP with ZPVE correction, so it's possible for the variation of the energy order when different methods or basis sets are used. 4'-d with a nearly planar pentagonal structure with nitrogen atom and the four oxygen atoms at the apexes is the first low-energy isomer at MP2/6-31+G(d,p) studied by J. Novoa et al [375]. 4'-d is also the first low-energy isomer in D. Bacelo's study using QCISD(T) for a single-point energy calculation based on the MP2/6-311++G(d,p) results. [373]. In addition, 4'-a to 4'-e are also the five low-energy isomers in D. Bacelo's study even the energy order is different. [373]. The results show the SCC- DFTB is good enough to find the low-energy isomers isomers for cluster $(\text{H}_2\text{O})_4\text{NH}_3$.

The relative binding energies of isomers 4'-a to 4'-e are shown in Table 3.2. Except 4'-d, the values of ΔE_{bind}^{whole} for 4'-a to 4'-e are smaller than the corresponding values of $\Delta E_{bind}^{sep.}$. The $\Delta E_{bind}^{sep.}$ of 4'-d is smaller than those of other isomers. 4'-d has a nearly planar pentagonal structure that only contains three O-H...O hydrogen bonds among the four water molecules while other isomers contain four O-H...O hydrogen bonds among the four water molecules. So the intermolecular interaction of the four water molecules in 4'-d is not as strong as it is in other isomers, this may explain the $\Delta E_{bind}^{sep.}$ of 4'-d is smaller than those of other isomers. In general, both relative binding energies $\Delta E_{bind}^{sep.}$ and ΔE_{bind}^{whole} are not big that indicates SCC-DFTB performs well compared to the MP2 method with BSSE correction for calculating the binding energy of cluster $(\text{H}_2\text{O})_4\text{NH}_3$.

Cluster $(\text{H}_2\text{O})_5\text{NH}_3$. For cluster $(\text{H}_2\text{O})_5\text{NH}_3$, 5'-a to 5'-e are the five low-energy isomers shown in Figure 3.10. 5'-a with four three-coordinated water molecules is the first low-energy structure at both MP2/Def2TZVP with ZPVE correction and SCC-DFTB levels. 5'-b and 5'-c

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into their behavior in aqueous medium, especially the effects on their structure, stability and dynamics.

The nucleobases in DNA and RNA play a significant role in the encoding and expression of genetic information in living systems while water is a natural medium of many reactions in living organisms. The study of the interaction between nucleobase molecules and aqueous environment has attracted a lot of interests among biologists and chemists. Exploring the clusters composed of nucleobase molecules with water is a good workbench to observe how the properties of nucleobase molecules change when going from isolated gas-phase to hydrated species.

The radiation can cause damages on RNA and DNA molecules, which is proficiently applied in radiotherapy for cancer treatment. The major drawback in radiotherapy is the unselective damage in both healthy and tumor cells, which has a big side effect. This makes it particularly important to explore the radiation fragments. Uracil, $C_4H_4N_2O_2$, is one of the four nucleobases of RNA, has been paid attention concerning radiation damage. Protonated uracil UH^+ can be generated by radiation damages.^[396] The reasons for such degradation can be due to the interaction with slow electrons, as shown by the work of B. Boudaiffa *et al.*^[397] Several studies have been devoted to the effect of hydration on the electron affinity of DNA nucleobases.^[398, 399, 400] For instance, A. Rasmussen *et al.* found that a water molecule is more likely to interact with a charged species than with a neutral one though the study of hydration effects on the lowest triplet states of cytosine, uracil, and thymine by including one or two water molecules explicitly,^[401] However, a lot of work is still needed to be performed to understand the role of aqueous environment on charged nucleobases of DNA and RNA.

Collision experiments is a useful tool that can be applied to understand the reactivity of molecules and provide access to structural information.^[141] Fragmentation of the bare protonated U has already been performed under collision-induced dissociation (CID) with tandem mass spectrometry,^[142, 402, 403] however, there are only few studies available concerning the effect of hydration on such process. Infrared photodissociation spectroscopy of singly hydrated protonated uracil shows that the most stable tautomeric form of the neutral uracil (diketo) differs from the most stable one for bare protonated uracil (keto-enol).^[404] However, fragmentation studies of such species under CID conditions have not been performed. **S. Zamith and J.-M. L'Hermite conducted such CID experiments on protonated uracil water species $(H_2O)_{1-15}UH^+$ during my thesis and I collaborated with them in order to provide a theoretical support to their measurements.**

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Theoretical studies have already been devoted to mixed uracil-water clusters and intended to describe the lowest energy structures. However, only neutral species $((\text{H}_2\text{O})_n\text{U})$ were considered. [405, 406, 407, 408, 409, 410] Those studies showed that for sizes up to with $n = 3$, the water molecules arrange in monomers or dimers in the plane of the uracil molecule [406, 407, 408, 409, 410] with no trimer formation. But for $n > 3$, very different structures were predicted depending on the considered study. For instance, M. Ghomi predicted that for $n = 7$, [408] water molecules arrange in dimers and trimers in the plane of the uracil molecule, whereas for $n = 11$, water molecules form locked chains. [405] 3D configurations were also proposed. For instance, all water molecules lie above the uracil plane for $n = 4, 5$ reported by F. Calvo *et al.* [410] Similarly, for $n = 11$, V. Danilov *et al.* also obtained a structure that consists of a water cluster above the uracil molecule. [409] Such structures are predicted to start with 4 water molecules reported by F. Calvo and collaborator [410] or with 6 water molecules (though 5 have not been calculated) reported by S. Gadre *et al.* [406] Those studies may suggest that for few water molecules (up to two), the proton should be located on the uracil molecule, whereas when a large number of water molecules surround the uracil, the charge is expected to be located on the water molecules. Of course, the excess proton is expected to strongly influence the structure of the lowest energy isomers of each species, as observed for pure water clusters, so the size at which the proton is transferred from uracil to water cannot be deduced from the aforementioned studies. Moreover, all those theoretical studies do not lead to the same low-energy structures as highlighted by V. Danilov and F. Calvo. [409, 410] Consequently, although it is instructive from a qualitative point of view, the analysis of the experimental data by S. Zamith and J.-M. L'Hermite cannot be based on those studies. I have therefore undertaken a theoretical simulation of hydrated protonated uracil clusters $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ to determine their lowest-energy structures to complete the experiments by S. Zamith and J.-M. L'Hermite at the *Laboratoire Collisions Agrégats Réactivité* (LCAR). This work has been published in 2019 in the *The Journal of Chemical Physics*. [104]

3.3.2 Results and Discussion

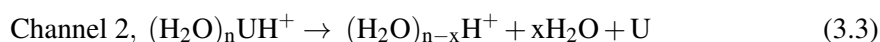
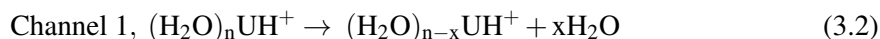
In the following section, section 3.3.2.1, I present in details the results obtained from the CID experiments of S. Zamith and J.-M. L'Hermite and the main concepts used to interpret the data. The following section, section 3.3.2.2, is devoted to the theoretical determination of the low-energy isomers of the $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ clusters. A more detailed presentation of CID

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experiments is also provided in section 4.1 of chapter 4, where these details are important to explicitly model CID experiments.

