Quantum chemical calculations of multidimensional dynamics probed in resonant inelastic X-ray scattering

Emelie Ertan

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Abstract
This thesis is devoted to the theoretical study of the dynamical processes induced by light-matter interactions in molecules and molecular systems. To this end, the multidimensional nuclear dynamics probed in resonant inelastic X-ray scattering (RIXS) of small molecules, exemplified by H_2O (g) and H_2S (g), as well as more complex molecular systems, exemplified by NH_3(aq) and kaolinite clay, are modelled. The computational methodology consists of a combination of \textit{ab initio} quantum chemistry calculations, quantum nuclear wave packet dynamics and in certain cases molecular dynamics modelling. This approach is used to simulate K-edge RIXS spectra and the theoretical results are evaluated against experimental measurements.

Specifically, the vibrational profile for decay back to the electronic ground state of the H_2O molecule displays a vibrational selectivity introduced by the dynamics in the core-excited state. Simulation of the inelastic decay channel to the electronic |1b_v^1,4u_v^{1/2}\rangle valence-excited state shows that the splitting of the spectral profile arises from the contribution of decay in the OH fragment. The character of the 1s\,^1 and 2p\,^1 core-excited states of the H_2S molecule has been investigated and distinct similarities and differences with the H_2O molecule have been identified. RIXS has also been used as a probe of the hydrogen bonding environment in aqueous ammonia and by detailed analysis of the valence orbitals of NH_3 and water, the spectral profiles are explained. Finally, it is shown that vibrations of weakly hydrogen bonding OH are excited in RIXS decay to the electronic ground state in kaolinite.

Keywords: quantum chemistry, X-ray spectroscopy, RASSCF, density functional theory, ultrafast nuclear dynamics.

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QUANTUM CHEMICAL CALCULATIONS OF MULTIDIMENSIONAL DYNAMICS PROBED IN RESONANT INELASTIC X-RAY SCATTERING

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Quantum chemical calculations of multidimensional dynamics probed in resonant inelastic X-ray scattering

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Populärvetenskaplig sammanfattning

Det latinska ordet *physica* betyder läran om naturen vilket är precis det fysiken handlar om även idag; strävan att förstå världen omkring oss. Jämfört med de tidigaste fysikerna har vi idag så klart avsevärt mer sofistikerade verktyg för att utföra våra studier, såsom datorer som kan lösa matematiska problem mångdubbelt så snabbt som den mänskliga hjärnan och strålkällor som kan skapa ljus som är otroligt mycket mer energirikt än det synliga ljuset. Dessa tekniska framsteg har lett till att den kollektiva kunskapen om de fysikaliska och kemiska processer som driver vår omvärld ständigt ökar.

Idag kan vi undersöka naturen ner på molekyl- och atomnivå och upplösa dessa beståndsdelars inneboende kemiska egenskaper och dynamiska processer, såväl som deras växelverkan med omgivningen. Syftet med forskningen som samlats i den här doktorsavhandlingen är att förstå sådana basala fysikaliska effekter i molekyler som finns i naturen omkring oss.

Ett sätt att undersöka de dynamiska processerna i molekyler är genom att bestråla dem med röntgenstrålning. Samverkanseffekter mellan den starka röntgenstrålningen och molekylen leder till att dynamiska processer som t.ex. molekylvibrationer, sätts igång. Röntgenspektroskopi, där röntgenstrålningen låts växelverka med det molekylprov som ska undersökas är därför en metod vi kan använda för dessa studier.

Stora framsteg har gjorts inom fysiken under de senaste hundra åren, likväl är det fortfarande en stor utmaning att detaljerat beskriva de dynamiska processerna och växelverkningarna som sker i ett komplext kemiskt system, t.ex. ett glas vatten. Även om det verkar som det vanligaste och allra vardagligaste kemiska systemet, så påverkas vattenmolekylerna i glaset av intrikata och komplicerade växelverkningar med varandra. Därför har vi börjat våra studier genom att först undersöka och utveckla teoretiska modeller för enstaka molekyler som inte påverkas av några växelverkanseffekter från omgivningen. Dessa modeller och den kunskapen vi samlat för det lilla systemet, fungerar sen som utgångspunkt när vi ska ta oss an utmaningen att förstå mer komplicerade system, såsom vattnet i ett glas eller en mineral.
Forskningen i denna doktorsavhandling, har bl.a. lett till att vi nu har en djup förståelse för vad det är för fysikaliska effekter som driver de dynamiska processerna i en vattenmolekyl. Denna kunskap lägger grunden för pågående studier av flytande vatten. Med utveckling av liknande metoder hoppas vi att i framtiden kunna undersöka ännu mer komplicerade system med stor detaljrikhet, t.ex. biologiska molekyler i vattenlösning vilket skulle kunna ge oss bild av de fysikaliska processerna som sker i människokroppen.

Emelie Ertan
Stockholm, 2018
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I: Selective gating to vibrational modes through resonant X-ray scattering.

PAPER II: A study of the water molecule using frequency control over nuclear dynamics in resonant X-ray scattering.

PAPER III: Ultrafast dissociation features in RIXS spectra of the water molecule

PAPER IV: Setting the stage for theoretical X-ray spectra of the H$_2$S molecule with RASPT2 calculations of the energy landscape
E. Ertan, M. Lundberg, L. K. Sørensen, and M. Odelius, In manuscript


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Author’s contribution

Paper I: I performed the electronic structure calculations and participated actively in the discussion of the results. I wrote the computational details section related to the electronic structure calculations and participated actively in the reviewing of the manuscript.

Paper II: I performed the electronic structure calculations and I participated actively in the discussion of the results. I wrote the computational details section related to the electronic structure calculations and participated actively in the reviewing of the manuscript.

Paper III: I performed the electronic structure calculations, participated actively in the discussion of the results and was co-responsible together with V. Kimberg for preparing the manuscript.

Paper IV: I performed all the calculations and analysis and was responsible for preparing the manuscript.

Paper V: I performed the RASPT2 calculations of gas phase NH$_3$ and participated in the discussion and writing of the manuscript.

Paper VI: I performed all calculations and analysis of the potential energy surfaces and the RIXS spectra and was responsible for preparing the manuscript.

This PhD thesis contains material that has been included in or reprocessed from my Lic thesis [1]: 'Ab initio simulations of vibrational and electronic structure evaluated against K-edge resonant inelastic X-ray scattering'. Below follows a list of the material in PhD that has been reused from Lic:

**Chapter 2:** The text, figures and layout in this PhD thesis have in large part been taken from chapter 2 in Lic with some adaptation.

**Chapter 3:** The text of sections 3.2-3.3 in this PhD thesis is in large part taken from chapter 3 in Lic with some adaptation. In this
PhD thesis some of the equations are reformulated.

**Chapter 4:** The text and figure of the introduction and section 4.1 in this PhD thesis have in large part been taken from the introduction and section 4.1 of chapter 4 in Lic with some adaptation.

**Chapter 5:** Text and figures of section 5.3 in this PhD thesis have in large part been taken from section 5.2 in Lic with some adaptations.
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## Abbreviations

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<th>Abbreviation</th>
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<tbody>
<tr>
<td>BO</td>
<td>Born-Oppenheimer</td>
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<tr>
<td>CAS</td>
<td>Complete Active Space</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Complete Active Space Self-Consistent Field</td>
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<tr>
<td>CI</td>
<td>Configuration Interaction</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>EY</td>
<td>Electron Yield</td>
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<tr>
<td>FC</td>
<td>Franck-Condon</td>
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<tr>
<td>FY</td>
<td>Fluorescence Yield</td>
</tr>
<tr>
<td>HCH</td>
<td>Half-Core-Hole</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock</td>
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<tr>
<td>KS</td>
<td>Kohn-Sham</td>
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<tr>
<td>MCSCF</td>
<td>Multi-Configuration Self-Consistent Field</td>
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<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>MP</td>
<td>Møller-Plesset</td>
</tr>
<tr>
<td>PES</td>
<td>Potential Energy Surface</td>
</tr>
<tr>
<td>RAS</td>
<td>Restricted Active Space</td>
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<tr>
<td>RASSCF</td>
<td>Restricted Active Space Self-Consistent Field</td>
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<tr>
<td>RIXS</td>
<td>Resonant Inelastic X-ray Scattering</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-Consistent Field</td>
</tr>
<tr>
<td>TDSE</td>
<td>Time-Dependent Schrödinger Equation</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XES</td>
<td>X-ray Emission Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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1. Introduction

1.1 Light-matter interaction in molecules

In physics and chemistry, the term spectroscopy refers to the technique of mapping the quantum energy levels in atoms and molecules. This mapping is in practice performed by observation of the radiation or particles absorbed and emitted as a result of the interactions of electromagnetic radiation with the sample. For molecules and molecular systems, we can investigate chemical, structural and electronic properties using spectroscopy. Insight into the properties mentioned helps us understand, for examples, chemical bonding, reaction dynamics, and charge transfer. The wide variety of the processes we can investigate with spectroscopy is a result of coupling of the broad electromagnetic spectrum (Fig. 1.1) with the different degrees of freedom in the system. By tuning the energy of the radiation that we apply on our sample, we can, in principle, select what processes we will activate.

With infrared (IR) spectroscopy, molecular vibrations can be probed to learn about structural properties, such as functional groups, bond strength and dynamics. Radiation in the visible (Vis) to ultraviolet (UV) range corresponds to the binding energy of the valence electrons. UV-Vis spectroscopy can therefore be used to study, e.g. chemical bonding, oxidation, and charge transfer. The main focus of this thesis is
the energy landscape of molecules and extended systems. Hence, for this, X-ray spectroscopy is a relevant technique. X-ray radiation contains enough energy to induce excitation and ejection involving strongly bound electrons in the core levels.

Spectroscopy in the X-ray regime has developed rapidly in the recent decades as a result of the improved light sources. Synchrotron radiation was first observed in the late 1940s at the General Electric Labs [2], and is the result of radiation emitted by particles accelerated on a bent trajectory. Since then, the synchrotron sources have developed from the first generation storage rings (where electron bunches are kept in a closed trajectory at constant energy) intended for high-energy physics research, to the storage rings devoted to producing synchrotron radiation that we use today in experiments. The modern storage rings use insertion devices (so called undulators and wigglers) to generate X-ray radiation of high brilliance.

Another source of high-energy radiation is the X-ray free electron lasers (XFEL), where a long undulator is used to generate microbunches of electrons emitting highly intense and coherent radiation about 10 orders of magnitude brighter than what can be generated by the modern synchrotron storage rings [3].

The rich information contained in the measured spectra can be challenging to extract and analyse, and for this theoretical modelling is an invaluable tool. Using quantum chemistry we get a model of the electronic structure and electronic states in the sample, and quantum dynamics simulations provides a description of the motion of the nuclei. Even the molecular structure in more complex coordinated molecular materials, such as liquids and solids, can be determined using classical molecular dynamics simulation and Monte Carlo modelling.

1.2 X-ray spectroscopy

X-ray spectroscopy refers to spectroscopic techniques wherein X-ray light is used to induce electron transitions, in particular involving the core-electrons. An electronic state with an electron vacancy in the core-level is referred to as a \textit{core-excited} state if the core-electron has been excited to an unoccupied valence or Rydberg level, or a \textit{core-ionized} state if the core-electron has been ejected. Important techniques to studie these processes include X-ray photoelectron spectroscopy (XPS) [4], X-ray absorption spectroscopy (XAS) [4; 5], X-ray emission spectroscopy (XES) [4], Auger electron spectroscopy [4], resonant photoemission spectroscopy [6], and resonant inelastic X-ray scattering (RIXS) [7].
The work of this thesis focuses on the theoretical simulation of RIXS. RIXS is a very powerful spectroscopic technique that makes it possible to study the electronic structure in molecules, such as gas phase H$_2$O [8; 9], aqueous ammonia [10], and gas phase H$_2$S, and more complex local chemical environments, such as in kaolinite clay [11] and NH$_3$ (aq) [10], through a combination of element specific excitations. In chapter 2, the quantum chemistry framework for calculating excited electronic states is presented in detail in chapter 3.

1.3 Core-excited state dynamics in RIXS

A molecule in a core-excited state may undergo a change in nuclear geometry on the femtosecond (10$^{-15}$ s) timescale, a nuclear relaxation process that is referred to as ultrafast core-excited state dynamics. At the same time, the core-excited state decays electronically, either elastically back to the ground state or inelastically to another, lower lying, excited state. When the RIXS process is affected by the core-excited state dynamics, it opens up the possibility to probe the nuclear degrees of freedom, such as, vibrational excitations [8; 9; 11–18]. The resulting vibrational signal in the quasi-elastic RIXS spectra may be used to map the quantized energy levels of the ground state, which was done for the H$_2$O molecule in Papers I and II and for kaolinite in Paper VI.

The core-excited state dynamics may also result in dissociation of the molecule into fragments, a process which is referred to as ultrafast dissociation. This is the case in the inelastic RIXS of the water molecule, presented in Paper III.

The theoretical concepts of quantum dynamics are presented in detail in chapter 4.