3.3.2.1 Experimental Results

Time-of-flight of mass spectrum. A typical fragmentation mass spectrum obtained by colliding $(\text{H}_2\text{O})_7\text{UH}^+$ with neon at a center of mass collision energy of 7.2 eV is shown in Figure 3.14. The more intense peak on the right comes from the parent cluster $(\text{H}_2\text{O})_7\text{UH}^+$, the next 7 peaks at the left of the parent peak correspond to the loss of 1-7 water molecules of parent cluster, and the next 5 peaks to the left results from the evaporation of the uracil molecule and several water molecules from parent cluster. This mass spectrum is obtained at the highest pressure explored in the present experiments. This is still true for the largest size investigated here, namely, $(\text{H}_2\text{O})_{15}\text{UH}^+$. From the result of the fragmentation mass spectrum displayed in Figure 3.14, it indicates multiple collisions are possible, which allows the evaporation of all water molecules. Moreover, the intensity of evaporation of water molecules is bigger than the one of evaporation of U. In the study, mainly focus on two specific channels. Channel 1 corresponds to the loss of only neutral water molecules, whereas channel 2 corresponds to the loss of neutral uracil and one or several water molecules,



Fragmentation cross section. The total fragmentation cross sections of clusters $(\text{H}_2\text{O})_{n-1}\text{UH}^+$, pure water clusters $(\text{H}_2\text{O})_{2-6}\text{H}^+$, [411] and deuterated water clusters $(\text{D}_2\text{O})_{5,10}\text{H}^+$ [412] are plotted in Figure 3.15 as a function of the cluster size n. Here n stands for the total number of molecules when the cluster includes uracil molecule. Different target atoms and molecules were used in these experiments: Water molecules or neon atoms in our experiments, xenon atoms in Dalleska's experiments. These experimental data are compared to the geometrical (*i.e.*, hard sphere) cross sections given by:

$$\sigma_{geo} = \pi \left([n_w \times r_w^3 + n_U r_U^3]^{1/3} + r_T \right)^2 \quad (3.4)$$

where n_w is the number of water molecules, and n_U is the number of uracil molecules ($n_U = 0$ or 1 in the present study). r_w , r_U , and r_T refer to the molecular radii of water, uracil, and

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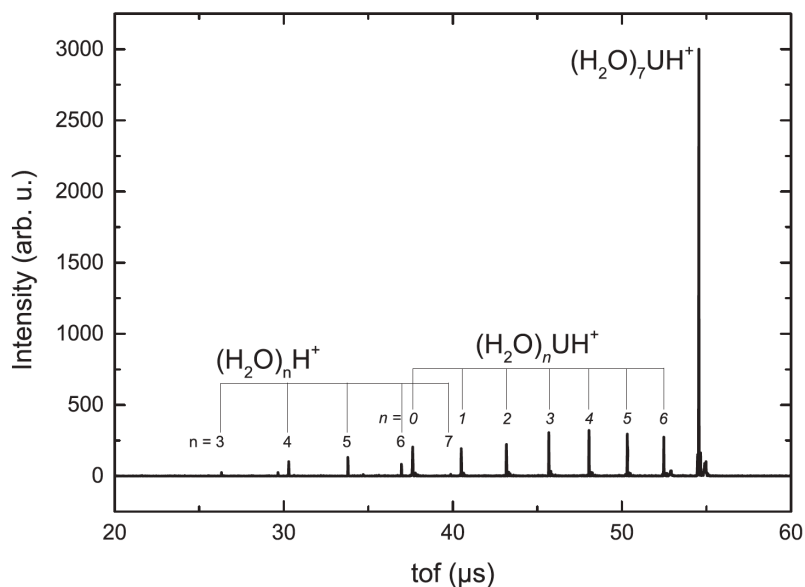


Figure 3.14: Time-of-flight mass spectrum obtained by colliding $(\text{H}_2\text{O})_7\text{UH}^+$ with Ne at 7.2 eV center of mass collision energy (93.5 eV in the laboratory frame).

the target atom or molecule, respectively. The molecular radii are deduced from macroscopic densities that gives $r_U = 3.2 \text{ \AA}$ [413] and $r_w = 1.98 \text{ \AA}$. The radii of rare gas target atoms are taken as their Van der Waals radii $r_{\text{Ne}} = 1.54 \text{ \AA}$ and $r_{\text{Xe}} = 2.16 \text{ \AA}$.

The main differences between the curves in Figure 3.15 can be rationalized as follows: The larger the size of the target atom (or molecule) is, the bigger the fragmentation cross section will be. The experimental fragmentation cross sections of clusters $(\text{H}_2\text{O})_{n-1}\text{H}^+$ colliding with water molecules are larger than the values obtained for collisions with Ne atoms. In the same vein, for a given number of molecules in the cluster, the cross section is larger for clusters containing uracil. The overall trend of all curves in Figure 3.15 is the same: The fragmentation cross sections increase with the size and seem to tend toward the geometrical one. The cross sections measured for clusters containing uracil colliding with water molecules (black squares) are of the same magnitude as the ones previously obtained for deuterated pure water clusters (green full circles) at a similar collision energy. [412] For clusters containing uracil, fragmentation cross sections are systematically larger than the one for pure water clusters by an amount of the same magnitude as the one predicted by the geometrical cross sections. For instance, the difference between red squares and blue stars, and the difference between red full line and blue dashed line has the same magnitude.

4

Dynamical Simulation of Collision-Induced Dissociation

This **fourth chapter of this thesis** merges two independent studies relating to the dynamical simulation of the collision-induced dissociation of $(\text{H}_2\text{O})_n\text{UH}^+$ clusters and pyrene dimer cation Py_2^+ . The two studies in this chapter share the same methodology to generate the collision trajectories for the collision of argon with $(\text{H}_2\text{O})_n\text{UH}^+$ and Py_2^+ . The collision process of the two studies involves dynamical simulations carried out at a QM/MM level where argon is treated as a polarisable MM particle and the lowest-energy targets $(\text{H}_2\text{O})_n\text{UH}^+$ and Py_2^+ are treated as SCC-DFTB level. The dynamical simulations performed in these two studies allow to visualise the collision trajectories from which it is possible to analyse in details a number of properties. The theoretical results are compared with the CID experimental results conducted on the same systems, *i.e.* $(\text{H}_2\text{O})_n\text{UH}^+$ and Py_2^+ , by S. Zamith and J.-M. l'Hermite, which facilitates their interpretation and complete the CID experiments.

4.1 Experimental Methods

The stability of cluster can be investigated from dissociation experiments. Clusters can be dissociated in electric field, magnetic field, high pressure environment, or by heating (such as absorption of photons) or colliding with energetic particles and so on. For instance, the sodium cluster ions and lithium cluster cation were dissociated with a pulsed UV laser source.[\[419\]](#) [\[420\]](#) Gaseous hydrated trivalent metal ions were dissociated using blackbody infrared radiative dissociation (BIRD).[\[421\]](#) [\[422\]](#) The collision between cluster and high or low energetic par-

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ticles at different pressure also have been investigated. Collisions between the high energetic projectile ions (such as 3 keV Ar⁺, 22.5 keV He²⁺) and neutral targets were investigated by M. Gatchell and A. Holm, [129, 134, 423]. Collisions between clusters and projectile have been also explored at low collision energy, which allows for the derivation of dissociation energies and the thermal evaporation and stability of clusters. [135, 424, 425]

By colliding a molecule, or a molecular aggregate, with a non-reactive rare gas atom (neon, argon) or a small molecule such as H₂O or N₂, it is possible to monitor the parent ions and collision products by use, for instance, of tandem mass spectrometry (MS/MS). [426, 427] The resulting mass spectra provide a wealth of information about the structure of the parent and product ions from which one can infer, for instance, dissociation mechanisms [142, 143] or bond and hydration enthalpies [144].

The overall process of collisional activation followed by dissociation/fragmentation is commonly referred to as the collision-induced dissociation (CID) that is also named collisionally activated dissociation (CAD). CID is a mass spectrometry technique to induce dissociation/fragmentation of selected ions in the gas phase, which is one of standard methods for the determination of dissociation/fragmentation pathways. [425, 428] The CID technique consists of accelerating a given ion into a collision gas thereby the ion getting energy and inducing fragmentation. The produced ionic fragments are then mass analyzed, yielding essentially a mass spectrum. [429] The CID technique has been applied in different context. Higher-energy C-trap dissociation is a CID technique specific to the orbitrap mass spectrometer in which dissociation/fragmentation occurs outside the trap [430, 431]. Sustained off-resonance irradiation collision-induced dissociation (SORI-CID) is a CID technique used in Fourier transform ion cyclotron resonance mass spectrometry which involves accelerating the ions in cyclotron motion, in a circle inside of an ion trap, in the presence of a collision gas. [432, 433]

CID and the dissociated/fragmented ions produced by CID are used for several purposes: First, partial or complete structural determination can be achieved. Second, CID can simply achieve more sensitive and specific detection. By detecting a unique dissociated/fragmented ion, the precursor ion can be detected in the presence of other ions of the same m/z value, mass-to-charge ratio, which reduces the background and increases the limit of detection.

CID has been applied to a variety of systems, in particular hydrated atomic ions [141, 434, 435, 436, 437] and molecular ions [137, 138, 140, 438]. In the second case, it has been used to understand the impact of high-energy radiations on living cells and DNA or RNA [139, 145, 146], as well as low-energy collisions on molecules of biological interest [147, 148].

Theoretical and experimental studies devoted to fragmentation of hydrated molecular aggregates are scarce, [139, 147, 395, 404, 439, 440] although CID has been applied to water clusters containing an atomic ion [141, 435, 436] and on charged water clusters [136, 404, 412, 434]. This is a real lack as understanding hydration of molecules and biomolecules is of paramount importance to get insights into their structure, stability, dynamics and reactivity in aqueous medium. In that respect, CID investigations could play an important role in understanding those properties in a environment free from long-range solvent effects but also for different hydration degrees or protonation states. This can be evidenced by the experimental study of B. Liu *et al.* on the fragmentation of the singly-charged adenosine 5'-monophosphate (AMP^-) which shows two different fragmentation channel depending on the solvation state of AMP^- . [139] However, to the best of our knowledge, no modelling was performed to complement these experiments except for a few static calculations. [141, 435, 436].

Threshold collision-induced dissociation (TCID) method has also been used, for instance to study the fragmentation patterns and to measure the dissociation energies of clusters. [441, 442] S. Zamith *et al.* did a CID study of the mass-selected protonated uracil water clusters with water molecules and noble gases, respectively. [104] In addition, they also reported the TCID study of pyrene cluster cations. [65] For these two projects, the single collision event is the predominant process. In this chapter, MD simulations based on a quantum chemical formalism are able to model such complex dissociation mechanism to provide an atomic-scale description for these collisions to explain and complete these experiments.

4.1.1 Principle of TCID

In usual TCID setups, experiments are done in ion guides, allowing to perform collisions with large mass atoms such as xenon without losing ions by deflection due to the collision. In order to unambiguously determine dissociation energies, one has to take care of a number of experimental parameters. First, the number of collisions should be as low as possible in order to insure single collision conditions. This can be achieved by performing experiments at various pressures and extrapolating results to zero pressure. Second, one has to consider the possible so-called kinetic shifts that can alter the dissociation energy measurement. Indeed, at threshold collision energy, the system under study might not dissociate during the timescale of the experiment. The apparent threshold has, therefore, to be corrected. This is usually done by extrapolating the experimental values using Rice-Ramsperger-Kassel-Marcus (RRKM) dissociation rates. [149, 150] Third, the initial thermal energy distribution has to be taken into

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account. Finally, TCID experimental results are usually fitted assuming a given form for the CID cross section, which can be expressed as [442]:

$$\sigma(E_{col}) = (\sigma_0 n / E_{col}) \sum_i g_i \int_{E_0 - E_i}^{E_{col}} [1 - e^{-k(\varepsilon + E_i)\tau}] \times (E_{col} - \varepsilon)^{n-1} d\varepsilon \quad (4.1)$$

where σ_0 is the collision cross section, n is the energy dependence of the reaction cross section, and E_{col} is the collision energy. The populations g_i of rovibrational states with energies E_i are used to carry out the thermal averaging. The dissociation rate k is usually calculated using RRKM type theories, and τ is the typical experimental time between the collision and detection. For comparison with experimental curves, eq 4.1 is further convolved with the kinetic energy distributions of both the ion and neutral reactants. If one needs to incorporate sequential fragmentation and/or competitive channels, these can also be included. [443, 444]

In this method, ion guides are not used. Therefore, it needs to simulate the full ion trajectories in order to ensure that ion losses are correctly taken into account. Collisions are, thus, described with a microscopic model rather than with the average curve given by eq 4.1. This approach allows to quite naturally include sequential dissociation and to potentially test energy transfer models. One advantage of the setup resides in the fact that the systems under study are thermalized at low temperature prior to collisions. This implies that averaging over thermal energies of the parent ion plays a minor role, thus leading to minor uncertainties.