1.4 Aim of thesis

The work included in this thesis aims to deepen the understanding of ultrafast nuclear dynamics processes in RIXS through accurate simulations of spectra that include both electronic transitions and nuclear dynamics in a combined model.$^1$

$^1$Atomic units are used throughout this thesis, if not otherwise specified:

$$e = \hbar = m_e = 1$$ (1.1)
My work has specifically been focused on calculating accurate potential energy surfaces (PESs) for the nuclear degrees of freedom relevant to the RIXS process. For the case of the H$_2$O and H$_2$S molecules, the strong coupling of the stretching modes was included by considering 2D PES. State-of-the-art quantum chemistry methods make it possible to include relativistic effects, low lying Rydberg states, and spin-orbit coupling. For more complex systems, like kaolinite clay, specific coordinates along the nuclear degrees of freedom in the ground state and core-excited state PESs are calculated more approximately using density functional theory.
2. Quantum chemistry

Molecules consist of smaller particles; positively charged protons and neutral neutrons make up the nuclei and the nuclei are surrounded by clouds of negatively charged electrons. These constituent particles, especially the electrons, have very small masses and therefore we need to use quantum mechanics to accurately describe the electronic structure of a molecule. In quantum mechanics the state of the system at time $t$ is obtained by solving the *time-dependent Schrödinger equation* (TDSE):

$$H(R, r)\Psi(R, r; t) = i\frac{\partial}{\partial t}\Psi(R, r; t).$$

For molecular systems the Hamiltonian operator, $H(R, r)$, is constituted by the sum of the kinetic energy operators of the electrons and the nuclei, the potential energy operators of the interactions of these particles, and is dependent on the positions of the nuclei $\{R\}$ and the positions of the electrons $\{r\}$. $\Psi(R, r; t)$ is the wave function at time $t$.

In this section I will describe the molecular Schrödinger equation and present the quantum chemistry methods used to solve it.

### 2.1 The molecular Schrödinger equation

![Figure 2.1: Schematic representation of the H₂ molecule. A and B denotes the nuclei, and i and j are the electrons.](image)

For a molecule or a molecular system we need to consider several particles that will interact with each other. Solving the Schrödinger equation even for a small molecule such as $\text{H}_2$ is not trivial. Here we

---

2The symbol $i$ is used to denote the imaginary unit throughout this thesis.
have four particles, two nuclei and two electrons, which will interact with each other, as can be seen in the schematic in Fig. (2.1). This must be considered when formulating the Hamiltonian for a multi-particle system.

In general terms, the molecular Hamiltonian can be formulated with the following two terms:

$$H(R, r) = T_{\text{nuc}} + H_{\text{el}}.$$  \hspace{1cm} (2.2)

$T_{\text{nuc}}$ is the purely nuclear kinetic energy operator for $N_{\text{nuc}}$,

$$T_{\text{nuc}} = -\sum_A \frac{\nabla^2 A}{2m_A}$$  \hspace{1cm} (2.3)

where $\nabla^2 A = \left( \frac{\partial^2}{\partial R^2_{x,A}} + \frac{\partial^2}{\partial R^2_{y,A}} + \frac{\partial^2}{\partial R^2_{z,A}} \right)$ and $m_A$ is the mass of nucleus $A$.

$H_{\text{el}}$ is called the electronic Hamiltonian and contains both kinetic and potential energy operators,

$$H_{\text{el}} = T_{\text{el}} + V_{\text{nuc-el}} + V_{\text{el-el}} + V_{\text{nuc-nuc}}.$$  \hspace{1cm} (2.4)

The first right-hand side term is the kinetic energy operator of the electrons,

$$T_{\text{el}} = -\frac{1}{2} \sum_i N_{\text{el}} \nabla^2_i$$  \hspace{1cm} (2.5)

where $N_{\text{el}}$ is the number of electrons and $\nabla^2_i = \left( \frac{\partial^2}{\partial r^2_{x,i}} + \frac{\partial^2}{\partial r^2_{y,i}} + \frac{\partial^2}{\partial r^2_{z,i}} \right)$ of electron $i$. The second term is the potential energy operator of the nucleus-electron interaction,

$$V_{\text{nuc-el}} = -\sum_A \sum_i \frac{Z_A}{|R_A - r_i|},$$  \hspace{1cm} (2.6)

where $Z_A$ is the atomic number of nucleus $A$, $|R_A - r_i|$ is the separation of the nucleus $A$ and electron $i$. The next to last term in Eq. (2.4) is the electron-electron interaction potential energy operator,

$$V_{\text{el-el}} = \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|}$$  \hspace{1cm} (2.7)

where $|r_i - r_j|$ is the separation of electrons $i$ and $j$. The last term in Eq. (2.4) is the nucleus-nucleus potential energy operator

$$V_{\text{nuc-nuc}} = \sum_A \sum_{B>A} \frac{Z_A Z_B}{|R_A - R_B|}.$$  \hspace{1cm} (2.8)
Here $Z_B$ is the atomic number of nucleus B and $|\mathbf{R}_A - \mathbf{R}_B|$ is the internuclear separation of nuclei $A$ and $B$. We note that only the second term in Eq. (2.4) depends both on nuclear and electronic degrees of freedom, whereas the first and third terms only depend on the electrons and the last term only requires the positions of the nuclei.

2.1.1 The Born-Oppenheimer (BO) approximation

We are ready to formulate the TDSE for a molecule (we now drop the $t$ variable for the wave function for simplicity of notation),

$$i \frac{\partial}{\partial t} \Psi(\mathbf{R}, \mathbf{r}) = [T_{\text{nuc}} + H_{\text{el}}] \Psi(\mathbf{R}, \mathbf{r}). \quad (2.9)$$

For each $R_i$, the total wave function can be expanded in terms of the complete set of electronic wave functions, $\psi_j(\mathbf{R}, \mathbf{r})$, as is seen in Eq. (2.10) below,

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_{j=1}^{\infty} \Psi_{\text{nuc}}^{(j)}(\mathbf{R}) \psi_j(\mathbf{R}, \mathbf{r}). \quad (2.10)$$

$\Psi_{\text{nuc}}^{(j)}(\mathbf{R})$ is the nuclear wave function acting as the expansion coordinates in Eq. (2.10). Inserting the expansion of the total wave function into the TDSE yields

$$i \frac{\partial}{\partial t} \left[ \sum_{j=1}^{\infty} \Psi_{\text{nuc}}^{(j)}(\mathbf{R}) \psi_j(\mathbf{R}, \mathbf{r}) \right] = [T_{\text{nuc}} + H_{\text{el}}] \left[ \sum_{j=1}^{\infty} \Psi_{\text{nuc}}^{(j)}(\mathbf{R}) \psi_j(\mathbf{R}, \mathbf{r}) \right]. \quad (2.11)$$

The electronic problem at fixed nuclear geometry can be solved time-independently,

$$H_{\text{el}} \psi_j(\mathbf{R}, \mathbf{r}) = E_j(\mathbf{R}) \psi_j(\mathbf{R}, \mathbf{r}). \quad (2.12)$$

The energy eigenvalue $E_j(\mathbf{R})$ is the electronic energy for state $j$ at a specific nuclear geometry and $\psi_j(\mathbf{R}, \mathbf{r})$ are the eigenfunctions. If we solve Eq. (2.12) for a large number of nuclear positions we get the so called potential energy surface (PES) of this state. Inserting Eq. (2.12) into the Eq. (2.11), and using $T_{\text{nuc}} = \nabla_{\text{nuc}}^2$ (hence, $\nabla_{\text{nuc}}$ contains the summation, sign and the dependence on the mass of the nuclear kinetic energy operator), we get for the $j$th state,

$$i \frac{\partial}{\partial t} \Psi_{\text{nuc}}^{(j)}(\mathbf{R}) = \left[ \nabla_{\text{nuc}}^2 + E_j(\mathbf{R}) \right] \Psi_{\text{nuc}}^{(j)}(\mathbf{R})$$

$$+ \sum_{k=1}^{\infty} \left( 2 \langle \psi_j | \nabla_{\text{nuc}} | \psi_k \rangle \nabla_{\text{nuc}} \Psi_{\text{nuc}}^{(k)} + \langle \psi_j | \nabla_{\text{nuc}}^2 | \psi_k \rangle \Psi_{\text{nuc}}^{(k)} \right). \quad (2.13)$$
Notice that to make Eq. (2.13) more legible, "bracket formalism" is used to denote the integrals over electronic coordinates and the coordinate dependencies are suppressed. The two last terms are cross-terms of the nuclear kinetic energy operator. These are referred to as the non-adiabatic coupling elements and these terms are neglected in the Born-Oppenheimer (BO) [19] approximation. Hence, within BO we get for state $j$:

$$i \frac{\partial}{\partial t} \Psi^{(\text{nuc}),\text{BO}}_j(R) = \left[ \nabla^2_{\text{nuc}} + E_j(R) \right] \Psi^{(\text{nuc}),\text{BO}}_j(R).$$

(2.14)

Here $\Psi^{(\text{nuc}),\text{BO}}_j(R)$ is the nuclear wave function for the $j$th state.

The BO approximation is very useful since it greatly simplifies the solution of the molecular TDSE. However, there are cases where the approximation breaks down. When several energy eigenvalues to Eq. (2.12) are close in energy, the non-adiabatic coupling terms can become very large and the nuclear and electron dynamics can no longer be assumed to be independent.

### 2.2 The Hartree-Fock (HF) method

Electron-electron interactions make the electronic SE very complex to solve for multi-electron systems. The computations can be simplified by assuming that the motion of each electron behaves as if it was moving in the average field of the surrounding electrons, an approximation referred to as the independent-particle approximation. This approximation implies that the total N-particle electronic wave function, $\Psi$, can be expressed as a product of one-electron wave functions, referred to as the molecular spin orbitals $\phi_i$. The spin orbitals contain both a spatial part, $\psi(r)$, and a spin function, $\alpha$ or $\beta$, e.g. $\phi_i(x) = \psi(x)\alpha$. We still need to somehow account for the electron-electron interactions to get a solution with acceptable accuracy.

Electrons are fermions, and the electronic wave function must obey the Pauli exclusion principle [20]. We therefore construct it using a Slater determinant [21], which ensures the anti-symmetry of the total electronic wave function,

$$\Psi = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc} \phi_1(x_1) & \phi_2(x_1) & \ldots & \phi_N(x_1) \\ \vdots & \vdots & & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \ldots & \phi_N(x_N) \end{array} \right|. \quad (2.15)$$

The orbitals in Eq. (2.15) are conveniently constructed to be orthonormal. With the (normalised) wave function $\Psi$ as a starting point, the
variational principle can be used to determine an upper bound to the "true" energy.

The energies of the orbitals are obtained as the eigenvalues to the one-electron Fock operator

\[ F_i = \hbar_i + \sum_j (J_j - K_j). \]  \hspace{1cm} (2.16)

The first term on the right hand side in Eq. (2.16) is the one-electron operator \( \hbar_i \), which is associated with the motion of the \( i \)th electron and the attraction of this electron to all the nuclei. In the Fock operator the explicit electron-electron interaction is reformulated into effective one-electron operators. \( J_j \) describes the average Coulomb repulsion between an electron in the \( i \)th orbital, \( \phi_i \), and all the surrounding electrons, and is called the Coulomb operator. \( K_j \) is a result of the quantum mechanical anti-symmetry requirement of the wave function, preventing two electrons of the same spin from occupying the same spatial orbital, and is referred to as the exchange operator. The Hartree-Fock (HF) equation is given by:

\[ F_i \phi_i(x) = \epsilon_i \phi_i(x), \]  \hspace{1cm} (2.17)

where \( \epsilon_i \) is the orbital energy. The operator \( F_i \) is dependent on all the occupied spin orbitals which are used to construct the Fock matrix, Eq. 2.16. By solving Eq. (2.17) we obtain a new set of orbitals that can be used to construct a new Fock matrix and so on. Hence, by iteratively solving the Fock equation, we can converge the solution self-consistently and find the wave function for which the energy is minimised (below the threshold value that we choose). Because of this the HF method is also referred to as the self-consistent field (SCF) method. To obtain the total HF energy, we finally add \( V_{\text{nuc-nuc}} \) to the orbital energy.

The spatial part of the spin orbital, \( \psi(r) \), is commonly referred to as the molecular orbital (MO). To solve the HF equation, the unknown MOs are expanded in terms of a set of basis functions that are known. It is often convenient to use a basis consisting of approximate atomic orbitals, \( \chi_a(r) \), which are centred on the nuclei,

\[ \psi_i = \sum_a c_{ai} \chi_a(r). \]  \hspace{1cm} (2.18)

By inserting Eq. (2.18) into the HF equation we obtain the Roothan-
Hall equations [22; 23],

\[ F_i \sum_a c_{ai} \chi_a(r) = \epsilon_i \sum_a c_{ai} \chi_a(r). \quad (2.19) \]

Eq. (2.19) can be written as matrices:

\[ Fc = Sc \epsilon, \]

\[ F_{ab} = \int dr \chi^*_a(r) F_i \chi_b(r) \]

\[ S_{ab} = \int dr \chi^*_a(r) \chi_b(r) \quad (2.20) \]

c is the matrix containing the coefficients, \( c_{ai} \). By diagonalising \( F \), we obtain the energies of the MOs, as diagonal elements of \( \epsilon \) (provided we use an orthonormal basis).