4.1.2 Experimental Setup

The experimental setup of Laboratoire Collisions Agrégats Réactivié (LCAR) by S. Zamith *et al.* for the collision of protonated uracil water clusters or pyrene dimer cation with noble gas atoms is set up as follows:

Clusters are produced in a gas aggregation source [445](a) and then thermalized (b) at 25 K through thousands of collisions with helium. The experimental setup can be used in two modes. In the first mode, only the first Wiley-McLaren acceleration stage (c) is used to work together with the reflectron (i). Clusters are detected using dual micro-channel plates (MCPs) (j) biased at 10 kV. This allows to perform regular Time of Flight Mass Spectrometry (TOFMS) and to optimize the cluster production. In this mode, the mass filter (d), the electrodes for energy focusing (e) and deceleration (f), and the second Wiley-McLaren acceleration stage (h), are grounded.

4.3 Dynamical Simulation of Collision-Induced Dissociation of Protonated Uracil Water Clusters

Whatever the considered isomer, the three P_{NUL} and σ_{frag} values from 200, 400, and 600 random argon orientations are very close. Indeed, the largest difference is observed for isomer 7a which has P_{NUL} values of 29.5 and 31.3 % for 200 and 600 random orientations, respectively. This demonstrates that even for 200 initial random orientations, simulations are close to statistical convergence. In the present study, all results discussed in the main text were obtained with 600 initial random argon orientations per impact parameter value which ensures statistical convergence of the results independently of cluster size.

4.3.3 Time-Dependent Proportion of Fragments

The time-dependent proportion of each fragment was extracted from collision trajectories. To illustrate the change in behavior resulting from the difference in cluster size, Figures 4.6-4.11 display the time-dependent proportion of fragments obtained from the dissociation of the low-lying energy isomers of $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$.

I will discuss the time-dependent proportion of one small cluster (7a) and one big cluster (12a) in detail as an example. For the sake of clarity, only the fragments displaying significant proportion, higher than 0.035 and 0.015 for 7a and 12a, respectively are considered in Figure 4.10. This corresponds to the eight and ten most prominent fragments for 7a and 12a, respectively. From Figure 4.10, it is clear that for both aggregates, the proportion of H_2O has the sharpest increase after collision and then stays almost constant as a function of time. For 7a, ~ 3 ps after collision, the proportion of almost all fragments does not change any more. Before that, the proportion of the $(\text{H}_2\text{O})_6\text{UH}^+$ fragment increases first and then decreases, which indicates a sequential dissociation of water molecules. For 12a, proportion of $(\text{H}_2\text{O})_{11}\text{UH}^+$ and $(\text{H}_2\text{O})_{10}\text{UH}^+$ fragments displays a sharp increase quickly after collision which is then followed by a fast decrease, and finally it keeps a minute decrease up to the end of the simulations. The decrease of proportion of $(\text{H}_2\text{O})_{10}\text{UH}^+$ and $(\text{H}_2\text{O})_{11}\text{UH}^+$, and the increase of proportion of $(\text{H}_2\text{O})_6\text{UH}^+$, $(\text{H}_2\text{O})_7\text{UH}^+$ and $(\text{H}_2\text{O})_8\text{UH}^+$ indicate sequential dissociation after collision is occurring. It is worth noting that, in contrast to 7a, the proportions of the main fragments of 12a do not tend to be constant at the end of the simulations. This implies that, for this large aggregate, structural rearrangements are more likely to occur prior to complete dissociation. Proportions of the main fragments of clusters 7d and 12c shown in Figure 4.11 display similar behavior as for 7a and 12a. As a first conclusion, Figure 4.10 suggests that clusters with 7 water molecules experience a direct dissociation mechanism as was hypothesised by I. Braud *et al.* [104]. A similar conclusion can be drawn for smaller cluster sizes as supported by Figures

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Table 4.1: The proportions of P_{NUL} and σ_{frag} of first lowest-energy isomer and the isomer whose P_{NUL} fits the experiment (in bold) of $(\text{H}_2\text{O})_{1-5}\text{UH}^+$ with simulations of 200, 400, and 600 as initial conditions.

Cluster	Simu	P_{NUL} (%)	σ_{frag} (\AA^2)
1a	200	0.1	28.4
1a	400	0.1	28.3
1a	600	0.2	28.9
1b	200	0.2	26.3
1b	400	0.1	25.7
1b	600	0.1	25.9
2a	200	0.0	35.9
2a	400	0.0	36.5
2a	600	0.0	36.3
2b	200	0.0	34.7
2b	400	0.1	34.8
2b	600	0.1	34.9
3a	200	5.4	37.4
3a	400	5.2	36.2
3a	600	5.7	36.3
3b	200	0.0	41.2
3b	400	0.0	41.5
3b	600	0.0	41.9
4a	200	26.9	40.1
4a	400	28.2	40.3
4a	600	29.4	40.1
4b	200	2.7	45.3
4b	400	2.6	45.6
4b	600	2.6	45.2
5a	200	37.2	45.7
5a	400	37.8	46.1
5a	600	38.2	46.6
5d	200	0.1	47.3
5d	400	0.1	47.3
5d	600	0.1	47.5

4.3 Dynamical Simulation of Collision-Induced Dissociation of Protonated Uracil Water Clusters

Table 4.4: Energies of different $(\text{H}_2\text{O})_6\text{UH}^+$ fragments selected from the dissociation of 7d at SCC-DFTB level, and the lowest energies $(\text{H}_2\text{O})_5\text{UH}^+$ and (H_2O) at SCC-DFTB level. The relative energy $\Delta E = E_{(\text{H}_2\text{O})_6\text{UH}^+} - (E_{(\text{H}_2\text{O})_5\text{UH}^+} + E_{\text{H}_2\text{O}})$. All energies here are given in eV.

$E_{(\text{H}_2\text{O})_6\text{UH}^+}$	$E_{(\text{H}_2\text{O})_5\text{UH}^+}$	$E_{\text{H}_2\text{O}}$	ΔE
-44.310	-40.312	-4.057	1.605
-44.322	-40.312	-4.057	1.279
-44.307	-40.312	-4.057	1.687
-44.344	-40.312	-4.057	0.680
-44.373	-40.312	-4.057	-0.109

contribution of structural re-arrangements on the short time scale, they are very likely to occur as in $(\text{H}_2\text{O})_{12}\text{UH}^+$.

One has to keep in mind that modeling the complete duration of the experiment (up to μs) is out of reach with MD/SCC-DFTB simulations. In this work, the simulation time was 15 ps, for all cluster sizes. Large fragments such as $(\text{H}_2\text{O})_{6-12}\text{UH}^+$ may lose more water molecules if long enough simulation time were available, as suggested from the time dependent evolution of selected trajectories in section 4.3.3. To certify this, the total energy of $(\text{H}_2\text{O})_6\text{UH}^+$ fragments at SCC-DFTB level is calculated originating from the dissociation of $(\text{H}_2\text{O})_7\text{UH}^+$ (7d) from all the 1421 trajectories producing fragment $(\text{H}_2\text{O})_6\text{UH}^+$ over the total 600×15 trajectories. Then the energies of the lowest-energy isomer of $(\text{H}_2\text{O})_5\text{UH}^+$ and H_2O at SCC-DFTB level are subtracted. The deduced relative energies ΔE are reported in Table 4.4 for five cases. When ΔE is greater than zero, it is possible for the $(\text{H}_2\text{O})_6\text{UH}^+$ fragment to lose a water molecule. The percentage of ΔE being positive in all the trajectories leading to fragment $(\text{H}_2\text{O})_6\text{UH}^+$ is 53.0 %, which indicates that many $(\text{H}_2\text{O})_6\text{UH}^+$ fragments have still the potential to lose one more water molecule after the end of the simulation.

4.3.7 Conclusions about CID of $(\text{H}_2\text{O})_n\text{UH}^+$

Collision-induced dissociation of protonated uracil water clusters $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ at constant center of mass collision energy has been investigated by molecular dynamics simulations using the SCC-DFTB method. The very good agreement between the simulated and measured P_{NUL} and σ_{frag} as well as branching ratios indicate that the essence of the dissociation induced by collisions is well captured by the simulations.

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The P_{NUL} values from the different isomers of the $(\text{H}_2\text{O})_{1-7}\text{UH}^+$ cluster show that the localization of the excess proton after dissociation is strongly determined by the initial configuration of the isomer undergoing the collision. This suggests that $(\text{H}_2\text{O})_{1-7}\text{UH}^+$ aggregates primarily engage a direct dissociation path after collision that takes place on a very short time scale, *i.e.* lower than 15 ps. More strikingly, in most cases, the proposed lowest-energy isomer does not lead to the best fit to the experiment. However, the relative energy between the lowest-energy isomers and the isomers best fitting to the experiment is less than $1.0 \text{ kcal.mol}^{-1}$ for $(\text{H}_2\text{O})_{1-4,7}\text{UH}^+$ clusters and less than $2.7 \text{ kcal.mol}^{-1}$ for $(\text{H}_2\text{O})_{5,6}\text{UH}^+$ clusters. This is in line with the strong sensitivity of the collision outcome with the nature of the isomer undergoing the collision. This even suggests that the LEP can help in determining the main characteristic of the isomer involved in the collision. For $(\text{H}_2\text{O})_{11,12}\text{UH}^+$, these conclusions do not apply any more which shows that significant structural rearrangements occur after collision. This is confirmed by the time-dependent proportion of fragments which continue to vary even at 15 ps for $(\text{H}_2\text{O})_{11,12}\text{UH}^+$ whereas it is almost flat for $(\text{H}_2\text{O})_{1-7}\text{UH}^+$. Analysis of the fragment branching ratios helps in clarifying these points. Indeed, for the smallest clusters, $(\text{H}_2\text{O})_{1-5}\text{UH}^+$, the short simulation time well reproduces the corresponding experimental results which is in line with a direct mechanism. In contrast, for $(\text{H}_2\text{O})_{6-7}\text{UH}^+$, although P_{NUL} is well reproduced by the simulations, the experimental and theoretical branching ratios differ which show that more time is needed to properly describe the dissociation. For $(\text{H}_2\text{O})_{11,12}\text{UH}^+$, neither theoretical nor experimental branching ratios and P_{NUL} are in agreement which is a strong indication that a significant contribution of structural rearrangements occur; This suggests that a contribution of a statistical mechanism is more likely to occur for larger species such as $(\text{H}_2\text{O})_{11,12}\text{UH}^+$.

This work demonstrates that explicit molecular dynamics simulations performed at a quantum chemical level can provide a wealth of information about collision-induced mechanism in molecular clusters, in particular, hydrated molecular species. Such simulations thus represent a key tool to complement CID experiments and hope the present study will motivate similar computational studies on future CID experiments of hydrated molecular aggregates.

4.4 Dynamical Simulation of Collision-Induced Dissociation for Pyrene Dimer Cation

4.4.1 Introduction

PAH clusters have been investigated in several scientific fields. In combustion science, the role of PAH clusters in combustion processes is still under debate, in particular they might or not be the intermediate systems in the growth of soot particles. [125, 458, 459, 460, 461] In atmospheric and environmental science, PAHs are known as the pollutants, which is harmful to human health. For instance, the carcinogenic PAHs associated with particulate matter in air pollution has showed clear evidence of genotoxic effects, such as DNA adduct, chromosome aberrations. [462, 463] In new energy resources field, for the understanding of the properties of organic crystal or the design of new organic solar cell devices, PAH stacks are investigated as the prototypes. [464] In astrophysics, PAHs species are believed to be ubiquitous and abundant in the interstellar medium because of their compact and stable structure. [117] The PAH clusters are important contributors to the diffuse interstellar bands and UV-visible absorption bands. PAH clusters have been proposed to be the origin of a series of infrared emission bands, which are ubiquitous in the Universe. [114, 115] The broadening of these bands in regions protected from the star's UV flux suggests the following scenario: PAHs are trapped in clusters in UV-protected regions and photo-evaporated by star's UV photons in the so-called photodissociated region. [465, 466] For all these topics, it is necessary to make a better understanding of the fundamental properties of PAH clusters. The crucial quantities are the stability, molecular growth processes, dissociation energies and their evolution with PAH charge, species, cluster size.

The investigation of PAH clusters has been performed in experiment. Many studies focused on the investigation of structural properties of these clusters at the most stable geometrical configurations [132, 461, 467, 468, 469]. Their energetic properties such as ionisation potentials have been recorded [122] as well as their spectral properties [470, 471]. clusters may evaporate, breaking the PAH units themselves or leading to chemical reactivity between the different units, which shows the role of PAH clusters in the growth of PAHs themselves. If free flying PAHs are possibly from the evaporation of larger clusters, then this calls for more experimental data on their dissociation properties. The evolution of PAH clusters has been explored from experiments following the evaporation after absorption of UV photons, collision with low or high energetic particles or in a high-pressure environment. [122, 129, 132, 133, 134, 135] The

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range of collision energies considered experimentally is quite large, ranging from eV to high energy collision at a few keV. Low energy collision experiments allow for the derivation of dissociation energies [135] whereas the oligomerization of PAHs within the cluster induced by high energy collisions [472] or photoabsorption [16] suggests the possible role of clusters in the interstellar PAHs growth process [131].

The quantitative data from experiments of PAH clusters are still rather limited, which motivates the modeling studies of them. In the calculation of PAH clusters, the size of the systems limits the use of *ab initio* wave function methods to the investigation of properties of the smallest clusters, namely dimers [473, 474], whereas larger clusters can be addressed either at the DFT level or with more semi-empirical schemes [233, 460, 475, 476]. Many of these studies, focused on structural properties, evidence a stacking growth process in agreement with experimental results. In addition, IR properties were also reported at the DFT level [477]. Most of the theoretical studies involve neutral clusters, mostly due to the fact that treating charge resonance process in ions is a challenging task for DFT based methods [478]. The singly charged PAH clusters are more stable than their neutral counterparts due to charge resonance stabilization.[121] Cationic PAH clusters are expected to be abundant in the photo-dissociation regions because the ionization energy of the PAH cluster is lower than that of the isolated PAH, which leads to the efficient formation of cationic PAH clusters. In addition, the ionized PAH clusters are easier to control, so it is more important to study them. It should be mentioned the recent studies computing ionisation potentials [122] as well as structural [457] and spectral (electronic [479] and vibrational [480]) properties of cations, performed with an original model combining DFTB [168, 218, 219, 448] with a configuration interaction scheme[481].