### 2.3 Electron correlation and the configuration interaction method

The difference between the electronic energy we obtain from the HF method and the true (non-relativistic) electronic energy is defined as the correlation energy [24]. The origin of this difference is the use of the single Slater determinant form of the HF wave function which provides a limited description of the electron interaction (correlation) effects. This is not to say that electron correlation is completely neglected in the HF method, as correlation of electrons with the same spin, referred to as Fermi correlation, is included in HF. It is a consequence of the Pauli exclusion principle, which does not permit two electrons with the same spin to occupy the same spatial orbital. Coulomb correlation, referring to the interactions of electrons with opposite spin is, however, not accounted for in HF. Generally, the accuracy of the results obtained by HF is also reliant on the choice of the basis set and limited by the non-relativistic Hamiltonian.

The electron correlation can also be discussed in terms of short-range and long-range correlation effects. As the individual electrons approach one another, they will instantaneously repel each other. This effect is the so called dynamic correlation and referred to as short-range. As consequence of the mean-field description of the electron correlation in

In this equation \( F_i \) is expressed for spatial orbitals and is taking into account the spin part.
Hartree-Fock, the electrons are allowed to be closer to one another than what would permitted if the dynamic electron correlation was properly accounted for. Long-range correlation, called static correlation, is related to the electrons more permanently avoiding one another.

In many cases, however, the static correlation becomes important. When a molecule undergoes dissociation, the electrons that formed the bond may distribute onto different atoms; the textbook case being the dissociation of $\text{H}_2$ where the electrons from the $\text{H}−\text{H}$ bond localise on different $\text{H}$ atoms. Hence, dissociation results in degenerate electron configurations, i.e., the distribution of the electrons in the MOs, which can not be accommodated by the single determinant trial wave function. For many electronically excited states, we need a more flexible trial wave function where permutations of electrons, corresponding to excited state electron configurations, can be represented. In such cases, we, in general, have to adopt a multi-determinant description of the wave function.

A natural step to improve the HF method is to choose a trial wave function constructed using more than one determinant, so we can account for both dissociation and excited states. One such approach is the configuration interaction (CI) method. In this method the wave function is expanded into a linear combination of Slater determinants, where all but the first one correspond to excited state electron configurations:

$$\Psi_{\text{CI}} = c_0 \Psi_{\text{HF}} + \sum_S c_S \Psi_S + \sum_D c_D \Psi_D + \cdots = \sum_i c_i \Psi_i. \quad (2.21)$$

The first term in Eq. (2.21) corresponds to the ground state HF wave function (Eq. (2.15)). The other terms are the wave function for states that are singly ($S$) and doubly ($D$) etc. excited state electron configurations. If all possible determinants representing all possible permutations of electrons over the number of basis functions are included, the wave function is referred to as the full CI wave function. Generally, to reduce the computational cost, the CI expansion is truncated so only limited number of determinants are included, e.g. only singlet and doublet excitation (CISD). The CI expansion coefficients are determined through energy minimisation and the weight of the contributions of the different electron configurations in the total wave function. The MOs are obtained from a HF calculation and remain unchanged. Similarly to the HF method, the accuracy of the CI result relies on the choice of basis set, but generally we may regard the full CI as the most accurate method within the chosen basis set.
2.4 Multi-configurational self-consistent field (MCSCF) - complete active space (CAS)

In the *Multi-configurational self-consistent field* (MCSCF) approach not only are the CI expansion coefficients energy minimised but simultaneously the orbital coefficients, $c_{ai}$, are optimised in a self-consistent fashion (much like the "regular" SCF, only in MCSCF the number of electron configurations is greater than one). The MO coefficients that we obtain in this manner minimise the CI energy. The strength of the MCSCF method is that we can recover the static contribution to the electron correlation at limited cost compared to CI in systems where the correlation effect is significant. Due to the optimisation of the MO coefficients, with MCSCF we also obtain a more flexible set of MOs, which is not the case in regular CI. This is important in cases where the electron density is affected by the static correlation effects.

Figure 2.2: Orbital space in the Complete Active Space (CAS) (left) and the Restricted Active Space (RAS) subspaces (right).

An application of MCSCF with good convergence properties is the *Complete Active Space Self-Consistent Field* (CASSCF) method \[25\]. In this approach we first have to divide the orbital space into an *active space*, an *inactive space*, and a *secondary space*. In the inactive space, all the MOs are doubly occupied and the secondary space contains the virtual MOs. In the active space all possible permutations of electrons are allowed, and a full CI is performed within this set of orbitals meaning that we can use CASSCF both to improve the description of the ground state wave function, $\Psi_{GS}$, and to describe excited states of a molecule. The active orbital space partitioning can be seen in Fig. (2.2). However, the CASSCF calculations grow computationally demanding when many MOs are included in the active space.

A variation of CASSCF is the *Restricted Active Space Self-Consistent*
Field (RASSCF) method [26] where we further partition the active space into three smaller restricted active spaces (RAS), hence limiting the computational cost. In the RAS, restrictions on the electron redistribution in the active space are employed; in RAS1 the number of holes in the orbital is restricted, in RAS2 all permutations are allowed (effectively a full CI is performed), and, in RAS3, the number of electrons is restricted. A schematic representation of the RAS space is displayed in Fig. (2.2).

The accuracy of the RASSCF method crucially depends on the choice of active MOs included in the different RAS subspaces. Splitting a pair of degenerate orbitals in different active spaces, like the $e$-orbital pairs in the NH$_3$ molecule, will result in an unphysical orbital space, yielding unbalanced energies and transition dipole moments. For the calculation of resonant inelastic X-ray scattering (RIXS) (chapter 3) transition energies and spectra, which has been the work of this thesis, we want to target the ground state, as well as core-excited states and final states (which could be a valence-excited state or a lower lying core-excited state), and we need to use an active space that is suitable to perform these calculations in. A peculiarity of our calculations in Papers I-II and Paper V is that we employed the RAS3 space to reach the core-excited states without having to calculate all lower-lying states; the 1s MO was placed in the RAS3 space, while the other active MOs were placed in RAS2. The recent development of the "highly-excited-state" (HEXS) method [27], makes it possible to eliminate one electron from the RAS1 and/or the RAS3 space, without having to calculate all the lower energy states. The difference of HEXS to the previous computational approach, is that in HEXS only the 1$s^{-1}$ configuration is present in the solution. This method was employed for the calculation of the core-excited states of the H$_2$O molecule in Paper III. In the case of simultaneously targeting both the S1$s^{-1}$ core-excited and the S2$p^{-1}$ core-excited states of the H$_2$S molecule in Paper IV in order to model K$\alpha$ RIXS, the HEXS method was used; the S1s MO was placed in RAS3 and the S2p MOs were placed in RAS1.

For the calculation of the PESs for simulation of the K-edge RIXS in the H$_2$O molecule (Paper I-III) we included the following MOs in the active space; 1$a_1$(O1s), 2$a_1$, 1$b_2$, 3$a_1$, 1$b_1$, 4$a_1$, 2$b_2$, 2$b_1$, in addition to three virtual MOs to obtain a improved description of the states. In the case of preparation of the PESs intended for simulation of K-edge RIXS in the H$_2$S molecule (Paper IV), the following MOs were included; 1$a_1$(S1s), 2$a_1$(S2s), 1$b_2$, 3$a_1$, 4$a_1$, 2$b_2$, 5$a_1$, 2$b_1$, 3$a_1$, 6$a_1$. The five 3$d$ MOs were not included for the calculation of the PESs to manage the
computational demands. However, the accuracy of our results was evaluated by calculations with an extended active space at the equilibrium geometry, where \( C_{2v} \) symmetry could be employed to make the calculation more efficient. In the calculation of the transition energies of \( K \)-edge RIXS in NH\(_3\) (Paper V), the following MOs were included in the active space: \( 1a_1(\text{N}1\text{s}), 2a_1, 1\epsilon, 3a_1, 4a_1, 2\epsilon, 5a_1, 3\epsilon, 4\epsilon \). In the case of the NH\(_3\) and the H\(_2\)O molecules, the 1s MO is frozen from a previous HF calculation. In H\(_2\)S, the 1s and 2\( p \) MOs are frozen from a RASSCF calculation. These MOs are frozen to prevent them from rotating at core-excitation.

All three molecules (H\(_2\)O, H\(_2\)S and NH\(_3\)) include low-lying Rydberg orbitals. To account for the character of these MOs, the main basis set was augmented with a diffuse basis set centred at the central atom (O, S, and N).

The RASSCF calculations were performed using the MOLCAS software (versions 7.4-8.2) [28–31].

2.5 Second-order perturbation theory

The MCSCF methods mainly account for the effect of static correlation. The solution can be improved using perturbation theory to recover more of the dynamic correlation. The basic assumption is that the solution we have found only differs from the exact solution by a small perturbation. We need then to formulate a perturbed Hamilton operator by selecting an unperturbed reference Hamiltonian and then add the perturbation, \( \mathbf{H} = \mathbf{H}^0 + \lambda \mathbf{H}' \), where \( \lambda \) is a dimensionless parameter describing the strength of the perturbation. The exact energy and wave function is then expanded in terms of the reference solutions, \( E = E^0 + \lambda E_1 + \lambda^2 E_2 + \ldots \) and \( \Psi = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \ldots \). In Møller-Plesset perturbation theory (MP) [32], the reference Hamiltonian is created by summing over all the Fock operators, \( \mathbf{F}_i \). The MP perturbation method is characterised by how many of the energy correction terms that are included; if all orders of correction terms are included, all dynamic correlation is recovered. If the terms up to the second order correction are included, the method is referred to as second order or MP2. By including some of these terms in the energy, we can get a more complete description of the electron correlation.

The CAS/RAS-SCF method manages to describe the static correlation well due to the multi-configurational wave function. However, to represent the dynamical correlation, we need to employ the CAS/RASP-PT2 [33; 34] method. CASPT2 combines second-order perturbation
with multi-configurational CASSCF reference states.

2.6 Relativistic effects

Up to this point, we have assumed that the system behaves non-relativistically. However, the relativistic correction is important for properties such as ionisation potentials and excitation energies, and will affect dissociation energies, etc. Taking the relativistic effects into account is, therefore, important for describing core-excited states. Relativistic quantum chemistry is described by the relativistic wave equation, the Dirac equation [35]. The solutions of the Dirac equation are four-component wave functions.

In the Douglas-Kroll-Hess (DKH) [36; 37] approach, the four-component wave function is transformed to a two-component formalism through block-diagonalisation of the Dirac Hamiltonian with a unitary operator composed of a sequence of simple unitary transformations. In our applications we have employed the second order Hamiltonian. The transformed two-component Hamiltonian can further be separated into a spin-free and spin-orbit parts. For the scalar relativistic effects, the one-electron term of the spin-free Hamiltonian is included but the relativistic contribution to the two electron interactions is neglected. For the spin-orbit coupling both one- and two-electron integrals are considered but, usually, approximations to the full SO-Hamiltonian have to be made. One such approximation is the Atomic Mean Field Integral [38; 39] approximation wherein the full SO Hamiltonian is expressed with a mean-field operator and only the spin-orbit coupling within an atom is considered, i.e., the multi-center integrals are neglected.

By adding the scalar relativistic corrections to the CASPT2 energies, we obtain accurate results in close agreement with experiment.

In Papers I-V, scalar relativistic corrections were included for the calculations of the H$_2$O, H$_2$S, and NH$_3$ molecules within the second order DKH approach implemented in MOLCAS software (versions 7.4-8.2) [28–31]. In kaolinite (Paper VI), relativistic effects are only implicitly included through the parameterisation of the pseudopotentials (see section 2.7).

2.7 Density functional theory (DFT)

An alternative method to determine the electronic energy of a system is by using Density Functional Theory (DFT). The fundamental idea be-
Hind DFT is that the electron density, $\rho(\mathbf{r})$, uniquely determines the electronic energy of the ground state, proven by Hohenberg and Kohn [40]. Hence, we do not need information about the wave function. The electronic energy is a functional of the electron density:

$$E_{\text{DFT}}[\rho] \equiv \int U_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho]$$

$$F[\rho] = T[\rho] + V[\rho].$$

Where $U_{\text{ext}}(\mathbf{r})$ is an external potential specific to every system, and $E_{\text{DFT}}[\rho]$ is the DFT functional of a specific electron density, $\rho$. $F[\rho]$ is an universal functional, i.e., it is independent of $U_{\text{ext}}(\mathbf{r})$, and $T[\rho]$ and $V[\rho]$ are the universal electronic kinetic energy and the potential energy functionals, respectively. The functional form of $F[\rho]$ is unknown, and needs to be determined (or rather approximated). The first attempts to approximate the functional $F[\rho]$ were formulated in an orbital-free framework based on a uniform electron gas using the Thomas-Fermi model [41; 42]. However, the functionals derived in this model was not useful in the case of molecules as the model does not describe molecular bonding. Furthermore, sufficiently accurate approximations of the functional for the kinetic energy were not available.