With respect to these studies, very few is known about the dynamical aspects of PAH clusters carrying internal energy. High energy collisions of PAH clusters with energetic ions have been simulated by M. Gatchel *et al.* [482, 483] at the semi-empirical and DFTB levels. Recently experiments at lower collision energies were performed by S. Zamith *et al.* [65] (the principle of this experiment and the experimental setup were shown in sections 4.1.1 and 4.1.2), which were analysed by treating statistically the dissociation after collision energy deposition. Namely, the dissociation rate of pyrene clusters has been computed using phase space theory (PST)[135]. A fair agreement with experimental results was obtained concerning the collision energy dependence of the dissociation cross section. However, the employed model failed at reproducing in details the shape of the peaks in the time-of-flight (TOF) spectra. In this section, it is aimed at extending the description of such low energy collision processes (less than several

4.4 Dynamical Simulation of Collision-Induced Dissociation for Pyrene Dimer Cation

tens of eV) combining a dynamical simulations to describe the fast processes in addition to the statistical theory to address dissociation at longer timescales. With this approach, (i) good agreement between simulated and experimental mass spectra will be shown, thus validating the model, (ii) dissociation cross sections as a function of the collision energy is derived, (iii) the kinetic energy partition between dissociative and non-dissociative modes will be discussed and (iv) the energy transfer efficiency between intra and intermolecular modes will also be discussed. This work focused on the experimental investigation has been published in 2020 in the *The Journal of Chemical Physics*.^[66] and focused on the theoretical simulation has been published in 2021 in the *Theoretical Chemistry Accounts*.^[66]

4.4.2 Calculation of Energies

In the analysis, I will discuss the kinetic energy contributors, applying the following decomposition of the total kinetic energy E_{tot}^k of the dimer:

$$\begin{aligned}
 E_{tot}^k &= E_{Ar}^k + E_{td}^k + E_{Py^1}^k + E_{Py^2}^k + E_{Re}^k \\
 E_{tot}^k &= \frac{1}{2} \sum_{i=1}^{52} m_i (\vec{v}_i)^2 \\
 E_{Ar}^k &= \frac{1}{2} m_{Ar} \vec{v}_{Ar}^2 \\
 E_{td}^k &= \frac{1}{2} m_{Py_2} \vec{v}_t^2(Py_2) \\
 E_{Re}^k &= \frac{1}{2} \frac{m_{Py^1} m_{Py^2}}{m_{Py^1} + m_{Py^2}} (\vec{v}_t(Py^2) - \vec{v}_t(Py^1))^2 \\
 E_{Py^n}^k &= \frac{1}{2} \sum_{i=1}^{26} m_i^n (\vec{v}_i^n - \vec{v}_t(Py^n))^2
 \end{aligned} \tag{4.5}$$

In these equations and in the following, Py_2 refers to the pyrene dimer (possibly dissociated) whereas Py^1 and Py^2 refer to the first and second monomers, respectively. E_{tot}^k can be also calculated from the masses m_i^n and velocities \vec{v}_i of its atoms. E_{Ar}^k refers to the kinetic energy of the argon (with mass m_{Ar} and velocity \vec{v}_{Ar}). E_{td}^k is the translation kinetic energy of the dimer (with mass m_{Py_2} and velocity $\vec{v}_t(Py_2)$). E_{Re}^k is the relative kinetic energy of the two pyrene monomers, computed from their masses of $m_{Py^1} = m_{Py^2}$ and monomer global translation velocities $\vec{v}_t(Py^{1,2})$. $E_{Py^n}^k$ is the rovibrational kinetic energy of the monomer n computed from the masses and velocities of its atoms (m_i^n and \vec{v}_i^n , respectively).

The intramolecular vibrational kinetic energy ($E_{intra^n}^k$) of monomer n obtained after removing the contributions associated to the monomer translation and rotation modes is calculated as

4. DYNAMICAL SIMULATION OF COLLISION-INDUCED DISSOCIATION

follows:

$$E_{intra}^k = \frac{1}{2} \sum_{i=1}^{26} m_i^n (\vec{v}_i^n - \vec{v}_t(Py^n) - \vec{v}_{ir}^n)^2 \quad (4.6)$$

where \vec{v}_{ir}^n is the velocity of atom i associated to the monomer global rotation. In addition, the dimer intermolecular kinetic energy (E_{inter}^k) is calculated as follows:

$$E_{inter}^k = E_{tot}^k - E_{Ar}^k - E_{td}^k - E_r^k - E_{intra}^k - E_{intra}^k \quad (4.7)$$

where E_r^k refers to the rotation kinetic energy of the dimer. \vec{v}_{ir}^n and E_r^k are calculated using the following formulas.

$$\begin{aligned} \vec{L}(Py^n) &= \sum_{i=1}^{26} m_i^n (\vec{r}_i^n - \vec{r}_{CM}(Py^n)) \times (\vec{v}_i^n - \vec{v}_t(Py^n)) \\ \vec{L}(Py_2) &= \sum_{i=1}^{52} m_i (\vec{r}_i - \vec{r}_{CM}(Py_2)) \times (\vec{v}_i - \vec{v}_t(Py_2)) \\ I &= mr^2 \\ \vec{\omega} &= [I]^{-1} \times \vec{L} \\ \vec{v}_{ir}^n &= \vec{\omega}(Py^n) \times (\vec{r}_i^n - \vec{r}_{CM}(Py^n)) \\ E_{tot}^k &= E_{r^n}^k + E_{td^n}^k + E_{intra^n}^k \\ E_{tot}^k &= \frac{1}{2} \sum_{i=1}^{26} m_i^n (\vec{v}_i^n)^2 \\ E_{td}^k &= \frac{1}{2} m_{Py^n} \vec{v}_t^2(Py^n) \\ E_r^k &= \frac{1}{2} \vec{\omega}(Py_2) \times [I](Py_2) \times \vec{\omega}(Py_2) = \frac{1}{2} \vec{L}(Py_2) \times [I]^{-1}(Py_2) \times \vec{L}(Py_2) \end{aligned} \quad (4.8)$$

E_{tot}^k is the total kinetic energy of monomer n . E_{td}^k is the translation kinetic energy of pyrene monomer n . $\vec{L}(Py^n)$ is the angular momentum of pyrene monomer n . $\vec{L}(Py_2)$ is the angular momentum of the dimer. $[I]$ refers to the moment of inertia tensor. $[I]^{-1}$ is the inverse of $[I]$. $\vec{\omega}$ is the angular velocity. \vec{r}_i^n and $\vec{r}_{CM}(Py^n)$ denote the coordinates of atom i and center of mass of dimer of monomer n , respectively. \vec{r}_i and $\vec{r}_{CM}(Py_2)$ and denote the coordinates of atom i and center of mass of dimer, respectively.