A development from the "orbital-free" DFT is the Kohn-Sham (KS) [43] DFT. In KS theory we make the ansatz that there exists a system of non-interacting electrons represented by a effective potential, which is constructed in such a way that it produces the same electron density as the desired system with interacting electrons. The DFT functional of KS theory is written in the following form:

$$F[\rho] = T_{\text{KS}}[\rho] + J[\rho] + E_{\text{XC}}[\rho].$$

$J[\rho]$ is the Coulomb energy functional and $E_{\text{XC}}[\rho]$ is the exchange-correlation energy functional. $T_{\text{KS}}[\rho]$ is the KS kinetic energy functional for the system of non-interacting electrons. It is constructed by non-interacting single particle KS orbitals (much like the HF wave function in Eq. (2.15) is constructed of one-electron orbitals). Compared to the orbital-free theory, the orbital description gives an improved representation of the kinetic energy,

$$T_{\text{KS}}[\rho] = -\frac{1}{2} \sum_i^{N_{\text{el}}} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{N_{\text{el}}} |\phi_i(\mathbf{r})|^2.$$
Hence, to obtain the electron density we need to know the KS orbitals. The electron density is determined in a self-consistent fashion similar to the HF method; starting with an initial guess of the electron density, generating the effective potential and calculating the KS orbitals and the new density, iterating until convergence is reached. The DFT energy functional in KS theory is given by:

\[ E[\rho] = \int U_{\text{ext}}(r)\rho(r) \, dr + T_{\text{KS}}[\rho] + J[\rho] + E_{\text{XC}}[\rho] \tag{2.25} \]

The exact exchange-correlation functional still remains unknown. However, there exist many different methods to derive approximate exchange-correlation functionals and the accuracy of the functional is crucial for the quality of the calculation. In HF, the exchange energy is evaluated exactly in terms of the antisymmetry of the wave function and in DFT, the exchange approximated in terms of the electron density and added to the total energy as a part of the exchange-correlation functional. However, the dynamical correlation energy that is also included in the exchange-correlation functional in DFT is not present in regular HF but can be added on top by perturbation theory or CI in higher order methods.

In Paper VI, the PESs of kaolinite are calculated within the periodic plane wave DFT implementation of the CPMD \cite{44, 45} computational software. Here we see the system as a Bravais lattice; a set of unit cells that are repeated to infinity where each point in this space is defined by a lattice vector in real space, \( \mathbf{R} = n_1a_1 + n_2a_2 + n_3a_3 \). We obtain the wave function of the periodic system of non-interacting electrons using the Bloch theorem:

\[
\psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) \, e^{i \mathbf{k} \cdot \mathbf{r}} \\
u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r}).
\tag{2.26}
\]

The total wave function is now expressed in terms of the wave vectors, \( \mathbf{k} \), mapping the first Brillouin zone. Hence, instead of obtaining the wave function in terms of an infinite number of KS orbitals, we now obtain it for the infinite set of \( \mathbf{k} \). \( u_{nk}(\mathbf{r}) \) is a periodic function with is repeated in each unit cell and \( n \) is referred to as the finite number of band indices. Eq. (2.26) implies that the periodic one-electron wave function needs only to be calculated for the unit cell in the periodic system. However, the wave function may still need to be evaluated in many \( \mathbf{k} \)-points. If the simulation cell is very large, the effect of dispersion is negligible, and we only need to sample the \( \Gamma \)-point, \( \mathbf{k} = (0,0,0) \), as in the case for the calculations of the PESs in Paper VI performed in CPMD \cite{44, 45}.
Each function \( u_k^n(r) \) is expanded in a basis set, \( e.g. \) plane wave basis functions, as in the method employed in Paper VI. There are several benefits of the plane wave basis functions; \( e.g. \) they are not reliant on the position of the atoms, they are orthogonal, convergence is controlled by a single parameter (the energy cutoff). However, a drawback of the plane wave basis is that the number of plane waves needed may grow very large, especially for the rapidly changing wave functions in the core region. A way to economise on the plane waves is therefore to use so-called \textit{pseudopotentials} to approximate the interactions of the nucleus and the core electrons. It is important that the pseudopotential reproduces the same physical valence properties, as the all electron potential for different chemical environments. This is referred to as the transferability of the pseudopotential. In competition with this requirement, we also want the pseudopotentials to be \textit{soft}, meaning that the pseudo valence orbitals can be described with as few plane waves as possible.

To calculate the X-ray absorption spectra in Paper VI a basis of \textit{Gaussian Type Orbitals} (GTO) was used to access O1s.
In this thesis we will in general discuss X-ray spectroscopy as X-ray induced transitions from an initial state to a final state (either directly or via an intermediate core-excited state), a perspective we refer to as the state or total energy representation. However, it may still be more transparent to give an overview of different X-ray spectroscopy techniques by first discussing one electron transitions between molecular orbitals, the molecular orbital (MO) representation. However, as will be seen, not only electronic transitions are probed with X-ray spectroscopy. The final states may also be vibrationally excited states, something that is not readily reflected in the one electron transitions.

In the MO representation, the molecular orbitals of the system are divided into core orbital(s), occupied valence orbitals, and unoccupied (virtual) orbitals. The core orbital(s) do not overlap significantly with the other molecular orbitals and, hence, they are not strongly influencing the chemical bonding in the system. Valence orbitals, on the other hand, strongly influence the chemical bonding. An incoming X-ray photon interacts with the core electrons in the system and can, with sufficient frequency, excite an electron from a core orbital to a virtual orbital, as in the case of X-ray absorption spectroscopy (XAS), or even cause ejection of core electron as a photoelectron, as in X-ray photoelectron spectroscopy (XPS). The process wherein an electron drops down to the core orbital from an occupied molecular orbital may result in emission of an X-ray photon, as in X-ray emission spectroscopy (XES). All three processes are illustrated in Figure (3.1).

To describe spectroscopic processes involving multiple electron transitions, it is more convenient to use the state representation. In resonant inelastic X-ray scattering (RIXS) the incoming X-ray photon is scattered against a core-excited state to the final state, emitting a secondary X-ray photon. In other words, RIXS is a coherent scattering process where both an X-ray absorption (XA) and an X-ray emission (XE) process takes place. However, the core-excited state may also decay by emission of an electron, as a result of the Auger effect, which is detected in Auger electron spectroscopy.
In the present section we will go deeper into the theoretical framework of the XAS and RIXS spectroscopic techniques, as these techniques are related to the results presented in the appended papers.

3.1 Note on conventions

In this and the following chapter, the equations relating to XAS and RIXS will be presented, both in time-independent representation (this chapter) and time-dependent representation (chapter 4). To make it easier to follow the derivations, we will first establish the convention of notation that will be used.

The ground, core-excited, and final electronic states are denoted $|0\rangle$, $|c\rangle$, and $|f\rangle$, respectively. The energy minimum of the PES of the ground, core-excited, and final states are denoted $E_0$, $E_c$, and $E_f$, respectively. We also introduce a notation for the frequency between the minima of the ground state and the core-excited state PESs, $\omega_{0c} = E_c - E_0$, and the frequency between the minima of the ground state and the final state PESs, $\omega_{0f} = E_f - E_0$.

The vibrational states of the ground, core-excited, and final states are denoted $|\nu_0\rangle$, $|\nu_c\rangle$, and $|\nu_f\rangle$, respectively, and the corresponding vibrational energies, $\epsilon_{\nu_0}$, $\epsilon_{\nu_c}$, and $\epsilon_{\nu_f}$, respectively.

The frequency of the incoming and emitted photons are denoted $\omega$ and $\omega'$, respectively. $\mathbf{e}$ and $\mathbf{e}'$ are the electronic polarisation vectors of the incoming and emitted photons, respectively. The transition dipole moment from the ground state, $|0\rangle$, to the core-excited state, $|c\rangle$ is denoted, $\mathbf{d}_{0c}$, and the transition dipole moment from the core-excited state, $|c\rangle$, to the final state, $|f\rangle$, is denoted, $\mathbf{d}_{cf}$.
3.2 X-ray absorption spectroscopy (XAS)

Using the notation we have established, XAS is described by Eq. (3.1),

\[ |0\rangle + \omega \rightarrow |c\rangle. \quad (3.1) \]

That is, an incoming X-ray photon of frequency \( \omega \) is absorbed in the ground state \( |0\rangle \), bringing the system to a core-excited state \( |c\rangle \).

Experimentally, the transmission in X-ray absorption can be detected directly by measuring the intensity of the incoming and the transmitted beam. An indirect way to detect the XAS transmission is to measure the photons that are emitted when an electron from a valence orbital fills the core hole. This method is referred to as *fluorescence yield* (FY) or *partial fluorescence yield* (PFY) if detection is limited to photons in a specific energy interval. If the *electron yield* (EY) method is used, the photoelectrons, Auger electrons, secondary electrons, etc, emitted by the X-ray absorption are detected. If all electrons, regardless of their energy, are detected, the *total electron yield* (TEY) is measured and if, based on their energies, only a fraction of the electrons are detected, it is called *partial electron yield* (PEY).

3.2.1 Absorption intensity

The probability of transition for a system in the initial state, say the vibrational ground state \( |\nu_0\rangle \), to a vibrational core-excited state \( |\nu_c\rangle \), is called the absorption cross section, and is given by Fermi’s golden rule [5]. Within the *dipole approximation*, Fermi’s golden rule takes the following form:

\[
\sigma_{0c}(\omega) = \sum_{\nu_c} \left| \langle \nu_c | (\mathbf{e} \cdot \mathbf{d}_{0c}) | \nu_0 \rangle \right|^2 \frac{\Gamma_c / \pi}{(\omega - \omega_{c0} - (\epsilon_{\nu_c} - \epsilon_{\nu_0}))^2 + \Gamma_c^2} \quad (3.2)
\]

Within the Franck-Condon approximation [46; 47] (see chapter 4), the transition dipole moment, \( \langle \mathbf{e} \cdot \mathbf{d}_{0c} \rangle \), of the absorption is constant, and can be lifted outside the sum in Eq. 3.2. \( \langle \nu_c | \nu_0 \rangle \) is then referred to as the Franck-Condon (FC) factor between the initial states, and the core-excited states and is summed over \( |\nu_c\rangle \). \( \Gamma_c \) is the lifetime broadening of the core-excited state, which will be discussed in more detail in the next section. If there are more than one core-excited state involved in XAS, we would also need to add a sum over all these states in Eq. (3.2).

We can define the transition intensity from the vibrational ground state to a specific vibrational core-excited state, \( |\nu_c\rangle \), as

\[ I_{0c} \propto \left| \langle \nu_c | \mathbf{e} \cdot \mathbf{d}_{0c} | \nu_0 \rangle \right|^2. \quad (3.3) \]
$I_0$ is dependent of the direction of the incoming radiation with respect to the orientation of the molecules in the sample. The intensity in Eq. (3.3) applies to transmission XAS. However, the intensity detected with FY, PFY or EY might deviate from this expression.

3.2.2 The core-hole lifetime

The core-excited state $|c\rangle$ is populated in the XAS process. A core-hole in heteronuclear molecules is localised [5] and therefore XAS can be used for element-specific investigations of the unoccupied valence. The core-excited state will undergo electronic relaxation exponentially with time $\tau$, referred to as the lifetime of the core-excited state, either through fluorescence (radiative) decay or Auger decay. The net lifetime of the core-excited state is decided by the sum of the respective decay rates of these two processes,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}}.$$  

(3.4)

For core-excitation in elements of small $Z$, $\tau_{\text{Auger}} \ll \tau_{\text{rad}}$. Hence, for light elements the core-excited state lifetime will be determined by the rate of the Auger decay. The lifetime broadening of the core-excited state, $\Gamma_c$, is characterised by the Heisenberg uncertainty relation,

$$\frac{1}{\Gamma_c} \leq \tau.$$  

(3.5)

Due to the uncertainty relation, Eq. (3.5), we will see a broadening of the spectral width in core-level excitation spectra for short core-hole lifetimes, commonly referred to as the natural lifetime broadening effect. Thus, as a consequence of the time-energy uncertainty relation, a shorter lifetime will result in broader spectra. This is the case for the $\text{H}_2\text{O}$ (Papers I-III) and $\text{H}_2\text{S}$ (Paper IV) molecules upon the $K$-edge excitation. The lifetime broadening is represented by a Lorentzian function. Another source of broadening of the spectral line shape originates from the resolution of the measuring equipment, the instrumental broadening. If the lifetime of the core-excited state is very short, the lifetime broadening may dominate, and we get a Lorentzian spectral shape. When the instrumental broadening is the limiting factor, we instead get a broadening that can be described by a Gaussian shape. Vibrations in molecules also give rise to broadening due to the nuclear dynamics of the core-excited state. In extended systems, such as liquids or a solid clay material like kaolinite (Paper VI), the vibrational modes are not as well separated and vibrational excitations will give rise to a Gaussian broadening of the spectral shape. There also arises a broadening from the statistical
distribution of configurations due to interactions with the environment, referred to as *configurational broadening*, which can be represented with a Gaussian distribution of the energy [48]. In most cases the combined effect of the different types of broadening means that the spectral shape is described by a convolution of the Gaussian and Lorentzian line shapes. For theoretical spectra presented in the papers included in this thesis, the broadening is accounted for by convoluting the calculated discrete spectrum Gaussians of a suitable full-width-at-half-maximum (Papers IV and V) or included explicitly as effects of nuclear motion and finite lifetime (Papers I-III and VI).

3.3 Resonant inelastic X-ray scattering (RIXS)

![Figure 3.2: Schematic representation of the states and transitions in the RIXS process.](image)

In RIXS, the incoming X-ray photon $\omega$ is scattered with frequency $\omega'$ as the molecule in the core-excited intermediate state decays to the
The final state can either be an electronically excited state and/or e.g. a vibrationally excited state. The process involving scattering back to the initial electronic state including vibrational excitations or excitations in other low energy degrees of freedom (e.g. rotations), such as RIXS in kaolinite (Paper VI) and the H$_2$O molecule (Papers I-III), is referred to as "quasi-elastic". For inelastic scattering, we gain site-specific information of the electronic structure of the excited states and the energy transferred in the process then corresponds to the energy of valence excitation (if the final state is valence-excited state) or core-excitation (if the final state is a low lying core-excited state) and vibrational excitation. For the quasi-elastic process, we probe the local vibrational structure of the initial(= final) state, and the energy transfer corresponds to the transitions between the vibrational levels. For example, RIXS can be used to probe rotational, magnetic and phonon (solids) excitations in molecular systems.

The relation between the frequency of the outgoing particle and the excitation energy is given by energy conservation:

$$\omega' = \omega - \omega_f,$$

which shows the Raman dispersion law. It is convenient to represent the RIXS spectra in terms of energy loss, defined as the difference in energy of the incoming and outgoing photon, $\omega - \omega'$, from which we can directly determine the energies of the quantum levels and electronic excitations in the system.

### 3.3.1 Kramers-Heisenberg equation and the RIXS cross section

The RIXS cross section for the transition to a vibrational state $|\nu_f\rangle$, is given by Kramers-Heisenberg [49] equation:

$$\sigma(\omega', \omega) = \sum_{\nu_f} |F_{\nu_f}|^2 \cdot \Delta(\omega - \omega_f - \omega_f^0 - (\epsilon_{\nu_f} - \epsilon_{\nu_0}), \Gamma_f).$$

(3.8)

Where $\Gamma_f$ is the lifetime broadening of the final state. The scattering amplitude, $F_{\nu_f}$, is given by:

$$F_{\nu_f}(\omega', \omega) = \sum_{\nu_c} \frac{\langle \nu_f | \mathbf{d}_{\mathbf{ef}} | \nu_c \rangle \langle \nu_c | \mathbf{d}_{\mathbf{0c}} | \nu_0 \rangle}{\omega - \omega_{\mathbf{0c}} - (\epsilon_{\nu_c} - \epsilon_{\nu_0}) + i\Gamma_c}.$$ 

(3.9)
In the denominator of Eq. (3.9) the lifetime broadening of the core-excited state, $\Gamma_c$, is taken into account.

To prepare for chapter 4, where the RIXS cross section is formulated in the time-dependent representation, we may alternatively use the following wave packet expression for the core-excitation:

$$|\Psi_{cf}(t=0)\rangle = i \sum_{\nu_c} \frac{\langle \nu_c | (e' \cdot d_{cf}) | \nu_0 \rangle}{\omega - \omega_{\nu_0} - (\epsilon_{\nu_c} - \epsilon_{\nu_0}) + i \Gamma_c}.$$

Eq. (3.10) highlights that core-excitation results in a coherent superposition of the core-excited states $|\nu_c\rangle$. Using Eq. (3.10) we obtain the following expression for the RIXS scattering amplitude:

$$F_{\nu_f}(\omega', \omega) = -i \langle \nu_f | \Psi_{cf}(0) \rangle.$$  

Eq. 3.11 shows that the scattering amplitude, in fact, the projection of the core-excited wave packet $|\Psi_{cf}(0)\rangle$ on the final states, $|\nu_f\rangle$. $\Delta = \Gamma_f/(\pi(x^2 + \Gamma_f^2))$ is a Lorentzian function with the half-width-at-half-maximum of the final state lifetime, $\Gamma_f$, describing the energy conservation law, Eq. (3.7), in the Raman process

$$\Delta(\omega - \omega' - \omega_{f0} - (\epsilon_{\nu_f} - \epsilon_{\nu_0}), \Gamma_f) = \frac{\Gamma_f/\pi}{(\omega - \omega' - \omega_{f0} - (\epsilon_{\nu_f} - \epsilon_{\nu_0}))^2 + \Gamma_f^2}.$$  

(3.12)

Just like in XAS, to reproduce the experimental measurements, the cross section in Eq. (3.8) has to be additionally convoluted to account for the instrumental broadening and incoming photon bandwidth, as well as the configurational broadening and the long-range interactions in extended systems [7].
4. The core-excited state dynamics

During the RIXS process the electronic and nuclear relaxation of the core-excited state gives rise to the energy loss channels corresponding to scattering to valence-excited, lower lying core-excited states, as well as vibrationally excited states. The nuclear relaxation is comparable to the core-excited state lifetime, as the nuclei move on a considerably slower timescale than the electrons. This means that for many systems the core-excited state lifetime is too short for the molecule to undergo any detectable geometric changes. Nevertheless, for some systems, nuclear dynamics on the timescale of the core-excited state lifetime, referred to as ultrafast nuclear dynamics, play an important role in the RIXS process [8; 9; 11]. The Franck-Condon approximation [46; 47] states that the transition dipole moment for a vertical electronic transition does not depend on the nuclear coordinates. This means that the transition dipole can be separated out from the cross section. For the initial core-excitation the Franck-Condon approximation holds, as the initial state is well localised around the energy minimum. However, for processes where, e.g. the molecular symmetry is broken or the electronic states are close in energy, the Franck-Condon approximation breaks down. This often occurs for RIXS transitions, which is exemplified by the water molecule in Paper III.

The nuclear dynamics is strongly affected by the character of the potential energy surfaces (PESs) of the ground, core-excited, and final states. The timescale of the nuclear relaxation depends on the gradient of the potential energy surface at vertical excitation or at decay. A difference of the equilibrium geometry of the molecule in the ground state, the core-excited state, and the final state, gives rise to vibrational excitation. If the core-excited state is dissociative, the timescale of the nuclear relaxation is comparable to the dissociation time, and the RIXS spectrum will be decided by the relationship between the decay rate and the dissociation rate, a process referred to as ultrafast dissociation. This is the case for the inelastic RIXS process of the H$_2$O molecule in Paper III, where we see contribution from scattering both in the intact
molecule as well as in the OH fragment.

![Figure 4.1: Schematic representation of 1D electronically elastic RIXS process in which the core-excited state is allowed to evolve in time, thereby resulting in excitation of the vibrational levels in the RIXS spectra.](image)

The dynamics in the core-excited state in the study of NH$_3$(g) in Paper V was simulated using a classical approach, and the emission energies of the 1e$^{-1}$ and 3a$^{-1}$ absorption lines at the equilibrium geometry were calculated using the RASPT2 method. In the following section, I will instead base the discussion of the simulation of the nuclear relaxation on the time-dependent wave packet approach to calculate the cross section employed to simulate the influence of core-excited dynamics in RIXS of the H$_2$O molecule and kaolinite, presented in Papers I-III and Paper VI, respectively. Fig. (4.1) displays the schematics of a quasi-elastic RIXS process, a process similar to the study of the local vibrations of the hydroxyl groups along one 1D vibrational mode in kaolinite in Paper VI.

4.1 Solving the time-dependent nuclear problem

To simulate nuclear dynamics of RIXS we explicitly solve the time-dependent Schrödinger equation (TDSE). This way we can account for the displacements of the nuclear geometry as a response to the electronic relaxation in the simulated RIXS spectrum. We remind ourselves of the formula for the TDSE for the nuclear wave function under the Born-Oppenheimer approximation from chapter 2 where the non-adiabatic
coupling elements are neglected,
\[ \frac{\partial}{\partial t} \Psi^\text{BO}_j (\mathbf{R}) = [\mathbf{T}_{\text{nuc}} + E_j (\mathbf{R})] \Psi^\text{BO}_j (\mathbf{R}) = \mathbf{H}_j \Psi^\text{BO}_j (\mathbf{R}). \] (4.1)

\( \Psi^\text{BO}_j \) is the Born-Oppenheimer nuclear wave function for the \( j \)th electronic state (where "nuc" index is now only implied), and \( E_j (\mathbf{R}) \) is the \( j \)th electronic potential energy surface at a nuclear geometry \( \mathbf{R} \).

To obtain the potential energy surface \( E_j (\mathbf{R}) \) we need to solve the electronic time-independent SE (Eq. (2.12)) for different nuclear geometries.

4.2 The wave packet picture

The cross section of RIXS can be expressed in terms of the frequencies of the incoming and emitted photons, as seen in Eq. (3.8). In this formulation we need to sum over the contributions of the different vibrational states of the core-excited and final states. However, for some processes or systems, i.e., for modelling of RIXS involving dissociative states or vibrationally resolved RIXS, it may be more efficient to calculate the RIXS cross section in a time-dependent formalism [50]. Let us therefore summarise the equations for derivation of the time-dependent RIXS cross section that we have applied in Papers I-III and Paper VI. The derivation can be found in full in the following publications [7; 50].

In line with the conventions we established in section 3.1, we denote the initial, intermediate core-excited and final electronic states with the indices 0, c, and f respectively and the corresponding vibrational states with indices \( \nu_0 \), \( \nu_c \), and \( \nu_f \), respectively. The dynamics of the wave packet on the core-excited states is defined as,

\[ |\psi_c (t)\rangle = e^{-i \mathbf{H}_c t (\mathbf{e} \cdot \mathbf{d}_0)} |\nu_0\rangle \] (4.2)

where \( |\nu_0\rangle \) is the ground state vibrational wave function, generally taken as \( \nu = 0 \), which is used as an initial condition for the dynamics in the core-excited state. \( \mathbf{H}_c \) is the nuclear Hamiltonian of the core-excited state. The integrated wave packet, hence containing the contribution of the core-excited state dynamics of the full time-evolution on the core-excited state potential, \( |\Psi_{cf} (0)\rangle \), is used as the initial condition to the nuclear dynamics of the final state(s), respectively,

\[ |\Psi_{cf} (0)\rangle = (\mathbf{e} \cdot \mathbf{d}_{cf}) \int_0^\infty dt e^{i (\omega - \omega_c 0 + \epsilon_{\nu_0} + i \Gamma_c) t} |\psi_c (t)\rangle, \]

\[ |\Psi_{cf} (t)\rangle = e^{-i \mathbf{H}_f t} |\Psi_{cf} (0)\rangle. \] (4.3)
\( H_f \) is the nuclear hamiltonian of the final state. Hence, the wave function \( |\Psi_{cf}(0)\rangle \) is nothing more than the wave packet in Eq. (3.10) rewritten in the time-dependent representation. By taking the half-Fourier transform of the autocorrelation function, the RIXS cross section, \( \sigma(t) \), is obtained,

\[
\sigma(\omega', \omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i(\omega - \omega' + \epsilon_{v_0} + i\Gamma_f)t} \sigma(t), (4.4)
\]

\[
\sigma(t) = \langle \Psi_{cf}(0)|\Psi_{cf}(t)\rangle.
\]

Here, the following relation has been used:

\[
\Delta(\omega - \omega' - \omega_{f0} - (\epsilon_{v_f} - \epsilon_{v_0}), \Gamma_f) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i(\omega - \omega' - \omega_{f0} - \epsilon_{v_f} + \epsilon_{v_0} + i\Gamma_f)t}. \tag{4.5}
\]

From the expression for \( |\Psi_{cf}(0)\rangle \) in Eq. (4.3), we may work out the following (conceptual) complex scattering duration time \([7; 51]\):

\[
\tau_d = \frac{1}{\Gamma_c - i\Omega}, \quad \Omega = \omega - \omega^{\text{XAS}}
\]

\[
|\Psi_{cf}(0)\rangle = (e' \cdot d_{cf}) \int_0^\infty dt e^{-t/\tau_d} e^{i\delta} |\psi_c(t)\rangle. \tag{4.6}
\]

Here, \( \omega^{\text{XAS}} \) is the vertical transition frequency corresponding to the maximum intensity of the XAS process and we have defined \( \delta = \omega^{\text{XAS}} - \omega_{c0} + \epsilon_{v_0} \) for convenience of notation. \( \Omega \) is the amount of detuning of the incoming photon frequency from \( \omega^{\text{XAS}} \). The scattering duration of RIXS is, hence, characterised by the core-excited state lifetime, \( 1/\Gamma_c \), that describes the depopulation of the core-excited state following the excitation, and the detuning, \( 1/|\Omega| \). It is common to refer to the real scattering duration:

\[
\tau = |\tau_d| = \frac{1}{\sqrt{\Gamma_c^2 + \Omega^2}}. \tag{4.7}
\]

Eq. (4.7) shows that \( \tau \) goes to zero for large detuning \( |\Omega| \). The detuning is, in other words, a powerful tool for controlling the dynamics of RIXS \([7]\).

### 4.2.1 Multidimensional nuclear dynamics

The nuclear dynamics of RIXS in polyatomic molecules and molecular systems can become very complex to evaluate due to the influence of multiple nuclear degrees of freedom. It may therefore be necessary to reduce the complexity by following the dynamics only along coordinates that are likely to be excited.
One approach is to generate nuclear geometries along normal mode coordinates, and represent the multidimensional PES of the state by 1D cuts along coordinates in which the nuclear dynamics occurs. This is the case for the simulation of the vibrationally resolved RIXS spectra of kaolinite presented in Paper VI. For this system we opted to decouple the vibrational motion of one species of hydroxyl from the environment and follow the core-excited state dynamics along the coordinate of the six vibrational degrees of freedom (1×stretching, 1×in-plane rotation, 1×out-of-plane rotation, 3×translation) individually. This approach was motivated by the locality of the of the RIXS probe. The "1D model" makes it possible to simulate vibrationally resolved spectra in complex environments at a relatively modest computational cost. In the case of kaolinite, we are able to identify which degrees of freedom are excited by RIXS. However, the 1D model does not account for mode coupling, which may often be necessary to describe the anharmonic PES of molecules. For kaolinite, the absence of mode coupling in our model results in strong RIXS features in the theoretical spectrum which are smeared by lower frequency vibrations (stretching and rotations) in the experimental spectrum.