From the endpoint of the simulation, the total energy transferred towards internal rovibrational modes of the pyrene dimer can also be computed as:

$$\Delta E_{int}^{Py_2} = E_{Ar}^{k,0} - E_{Ar}^k - E_{td}^k \quad (4.10)$$

4.4 Dynamical Simulation of Collision-Induced Dissociation for Pyrene Dimer Cation

that the essence of the collision-induced dissociation is captured by the simulation. It appears that the TOF spectra mostly result from dimers dissociating on short timescales (during the MD simulation) and the remaining minor contribution is from dimers dissociating at longer timescales (the second step, during PST calculation). This indicates that Py_2^+ primarily engages a direct dissociation path after collision.

The extraction of snapshots from the MD simulations allows to visualize the collision processes. It shows that the evolution of the trajectories either toward a dissociation or a redistribution of the transferred energy strongly depends on the initial collision conditions. Intramolecular fragmentation of the monomers occurred only for collision energies above 25 eV. The dissociation cross sections show a steep increase for collision energies below 7.5 eV and remain almost constant for collision energies greater than 10 eV. The dissociation cross section of Py_2^+ increases when dissociation occurring on longer timescale is included. As such, the dissociation cross section computed from the MD+PST model at the centre of mass collision energy of 17.5 eV is slightly higher than the value derived from pure MD simulations. The analysis of the partition of the final kinetic energy as a function of the collision energy shows how the absorbed energy is shared between the dissociative modes and the heating of individual monomers. It shows that above 7.5 eV, increasing the collision energy mostly results in an increase of the intramolecular energy. The qualitative analysis of the different timescales involved in the collision further supports the kinetic energy partition analysis. Finally, the analysis of energy transfer efficiency within the dimer suggests that direct dissociation is too fast to allow significant thermalization of the system. On the other hand, when there is no dissociation, thermalization can occur with a faster equilibration between the intramolecular modes of the two units than with the intermolecular modes.

The present results can be compared with experimental and theoretical works discussing the direct and indirect fragmentation of PAH and PAH clusters submitted to higher energy collisions [483, 485]. These authors showed that the nuclear stopping power dominates over the electronic one below 1 keV, giving a justification to our approach based on classical MD and PST. They also showed that the direct non-statistical PAH fragmentation (knock-out) is an efficient process above 20 eV. This is in line with the fact that monomer fragmentation was only observed in our MD simulations above 25 eV. Our work shows that, for PAH clusters, a regime exists below this collision energy where the dimer dissociation is governed by non-statistical processes.

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In this study, the collision process, dissociation path, energy partition and distribution, and the efficiency of energy transfer were deeply explored for the Py_2^+ system, which can provide valuable reference for the CID study of larger PAH cation clusters.

5

General Conclusions and Perspectives

5.1 General Conclusions

As stated in the general introduction, the goal of this thesis was to go a step further into the theoretical description of properties of molecular clusters in the view to complement complex experimental measurements. It has focused on two different types of molecular clusters. I have first investigated water clusters containing an impurity, *i.e.* an additional ion or molecule. First, I have studied ammonium and ammonia water clusters in order to thoroughly explore their PES to characterize in details low-energy isomers for various cluster sizes. I have then tackled the study of protonated uracil water clusters through two aspects: characterize low-energy isomers and model collision-induced dissociation experiments to probe dissociation mechanism in relation with recent experimental measurements by S. Zamith and J.-M. l’Hermite. Finally, I have addressed the study of the pyrene dimer cation to explore collision trajectories, dissociation mechanism, energy partition, mass spectra, and cross-section. These four studies have been organized in two chapters, each one gathering two studies involving similar computational tools. Below are gathered the main conclusions obtained along this thesis.

Structural and energetic properties. The structures and binding energies of the lowest-energy isomers of $(\text{H}_2\text{O})_{1-10}\text{NH}_4^+$ and $(\text{H}_2\text{O})_{1-10}\text{NH}_3$ clusters were obtained through a synergistic use of SCC-DFTB and PTMD. The reported low energy isomers were further optimized at the MP2/Def2TZVP level of theory. In order to improve the description of sp^3 nitrogen, I have proposed a modified set of N-H parameters. Through comparing the configurations and binding energies of the lowest-energy isomers obtained at SCC-DFTB an MP2/Def2TZVP levels and by comparing the corresponding results to the literature, I demonstrated that this

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modified set of NH parameters is accurate enough to model both ammonia and ammonium water clusters. This work has thus allowed to report a number of new low-energy isomers for the studied species. Finally, PTMD simulation of $(\text{H}_2\text{O})_{20}\text{NH}_4^+$ was conducted and the heat capacity curve of this aggregate was obtained. It is in agreement with previous results reported in the literature.

A similar exploration of the PES of $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ clusters was also performed. The reported low-energy isomers for these systems are all new and therefore constitute new data set to discuss and analyse the hydration properties of RNA nucleobases. They also complement available structures already reported for the non-protonated $(\text{H}_2\text{O})_n\text{UH}^+$ species. These structures have also helped use to provide preliminary explanations to recent collision-induced measurements performed by S. Zamith and J.-M. l’Hermite. In particular, I show that when there are only 1 or 2 water molecules, the excess proton is chemically bond to the uracil. When there are 3 or 4 water molecules, the proton is still bound to the uracil but it has a tendency to be transferred toward an adjacent water molecule. From $n = 5$ and above, clusters contain enough water molecules to allow for a net separation between uracil and the excess proton. The latter is often bound to a water molecule which is separated from uracil by at least one other water molecule. In the context of a direct dissociation mechanism, the nature of these isomers and the localisation of the proton as a function of cluster size, helps in analysing the nature of the fragments and the location of the proton on them.

These two studies finally provide a new proof that SCC-DFTB, when combined to efficient enhanced sampling methods, is a powerful tool to explore complex potential energy surfaces of molecular aggregates. They have already given rise to two publications [104, 384] and one other publication is in preparation.

Collision-induced dissociation. The SCC-DFTB simulations conducted to model collision-induced dissociation of $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ clusters and pyrene dimer cation were presented. These simulations have provided a wealth of important information to complement recent experimental CID measurements.