For systems where the coupling between the vibrational modes is strong, the 1D model may not be sufficient for describing the nuclear dynamics. In such systems, we need to represent the mode coupling in the PES. This is the case for the H$_2$O molecule, investigated in Papers I-III, where the strong mode coupling of the symmetric and asymmetric stretching modes combined with anharmonicity of the PES, makes it necessary to explicitly treat the stretching motions in 2D. However, the coupling of the bending mode with the stretching mode is weak in comparison to the coupling of the symmetric-asymmetric stretching modes. Hence, we may reduce the complexity of the dynamics by treating the bending mode in 1D. The "2D+1D model" [8] makes it possible to simulate accurate spectra for quasi-elastic RIXS of H$_2$O presented in papers I-II, without having to do a potentially more computationally arduous 3D treatment of the nuclear dynamics. In paper III both the quasi-elastic scattering and the inelastic scattering to the $|1b_1^{-1}, 4a_1^1\rangle$ valence-excited state against the lowest resonance are modelled. The bending mode is not excited in the lowest core-excited state [8; 9] nor in the valence-excited state. Hence a "2D model", where the bending mode is neglected, was employed.

The 2D, or alternatively the 2D+1D (if there is excitation of the bending mode) model will also be necessary to simulate the K-edge RIXS spectra of H$_2$S molecule (Paper IV), due to the same mode cou-
pling of the stretching mode as in the H$_2$O molecule.

Another aspect to consider for multidimensional nuclear dynamics is the Hamiltonian nuclear kinetic operator. As mentioned in chapter 2, the normal modes coordinates are only well defined for a harmonic PES, i.e., in general they only give a good description for small displacements from the minimum. If the RIXS process is affected by dynamics for large nuclear distortions, normal modes coordinates may not be a suitable choice. Instead we can use a coordinate system where the molecular bonds and angles are defined explicitly, e.g., the valence coordinate system ($R_1, R_2, \theta$). In the H$_2$O molecule, the 2D stretching PES of both the first core-excited and the first valence-excited states are dissociative, and the PES of the second core-excited state also deviates from the harmonic approximation. It therefore makes sense to express the 2D stretching PESs in valence coordinates. The 1D PESs of the bending modes of H$_2$O are bound, and there are only small nuclear distortions at core-excitation. Hence, we can use normal modes coordinates. However, the normal modes distortion vector of bending contains a small contribution of stretching. So, to ensure a symmetric bending PES, we performed the angular distortion at a fixed bond length.

For kaolinite we used normal modes coordinates to generate the PES of the ground state and core-excited state. However, motivated by the locality of the excitation, we extracted the normal mode coordinates in a frozen environment.

4.2.2 Simulating 1D RIXS

The RAM wave packet propagation program [52; 53] was used to simulate the 1D RIXS spectra of kaolinite, presented in Paper VI. The 1D nuclear dynamics were performed by solving the TDSE for the nuclear Hamiltonian in normal modes coordinates, $Q$:

$$
H_j = -\frac{1}{2\mu_i} \frac{\partial^2}{\partial^2 Q_i} + E_j(Q_i).
$$  \hspace{1cm} (4.8)

The states are denoted by $j = c, f$. $E_j(Q_i)$ is the 1D PES calculated along the normal mode coordinate $Q_i$, and $\mu_i$ is the reduced mass for this mode.

The RIXS cross section is calculated along each mode individually using Eqns. (4.2-4.4) for a quasi-elastic process.
4.2.3 Simulating 2D + 1D RIXS

The eSPec wave packet propagation program \[54; 55\] was used for simulating the RIXS spectra of the H$_2$O molecule. The nuclear dynamics of the 2D stretching mode is obtained by solving the TDSE, Eq. (4.1), for the following nuclear Hamiltonian in valence coordinates $(R_1, R_2, \theta_0)$ \[8; 56\]:

$$H_j = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial^2 R_1} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial^2 R_2} - \frac{\cos \theta_0}{m_O} \frac{\partial^2}{\partial R_1 \partial R_2} + E_j(R_1, R_2, \theta_0). \tag{4.9}$$

The states are denoted by $j = c, f$. The equilibrium angle is $\theta_0 = 104.2^\circ$, and $E_j(R_1, R_2, \theta_0)$ is the 2D stretching PES of state $j$. The reduced masses are given as:

$$\mu_1 = \frac{m_1 m_O}{m_1 + m_O}, \quad \mu_2 = \frac{m_2 m_O}{m_2 + m_O}, \tag{4.10}$$

where $m_1 = m_2 = m_H$ for the H$_2$O molecule, $m_1 = m_2 = m_D$ for the D$_2$O and $m_1 = m_H$, $m_2 = m_D$ for the HDO molecule. In case of the quasi-elastic RIXS spectra presented in Papers I-II, the R-dependence of the decay transition dipole moment was neglected and $d_{0c} = d_{0f}$. In Paper III we have taken the R-dependence into account, and use the full expressions from Eqs. (4.2-4.4). However, the bending mode is neglected. Hence, note that the following derivations apply only to the simulations of the 2D + 1D model \[8\] from Papers I-II.

In the 2D + 1D model \[8\], the total vibrational wave function is given as the product of the wave functions of the 2D symmetric-asymmetric stretching mode, $\psi_{n_s,n_a}$, and the bending mode, $\nu_f$, resulting in a final state for RIXS on the format:

$$|\nu_f\rangle |\psi_{n_s,n_a}\rangle. \tag{4.11}$$

The contribution from the bending mode is treated time-independently, and the contribution of the 2D stretching mode is treated using the time-dependent wave packet formalism. Hence the RIXS cross section is defined by the Franck-Condon (FC) amplitudes of the bending mode: $\langle \nu_f | \nu_c \rangle \langle \nu_c | \nu_0 \rangle$ and the overlap of the integrated core-excited wave packet of the 2D stretching mode (Eq. 3.11),

$$|\Psi_{\nu_c}(0)\rangle = \int_0^\infty dt e^{i(\omega_c t - \epsilon_{\nu_c} + i\Gamma_c t)} |\psi_c(t)\rangle, \tag{4.12}$$

$$|\Psi_{\nu_c}(t)\rangle = e^{-iH_f t} |\Psi_{\nu_c}(0)\rangle,$$

with the ground state vibrational wave functions, $\psi_{n_s,n_a}$. The energy of the core-excited bending vibrational state is given by $\epsilon_{\nu_c}$, and $\epsilon_{\nu_0}$ is the
sum of the zero-point energies of the bending and the stretching mode. Here the core-excited wave packet is given by,

$$|\psi_c(t)\rangle = e^{-iH_c t}|\nu_0\rangle.$$  

(4.13)

The RIXS cross section is given by

$$\sigma(\omega', \omega) = \frac{1}{\pi} \sum_{\nu_f, \nu_c, \nu_c'} \langle \nu_0 | \nu_c' \rangle \langle \nu_c' | \nu_f \rangle \langle \nu_f | \nu_c \rangle \langle \nu_c | \nu_0 \rangle$$

$$\times \text{Re} \int_0^\infty dt e^{i(\omega - \omega' - \omega_f + \epsilon_{\nu_f} + i\Gamma_f)t} \sigma_{\nu_c', \nu_c}(t),$$

(4.14)

where $\epsilon_{\nu_f}$ is the energy of the final bending vibrational state, and the autocorrelation function is given by

$$\sigma_{\nu_c', \nu_c}(t) = \langle \Psi_{\nu_c'}(0) | \Psi_{\nu_c}(t) \rangle.$$ 

(4.15)
5. Summary of results

![Chemical structures](image)

**Figure 5.1:** Organisation of this chapter. The first two sections are related to the study of RIXS in simple systems with three degrees of freedom. The last two sections are devoted to RIXS in more complex systems with multidimensional degrees of freedom.

This section is devoted to discussion of the results from the included papers. Fig. 5.1 contains an overview of the organisation of the chapter. The first two sections are devoted to the study of RIXS in simple triatomic molecules. In particular, in section 5.1, the main results from the investigation of $K$-edge RIXS in the water molecule, relating to Papers I-III, are summarised and discussed. Section 5.2 is devoted to the particular characters of potential energy surfaces (PESs) related to $K_\alpha$ and $L$-edge RIXS in the $H_2O$ molecule. The last two sections cover RIXS studies in more complex systems. In section 5.3, the investigation of the hydrogen bonding in aqueous ammonia using $N$ $K$-edge XES and RIXS is summarised and discussed. Finally, in section 5.4, local vibrations of the kaolinite clay mineral are discussed.
5.1 Studies of RIXS in the water molecule

Sections 5.1.1-5.1.4 cover the quasi-elastic RIXS process into the $4a_1$ and $2b_2$ resonances of the water molecule, studied in Papers I-II. Details on the RIXS process into $2b_1$ is found in Ref. [8; 9]. In particular, the anharmonicity of the ground state PES of H$_2$O and the implications for RIXS, the characters of the core-excited state PESs, and the RIXS propensity rule following from the spatial distribution of the core-excited wave packet, are discussed.

Sections 5.1.5-5.1.6 presents the main results of Paper III, where the quasi-elastic scattering and the inelastic scattering to the $|1b_1^{-1},4a_1^1\rangle$ valence-excited state for RIXS against the $|01s^{-1},4a_1^1\rangle$ core-excited state are studied. In particular the spectral features originating from ultrafast fragmentation in RIXS against $|1b_1^{-1},4a_1^1\rangle$ and the breakdown of the Franck-Condon approximation for the quasi-elastic RIXS channel are discussed.

5.1.1 Anharmonicity of the ground state potential energy surface in the H$_2$O molecule

![Ground state potential energy surface (PES) of the gas-phase H$_2$O molecule. The energy (eV) relative to the ground state minimum is shown in the panel above the PESs.](image)

**Figure 5.2:** Ground state potential energy surface (PES) of the gas-phase H$_2$O molecule. The energy (eV) relative to the ground state minimum is shown in the panel above the PESs.

The lowest few ground state vibrational levels behave in the manner predicted by the harmonic approximation, wherein two independent harmonic oscillators can be used to represent the 2D stretching vibration, producing eigenvalues with a monotonically varying energy spacing. However, due to the anharmonicity of the ground state PES, illustrated
Fig. 5.2, the approximation breaks down for the higher vibrational levels. To denote the coupled 2D stretching vibration levels, we, nevertheless, retain the format of the wave function, \( \psi_{n_s,n_a} \), where \( n_s \) and \( n_a \) are the quantum numbers relating to the symmetric and asymmetric stretching modes, respectively, and each vibrational level is denoted by the quantum number \( n \), referred to as the group number, where

\[
n = n_s + n_a.
\]  

(5.1)

Each group \( n \) consists of \( n + 1 \) vibrational levels formed by combination of the symmetric and asymmetric quantum numbers in the manner of \( (n_s, n_a) = (n - n_a, n_a) \).

**Figure 5.3:** Theoretical eigenvalues and eigenfunctions (vibrational wave functions) of the \( \text{H}_2\text{O} \) molecule computed using the 2D ground state stretching PES. (a) Discrete vibrational spectrum. The group number \( n \) is given on top of the bars. (b) Ground state vibrational wave functions \( (\psi_{4,0}, \psi_{3,0}, \psi_{2,0} \text{ and } \psi_{1,0}) \), the bifurcation is illustrated by the black lines.

The simulated discrete vibrational spectrum in Fig. 5.3(a) displays the vibrational levels for \( n \leq 5 \), where, for instance, the \( n = 4 \) group consists of 5 vibrational levels denoted by \( (4,0), (3,1), (2,2), (1,3) \) and \( (0,4) \). The energy spacing of the vibrational levels of the vibrational spectrum for \( n \leq 2 \) behaves in line with the prediction of the harmonic approximation. However, for larger \( n \), this is does not seem to be the case. We observe that for \( n \geq 3 \), the eigenvalues of the \( (n,0) \) and the
(n − 1, 1) vibrational levels become degenerate, thereby deviating from the harmonic approximation.

Vibrational wave functions for ψ_{4,0}, ψ_{3,0}, ψ_{2,0} and ψ_{1,0} are displayed in Fig. 5.3(b), where the bifurcation is shown by black lines. For n ≥ 3, the vibrational wave functions has density lobes along the coordinates of the OH bonds.

5.1.2 Character of the core-excited state potential energy surfaces and the relation to the XAS spectrum

![Figure 5.4](image_url)

Figure 5.4: (a) PESs of the ground state (GS), the |O_1s−1, 4a_1⟩, and the |O_1s−1, 2b_2⟩ core-excited states along the two stretching modes in valence coordinates (R_1, R_2). The diagonal line in the PESs show the symmetric (Q_s ∼ R_1 + R_2) stretching coordinate. The energy (eV) relative to the ground state minimum is shown in the panel above the PESs. (b) 1D PES of the ground state, the O_1s−1, 4a_1⟩, and the O_1s−1, 2b_2⟩ core-excited states along the bending mode (normal coordinate representation). (c) Theoretical XAS spectra corresponding to excitation into the |O_1s−1, 4a_1⟩ and the |O_1s−1, 2b_2⟩ core-excited states. The XAS energy corresponds to absorption from the lowest vibrational level of the ground state (∼ 0.5 eV from the bottom of the GS potential).

The RIXS spectrum is strongly dependent on the nuclear dynamics in the core-excited state, and the wave packet propagation is affected
by the shape of the core-excited PES. It is therefore important to spend
time to analyse the characters of the PESs of the core-excited states in
Fig. 5.4. Fig. 5.4(a) displays the 2D PES in the coupled stretching mode
and Fig. 5.4(b) the 1D bending PES.

The 2D stretching PESs of the two core-excited states have distinctly
different characters, as seen in Fig. 5.4(a). The PES of the $|O1s^{-1}, 4a_1\rangle$
core-excited state is dissociative along the OH-bonds, while the PES of the $|O1s^{-1}, 2b_2\rangle$ core-excited state is bound. However, both PESs have
a clearly different character from the ground state PES. The PES of the
bending mode of the core-excited states, plotted in Fig. 5.4(b), are all
bound. The minimum of the lowest core-excited state $|O1s^{-1}, 4a_1\rangle$ is
parallel with the minimum of the ground state PES. The minimum of the
$|O1s^{-1}, 2b_2\rangle$ core-excited state PES is slightly shifted with regards
to the ground state minimum.

The simulated XAS spectrum, plotted in Fig. 5.4(c), reflects the
different characters of the core-excited state PESs. The spectral profile
for the $|O1s^{-1}, 4a_1\rangle$ state is smooth and broad, due to the dissociative
character of the 2D stretching PES. For the $|O1s^{-1}, 2b_2\rangle$ state, where
the 2D stretching PES is bound, we see broad vibrational excitation in
the XAS profile.

5.1.3 On-resonance RIXS spectrum into the $4a_1$ and $2b_2$ reso-
nances

![Figure 5.5: Experimental (black lines) and theoretical (coloured lines)
RIXS spectra at the $4a_1$ and the $2b_2$ resonances. The following detuning
is used: $\Omega_{4a_1} = +0.05$ eV and $\Omega_{2b_2} = -0.025$ eV. The experimental data is
reproduced from Ref. [8; 9]
The distinct spectral profiles of the on-resonance RIXS spectra, seen in Fig. 5.5, display the effect of core-excited state dynamics. The theoretical spectra (coloured lines) reproduce the experiment (black lines) very well. For the \(|O1s^{-1}, 2b_1^2\rangle\) state, the vibrational progression is relatively long and both bending and stretching vibrations are excited. The vibrational progression of the \(|O1s^{-1}, 4a_1^1\rangle\) state, on the other hand, contains only excitation of stretching vibrations, as the minimum of the bending PES is parallel with the minimum of the ground state bending PES (Fig. 5.4(b)).

Hence, for excitation into the 4\(a_1\) and 2\(b_2\) resonances, we probe specific vibrational modes, due to the core-excited dynamics determined by the distinct characters of the core-excited PESs.

5.1.4 RIXS propensity rule relating to the spatial distribution of the core-excited wave packet

Upon closer inspection of the RIXS spectrum of the \(|O1s^{-1}, 2b_1^2\rangle\) and the \(|O1s^{-1}, 4a_1^1\rangle\) state, we notice that, in particular, for \(n \geq 3\), the vibrational progressions are shifted with respect to each other. This is shown in Fig. 5.6(a). To investigate the origin of this shift we look closer at the RIXS transitions to the discrete vibrational states, marked with red and green bars in Fig. 5.6(b). The vibrational states are characterised by the vibrational wave functions of the ground state, \(\psi_{n_s,n_a}\). Transitions to vibrational states where \(n_a\) is odd are not allowed due to the RIXS dipole selection rule. We notice that for excitation into the 4\(a_1\) resonance, only vibrational states with \(n_a = 0\) are populated by RIXS, while for excitation into the 2\(b_2\) resonance, the population of vibrational states with \(n_a \neq 0\) dominates.

This peculiar observation can be explained by looking at the overlap of the integrated core-excited wave packet, \(\Psi_0(0)\), and the ground state vibrational wave function, \(\langle\psi_{n_s,n_a} | \Psi_0(0) \rangle^2\) (referred to as the Franck-Condon factor), which defines the intensity of the RIXS transition to a given vibrational state (see chapter 4 for more general formulation). Due to the different characters of the PES, the wave packets in the \(|O1s^{-1}, 2b_1^2\rangle\) and the \(|O1s^{-1}, 4a_1^1\rangle\) states display distinctly different propagation dynamics, resulting in different spatial distribution of \(\Psi_0(0)\).

Fig. 5.6(c) displays the projection of \(|\Psi_0(0)|^2\) onto the specific vibrational wave functions, where we observe that the overlap varies significantly with the wave function due to the anharmonicity of the ground state PES. The spatial distribution of the wave packet of the \(|O1s^{-1}, 4a_1^1\rangle\) state has a very good overlap with the lobes oriented along the OH-bond.
Figure 5.6: (a) Experimental RIXS spectra at the $4a_1$ (green) and $2b_2$ (red) resonances compared to the corresponding theoretical spectra. The experimental spectra are smoothed by spline interpolation. The detuning is +0.05 eV for the $4a_1$ resonance and −0.025 eV for the $2b_2$ resonance. (b) A closer look at the theoretical RIXS spectra for $n = 4$ and $n = 3$. The ground state vibrational wave functions are shown on the top. The Franck-Condon factors between the ground state vibrational wave functions and the core-excited wave packets $|\langle \psi_{n_s,n_a} | \Psi_0(0) \rangle |^2$ are displayed by the coloured bars below. The grey dashed lines show the energies of vibrational states, to which transitions are forbidden in RIXS according to the dipole selection rule. (c) The overlap between the core-excited wave packet $|\Psi_0(0) \rangle^2$ of the $|O_1s^{-1}, 4a_1 \rangle$ and $|O_1s^{-1}, 2b_2 \rangle$ core-excited states and the ground state vibrational wave functions $\psi_{n_s,n_a}$. The classical turning point of the ground state PES are shown by the contour lines in the wave function plots. The figure is reproduced from Ref. [8] with permission from the PCCP Owner Societies.

of the purely symmetric stretching $\psi_{4,0}$ wave function. The overlap is instead poor with the wave function of mixed symmetric/antisymmetric stretching $\psi_{2,2}$, which has lobes along the symmetric stretching coordinate. In contrast, the spatial distribution of the wave packet of the $|O_1s^{-1}, 2b_2 \rangle$ state has an excellent overlap with the lobes of $\psi_{2,2}$ and a poor overlap with $\psi_{4,0}$. In other words, by exciting into the $4a_1$ resonance RIXS will probe only the symmetric stretching vibrational states, while mixed symmetric/asymmetric stretching vibrational states
are probed for excitation into the $2b_2$ resonance. Hence, this "propensity rule", together with the dipole selection rule, characterises the profile of the RIXS spectrum.

5.1.5 Ultrafast fragmentation features in 1D RIXS via the lowest core-excited state

The consequence of the dissociative character and the potential gradient at vertical excitation from the ground state minima of the lowest core-excited state, $|O1s^{-1},4a_1^1\rangle$, is that the core-excited state dynamics will lead to a fragmentation of the H$_2$O molecule into OH and H fragments on the timescale of the core-excited state lifetime. This process is referred to as ultrafast dissociation (UFD). The fluorescence decay in the OH fragment will give a signal in the RIXS spectrum; a narrow "atomic-like" feature, which we consider as the fingerprint of the UFD process. However, as we will soon see, dissociative configurations in the slightly dissociated H$_2$O molecule also gives rise to a narrow "pseudo-atomic" RIXS feature. Fig. 5.7 shows how the atomic-like feature is formed for the 1D PESs. Initially the wave packet is residing in the minimum of the ground state PES, $U_0$. The wave packet is promoted to the core-excited state PES, $U_c$, where it propagates along the gradient of the localised stretching of the OH-bond ($R_1$) towards the dissociative region (corresponding to $R_1 \sim 6$ a.u.). The wave packet has reached the dissociation region at $\tau \sim 6$ fs. While a 1D RIXS model does not reproduce the distinct profile of the RIXS spectrum, it gives the correct behaviour of atomic-like feature [8]. Hence, the conclusions concerning the atomic-like feature in the 1D model can be fully generalised to the 2D RIXS case.

The theoretical 1D RIXS profile displays a clear excitation energy dependence, as can be seen from Fig. 5.8. The black line shows the total RIXS spectra, where the contribution from decay to the valence-excited state is shown by the red lines, and the decay to the ground state is shown by the blue lines. Both the quasi-elastic decay channel, and the decay to the valence-excited state, the inelastic decay channel, yield an atomic-like feature at the same photon emission energy (526.2 eV), due to the degeneracy of the ground state and the valence-excited state in the dissociation region, as seen in Fig. 5.7. As it originates from decay in the OH fragment, the energy of the atomic-like feature does not depend on the excitation energy, (see the dashed line in Fig. 5.8). However, the strength of the atomic-like feature in the spectrum is strongly related to the excitation energy. The strongest signal is seen for excitation
energy around the X-ray absorption resonance. For large positive detuning, the atomic-like feature vanishes, a behaviour which is explained by the effective scattering duration of the RIXS process, as is described by Eq. 4.7. The effective shortening of the scattering duration for large detuning means that the wave packet has no time to reach the dissociation region, hence, the atomic-like contribution to the RIXS spectrum vanishes. In this case, decay in the none or slightly distorted H$_2$O molecule, yielding the so called molecular band, will mainly contribute to the RIXS spectrum. As opposed to the atomic-like feature, the energy of the molecular band is dependent on the excitation energy following the Raman dispersion law, Eq. 3.7 (see the dotted line in Fig. 5.8).

To first approximation, the detuning dependence is related to the absolute value of the detuning $|\Omega|$, e.g. in this case we would expect to observe a significant decrease of the atomic-like feature as compared to the molecular band for both large negative and large positive detuning. Indeed, for the elastic decay channel, we see how the atomic-like feature vanishes for large $|\Omega|$ (note that the molecular band for the quasi-elastic decay channel is found at higher emission energy). However, at $\Omega = -1$ eV we see, quite unexpectedly, a strong atomic-like feature in the RIXS.

Figure 5.7: Schematic illustration of the formation of atomic-like and "pseudo-atomic" features following core-excitation of the water molecule to the $[1s^{-1}, 4s]$ state. The 1D cuts of the 3D stretching PES of the ground, $U_g$, core-excited, $U_c$, and final, $U_f$, states are shown along the localised stretching of one OH-bond ($R_1$), while the second bond is kept fixed ($R_2 = R_0 = 1.81$ a.u.). The top panel displays the energy difference between the core-excited state and the two final states of the RIXS process. Shown by shaded area is the square of the core-excited wave packet at different propagation times, $\tau$. 

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Figure 5.8: Theoretical RIXS spectra in 1D RIXS model illustrating the formation of the atomic-like feature. The spectra display the X-ray detuning dependence of the spectral contribution from the quasi-elastic decay channel (blue) and the inelastic decay channel to the lowest valence-excited $|1b^{-1}_{1}, 4a_{1}^{1}\rangle$ state (red), as well as the total profile (black) containing both contributions. The detuning, $\Omega$, is related to the X-ray absorption resonance with the core-excited $|1s^{-1}, 4a_{1}^{1}\rangle$ state at $\omega = 534.15$ eV. The figure is reproduced from Paper III.
profile from the inelastic decay channel (see the red spectrum in bottom panel of Fig. 5.8).

This unexpected behaviour of the atomic-like feature for the inelastic decay channel can be explained by comparing the characters of the $|O1s^{-1}, 4a_1^1\rangle$ core-excited state and the $|1b_1^{-1}, 4a_1^1\rangle$ valence-excited state PESs, $U_c$ and $U_f$, respectively. The difference curve of $U_c - U_f$ is displayed in the top panel of Fig. 5.7. The difference curve shows that beginning from a distortion of 1.2 a.u. from the equilibrium geometry (corresponding to a bond length of 3 a.u.), the PESs of the core-excited state and the valence-excited state are parallel. For a RIXS process where the core-excited state and final state PESs are very similar, the consequence is a collapse of the vibrational structure [7]. For the inelastic decay channel, where both the core-excited and final state PESs are dissociative, this results in a significant narrowing of the of the spectral feature. This means that the molecular contribution to the RIXS profile at energy 526.2 eV, will have a shape similar to the characteristic atomic-like feature. In other words, what we have observed is a "pseudo-atomic" peak resulting from decay in the slightly distorted H$_2$O molecule. Hence, the RIXS profile for $\Omega = -1$ eV looks different than the RIXS profile at $\Omega = 1$ eV. In contrast, the characters of the ground state and the core-excited state PESs are very dissimilar, see the $U_c - U_0$ curve in top panel of Fig. 5.7. Hence, for the quasi-elastic decay channel, only decay in the OH fragment will yield the atomic-like feature.