For the collision simulations of $(\text{H}_2\text{O})_{1-7,11,12}\text{UH}^+$ clusters at constant center of mass collision energy, the theoretical proportion of formed neutral vs. protonated uracil containing clusters, total fragmentation cross sections as well as the mass spectra of charged fragments are consistent with the experimental data which highlights the accuracy of the simulations. They allow to probe which fragments are formed on the short time scale and rationalize the location

of the excess proton on these fragments. Analyses of the time evolution of the fragments populations and theoretical and experimental branching ratios indicate that $(\text{H}_2\text{O})_{1-7}\text{UH}^+$ engage a direct/shattering mechanism (dissociation on a very short time scale) after collision whereas for $(\text{H}_2\text{O})_{11-12}\text{UH}^+$ a significant contribution of structural rearrangements occur. This suggests that a contribution of a statistical mechanism is more likely to occur for larger species such as $(\text{H}_2\text{O})_{11-12}\text{UH}^+$. Such study is almost unique as the modelling of the dissociation of aqueous aggregates is very scarce in the literature. This study thus demonstrates that explicit molecular dynamics simulations at the SCC-DFTB level appear as a key tool to complement collision-induced dissociation experiments of hydrated molecular clusters. This study opens new possibility in the domain and I hope it will motivate new experimental measurements. One publication devoted to this study is in preparation.

Dynamical simulations of collision between Py_2^+ and argon at different center of mass collision energies, between 2.5 and 30.0 eV, were conducted. Collision process, dissociation path, energy partition and distribution, and the efficiency of energy transfer were deeply explored from these simulations that have provided valuable reference for the CID study of larger PAH cation clusters. The simulated TOFMS of parent and dissociated products were obtained from the combination of MD simulations and PST to address the short and long timescales dissociation, respectively. The agreement between the simulated and measured mass spectra suggests that the main processes are captured by this approach. It appears that the TOFMS spectra mostly result from dimers dissociating on short timescales (during the MD simulation) and the remaining minor contribution results from dimers dissociating at longer timescales (the second step, during PST calculation). This indicates that Py_2^+ primarily engages a direct dissociation path after collision. The dynamical simulations show that the outcome of the trajectories either toward a dissociation or a redistribution of the transferred energy strongly depends on the initial collision conditions. Intramolecular fragmentation of the monomers occurs only for collision energies above 25 eV. At low collision energies, the dissociation cross section increases with collision energies whereas it remains almost constant for collision energies greater than 10-15 eV. The analysis of the kinetic energy partition as a function of the collision energy shows the absorbed energy is shared between the dissociative modes and the heating of individual monomers. It shows that above 7.5 eV, increasing the collision energy mostly results in an increase of the intramolecular energy. Finally, the analysis of energy transfer efficiency within the dimer suggests that direct dissociation is too fast to allow significant thermalization of the system. On the other hand, when there is no dissociation, thermalization can occur with a faster

5. GENERAL CONCLUSIONS AND PERSPECTIVES

equilibration between the intramolecular modes of the two units than with the intermolecular modes. This study has given rise to two publications. [65, 66]

5.2 Perspectives

This thesis has addressed various problems, on different molecular clusters, and has involved a range of theoretical methodologies that are not common way in computational chemistry. Various and very exciting perspectives can be therefore be considered in future studies:

- The newly proposed set of N-H parameters could be used to explore the low-energy structures and properties of a much larger range of systems of atmospheric interest. Indeed the structure of pure $(\text{NH}_3)_m$ clusters as well as $(\text{NH}_3)_m\text{H}^+$, $(\text{H}_2\text{O})_n(\text{NH}_3)_m$, and $(\text{H}_2\text{O})_n(\text{NH}_3)_m\text{H}^+$ clusters have been hardly addressed in the literature mainly due to the lack of properly defined force field for these systems. The transferability of SCC-DFTB would suggest that the potential I developed could also be applied to these systems. This is an ongoing work that I have recently initiated. More interesting and also complicated is the study of water clusters containing a mix of nitrogen and sulphur compounds, for instance, ammonium and sulfate ion. These species, their conjugated basis and acid in combination with dimethylamine and water molecules represent the basis for nucleation of atmospheric particles. The chemical complexity induced by their mixing in force field simulations on the one hand, and the system size needed for proper molecular simulations on the other hand, suggest that SCC-DFTB has a major role to play in the theoretical description of these species.
- It would also be of great interest to pursue dynamical simulations of protonated uracil water clusters. Indeed, the work I have presented in this thesis still suffers from some lacks. First, it would be of high interest to look at the influence of collision energy, both lower or higher, on the dissociation mechanism as a function of the cluster size. By implementing a similar methodology as for the study of Py_2^+ , it would be possible to extract important new information about energy partition and dissociation mechanism. Those can be of interest to other aqueous aggregates. In other important point is the inclusion of nuclear quantum effects in the simulations. Indeed, as the experiments are performed at very low temperatures, the quantum nature of the proton can play an important role that has been neglected in the present thesis.

- The dynamical simulations for collision-induced dissociation of pyrene dimer cation can be extended to PAHs water clusters to complement recent experiments on these systems.
- Finally, all the simulations of water clusters performed within this thesis were performed in the electronic ground state. To model what can occur in the atmosphere or interstellar medium, it would be of interest to investigate solvation effects on organic/inorganic molecules brought in an electronic excited state. To do so, the TD-DFTB method need to be implemented and tested as such simulation would involve a number of additional theoretical complexities. This would allow to calculate both absorption spectra from electronic ground state and emission spectra from electronic excited state of organic/inorganic molecule containing water clusters.

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Publications

- [1] A. Simon, M. Rapacioli, E. Michoulier, **L. Zheng**, K. Korchagina & J. Cuny, *Contribution of the density-functional-based tight-binding scheme to the description of water clusters: methods, applications and extension to bulk systems*, Mol. Simul., 2019, 45, 249-268.
- [2] I. Braud, S. Zamith, J. Cuny, **L. Zheng**, and J. -M. L'Hermite, *Size-dependent proton localization in hydrated uracil clusters: A joint experimental and theoretical study*, J. Chem. Phys., 2019, 150, 014303.
- [3] S. Zamith, J. -M. L'Hermite, L. Dontot, **L. Zheng**, M. Rapacioli, F. Spiegelman, and C. Joblin, *Threshold collision induced dissociation of pyrene clusters cations*, J. Chem. Phys., 2020, 153(5), 054311.
- [4] **L. Zheng**, S. Zamith and M. Rapacioli, *Dynamical simulation of collision-induced dissociation of pyrene dimer cation*, Theor. Chem. Acc. 2021, 140(19), 1-14.
- [5] **L. Zheng**, M. Rapacioli, S. Zamith, J. -M. L'Hermite and J. Cuny, *Collision-induced dissociation of protonated uracil water clusters probed by molecular dynamics simulations*, to be submitted soon.
- [6] **L. Zheng**, and J. Cuny, *Structure and stability of $(H_2O)_nNH_4^+$ and $(H_2O)_nNH_3$ clusters: A SCC-DFTB study*, to be submitted soon.

Declaration

I herewith declare that I have produced this paper without the prohibited assistance of third parties and without making use of aids other than those specified; notions taken over directly or indirectly from other sources have been identified as such. This paper has not previously been presented in identical or similar form to any other examination board.

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