5.1.6 Breakdown of the Franck-Condon approximation for the quasi-elastic decay channel

We have also investigated the effect of the R-dependence of the transition dipole moment on the quasi-elastic decay channel on the RIXS cross section. To this end, we will look at the $y$ and $z$ components of the transition dipole moment of the quasi-elastic decay channel, $d_{cg}$. Fig. 5.9(a) shows how the $d_{cg}^y$ (red line) and $d_{cg}^z$ (blue line) components are affected by distortion along the localised stretching mode. At equilibrium geometry, $R_{eq}$, only the $d_{cg}^z$ component contributes, i.e. the transition dipole moment points purely in the $z$-direction (= along the molecular axis). However, the dipole moment rotates to point in a direction orthogonal to the remaining OH bond in the course of the dissociation, which is seen from the growing $d_{cg}^y$ component in Fig. 5.9(a). The constant transition dipole moment within the Franck-Condon (FC) approximation (see definition in chapter 4) is displayed by the horizontal black line in Fig. 5.9(a).
Figure 5.9: R-dependence of the $d_{cg}^y$ and $d_{cg}^z$ components in the atomic-like feature formation. a) R-dependence of the transition dipole moment components in the 1D case $d_{cg}^y(R_1)$ (blue) and $d_{cg}^z(R_1)$ (red), where $R_2 = R_1 = 1.81$ a.u. The black line $d_{cg}(R_0) = d_{cg}^z = 0.018$ a.u., displays the R-independent dipole moment in the FC approximation b) 1D model: $\sigma_g$ cross section (violet line) computed taking into account the R-dependence of the transition dipole moment compared to the cross section $\sigma_{gFC}$ (black line) computed using $d_{cg} = \text{const}$. The lower panel show the contribution from the $\sigma_g^y$ (red) and $\sigma_g^z$ (blue line) components. c) Corresponding spectra to (b) from the 2D model. Calculations were performed for $\chi = 90^\circ$. Figure is reproduced from Paper III.
By comparing the spectra calculated within the FC approximation with the spectra calculated taking the R-dependence into account (beyond FC), we can evaluate the effect of the breakdown of the FC approximation on the RIXS cross section. Simulations for the 1D RIXS model are displayed in Fig. 5.9(b); the black line shows the total RIXS cross section for the constant (FC) transition dipole moment, $\sigma_0^{\text{FC}}$, and the violet line shows the total RIXS cross section, $\sigma_g$ beyond FC. The red and blue lines show the contributions of the $\sigma_y^g$ and $\sigma_z^g$ components, respectively. Comparing the $\sigma_0^{\text{FC}}$ and the $\sigma_g$ cross sections, we observe that the intensity of the RIXS spectrum (apart from the $\nu = 0$ at 0 eV) is underestimated within the FC approximation. This means that within the FC approximation, decay in the distorted H$_2$O molecule that is contributing to spectral features at high energy, is not fully accounted for. The rotation of the transition dipole moment means that the deviation from the constant FC transition dipole moment is great at large distortion. Hence, the effect of the breakdown of the FC approximation is greatest for the atomic-like feature, resulting in a fivefold increase of the intensity. The cross sections of the $\sigma_y^g$ and $\sigma_z^g$ components display how the former contributes mainly to the higher vibration peaks, while the latter gives the greatest contribution to the lower vibration peaks.

We see the same effects of the breakdown of the FC approximation for the 2D RIXS spectra, displayed in Fig. 5.9(c), as for the 1D case. However, the effect of the breakdown of the FC approximation on the intensity of the atomic-like feature is even greater in the 2D spectra as compared to the 1D case; we see a tenfold increase of the intensity of the atomic-like feature.
5.2 RASPT2 calculations of the potential energy landscape in RIXS of H$_2$S

We have used the same computational approach as employed for the H$_2$O molecule to calculate 2D stretching PESs of the H$_2$S molecule for the ground state, $K_\alpha$ RIXS and L-edge XA final states, and K-edge XA final states (RIXS intermediate states). The $K_\alpha$ RIXS and L-edge XA final states are $S2p^{-1}$ core-excited states, corresponding to promotion of an electron from a $Sp^{-1}$ MO ($1b_1$, $3a_1$ and $1b_1$) to $3b_2$ and $6a_1$. The K-edge XA final states are $S1s^{-1}$ core-excited states, corresponding to excitation of an electron from $S1s$ to the unoccupied $6a_1$ and $3b_2$ MOs. The $S2p^{-1}$ final states will be strongly influenced by spin-orbit coupling (SOC).

5.2.1 Near-degeneracy of the two lowest $S1s^{-1}$ core-excited states

The calculated energies for vertical excitation from the equilibrium geometry ($R_{eq} = 2.52$ a.u.) are $2486.23$ eV and $2486.38$ eV for $|S1s^{-1},3b_2\rangle$ and $|S1s^{-1},6a_1\rangle$, respectively. Our calculations, hence, predict a small energy splitting (0.15 eV) of the two lowest $S1s^{-1}$ core-excited states. We calculate the 2D stretching PESs of the $S1s^{-1}$ core-excited states. 1D cuts along the symmetric stretching coordinate and the localised S-H stretching coordinate, where one S-H bond is fixed at $R_{eq}$, are displayed in Fig. 5.10. We start with discussing the character and particular features of the PESs along the symmetric stretching coordinate, as plotted in Fig. 5.10(a). We see from Fig. 5.10(a) that also in distorted geometries, the $|S1s^{-1},3b_2\rangle$ and $|S1s^{-1},6a_1\rangle$ core-excited states display small energy splitting. There are two conical intersections on either side of the equilibrium geometry. The PES around the right conical intersection at $R_{S-H} = 3.12$ a.u. is displayed in the inset in Fig. 5.10(a). We note that this conical intersection could possibly influence the dynamics, as it is situated in a PES region that can be reached by a core-excited wave packet. Consequently, the K-edge RIXS and X-ray absorption (XA) signals could be affected by this conical intersection. The probability of the propagation of the core-excited wave packet to be influenced by the left conical intersection ($R_{S-H} = 2.14$ a.u.) in K-edge XA is limited due to the higher energy. At large distortion, corresponding to "complete" dissociation of the H$_2$S molecule into S and H+H fragments, these two core-excited states become degenerate.

The PESs along the localised stretching coordinate are displayed in
Figure 5.10: 1D cuts in the adiabatic potential energy surfaces of two lowest $S_1s^{-1}$ core-excited states, calculated using RASPT2. $R_{\text{eq}}$ is denoted by a dashed vertical line. (a) 1D cut along the symmetric stretching coordinate, where we see a change of PES character at two conical intersections at $R_{\text{S-H}} = 2.14$ a.u. and $R_{\text{S-H}} = 3.12$ a.u. Inset: Potentials zoomed in where we see the change of character at conical intersection $R_{\text{S-H}} = 3.12$ a.u. (b) 1D cut along the localised stretching coordinate of one S-H bond ($R_1$), the other bond is fixed at $R_2 = R_{\text{eq}}$. Inset: Potentials zoomed in around the equilibrium, where we see the avoided crossing. The figure is reproduced from Paper IV.

Fig. 5.10(b). By inspection of Fig. 5.10(b), we see that the energy splitting is related to an avoided crossing (seen in the inset in Fig. 5.10(b)) in the PESs when symmetry is broken. At large distortion, corresponding the dissociation of the $H_2S$ molecule into HS and H fragments, the core-excited states become separated with 7 eV. Giving rise to this separation is the electron configuration in the core-excited HS fragment where an electron is excited into $2\pi$; the first core-excited state corresponds to a closed shell configuration with $2\pi^4$, while the second core-excited state corresponds to an open-shell configuration with $2\pi^3$ and one electron in the anti-bonding $3\pi^*\text{MO}$.

The full 2D PES of the ground state and the $|S_1s^{-1},3b_2^1\rangle$ and $|S_1s^{-1},6a_1^1\rangle$ core-excited states are displayed in Fig. 5.11. As we saw from the 1D cut along the symmetric stretching coordinate, shown in Fig. 5.10(a), the
PESs of the S1s\(^{-1}\) core-excited states change character at two conical intersections. This means that it is not entirely straightforward to associate the |S1s\(^{-1}\), 3b\(_1^2\rangle\rangle and |S1s\(^{-1}\), 6a\(_1^1\rangle\rangle core-excited states with the 2D surfaces in Fig. 5.11(b-c). Nevertheless, we notice that there is a close similarity of the 2D PESs at K-edge XA of H\(_2\)S and the corresponding PESs of the two lowest core-excited states of the H\(_2\)O molecule, seen in Fig. 5.4(a); in both cases we see one bound and one dissociative PES. By comparison of 1D cuts in the PESs, at equilibrium geometry we observe that the gradient of the S1s\(^{-1}\) core-excited states is significantly smaller than the gradient of the corresponding O1s\(^{-1}\) core-excited state. We also notice that the O1s\(^{-1}\) core-excited state PESs are more narrow around the minima than the S1s\(^{-1}\) core-excited state PESs along the symmetric stretching coordinate. The O1s\(^{-1}\) and the corresponding S1s\(^{-1}\) core-excited states have comparable gradients along the localised stretching coordinate.

The significant difference between the PESs of the water molecule and the PESs of the H\(_2\)S molecule is, nevertheless, the near-degeneracy of the S1s\(^{-1}\) core-excited states at vertical excitation. Consequently, coherent core-excited state dynamics should be strongly influencing the K-edge RIXS process in H\(_2\)S, while such effects are absent in the corresponding RIXS process for the H\(_2\)O molecule. The reason for the near-degeneracy of the two lowest core-excited states in H\(_2\)S is the longer equilibrium bond length which gives a smaller splitting of the bonding and anti-bonding MO's.
Nevertheless, in analogy with the assignment in the H$_2$O molecule and motivated by analysis of the MO character, we associate upper bound core-excited state, Fig. 5.11(b), with $|S_1s^{-1},3b_1^1\rangle$ and the lower dissociative core-excited state, Fig. 5.11(c), with $|S_1s^{-1},6a_1^1\rangle$. This assignment is, however, in disagreement with the assignment along the symmetric stretching coordinate, Fig. 5.10(a). Therefore, we will refer to the 2D PESs of the core-excited states with the notation $|\text{Bound}_{S_1s}\rangle$ and $|\text{Dissoc}_{S_1s}\rangle$ in the remaining discussion.

To analyse the character of the 2D PES of the core-excited states, we look at the valleys along $R_{S-H_1}$ and $R_{S-H_2}$. The valley along the symmetric stretching coordinate for the PES of $|\text{Bound}_{S_1s}\rangle$, Fig. 5.11(b), indicates ultrafast bond elongation following core-excitation. The PES of $|\text{Dissoc}_{S_1s}\rangle$, Fig. 5.11(c), displays clear potential valleys spreading out along the individual bond stretching coordinates, indicating that the PES is strongly dissociative.

### 5.2.2 Spin-orbit coupling of the S$2p^{-1}$ core-excited states

The S$2p^{-1}$ core-excited states are split into S$2p_{3/2}$ and S$2p_{1/2}$ multiplets by SOC. This is generating the following four sets of SOC states; $|S_2p_{3/2},3b_1^1\rangle$, $|S_2p_{1/2},3b_1^1\rangle$, $|S_2p_{3/2},6a_1^1\rangle$ and $|S_2p_{1/2},6a_1^1\rangle$. A total of 24 SOC states are formed from the lowest six singlet and six triplet states at equilibrium geometry.

We calculate PESs along the 2D stretching coordinate for the S$2p^{-1}$ core-excited states. 1D cuts along the symmetric stretching coordinate and the localised stretching coordinate are displayed in Fig. 5.12(a-b) excluding SOC and in Fig. 5.12(c-d) including SOC. In the following discussion, we refer to the states including SOC as ”SOC states” and the states not including SOC as singlet and triplet states, respectively.

The shape of the singlet and triplet S$2p^{-1}$ core-excited states are nearly parallel with the S$1s^{-1}$ for distortion along the localised stretching coordinate, Fig. 5.12(b). After SOC, the PESs of a number of states at higher energies do not form the avoided crossing at equilibrium geometry that we see for the S$1s^{-1}$ core-excited states and S$2p^{-1}$ core-excited state before SOC. Along the symmetric stretching coordinate, Fig. 5.12(a) and Fig. 5.12(d), the PESs of the S$2p^{-1}$ core-excited states have a general character closely resembling the PESs S$1s^{-1}$ core-excited states. The local minima of the PESs of the S$2p^{-1}$ core-excited states are slightly shifted with regards to the minima in the PESs of the S$1s^{-1}$ core-excited states. The dissociative PES at lower energy are associated with S$2p^{-1}$ core-excited states where there is population of the 6$a_1$ MO, and the
Figure 5.12: 1D cuts in the adiabatic potential energy surfaces, derived from RASPT2, of singlet and triplet $S_2p^{-1}$ core-excited states are displayed in (a) and (b) and SOC states are displayed in (c) and (d). (a) 1D cut of PESs along the symmetric stretching coordinate. (b) 1D cut of PESs along the localised stretching coordinate of one S-H bond. (c) 1D cut of PESs along the symmetric stretching coordinate. (d) 1D cut of PESs along the localised stretching coordinate of one S-H bond.

Bound PESs at higher energy are associated with $S_2p^{-1}$ core-excited states where there is population of the $3b_2$ MO, in analogy with the $S_1s^{-1}$ core-excited states.

We identify three conical intersections in the PESs of the triplet states along the symmetric stretching coordinate, seen in Fig. 5.12(a). At $R_{S-H} = 3.34$ a.u. there is a conical intersection between the PESs of the singlet $|1b_1^{-1}, 6a_1^1\rangle$ and $|1b_1^{-1}, 3b_2^1\rangle$ states. At $R_{S-H} = 3.11$ a.u. there is a conical intersection in the PESs of the triplet $|1b_1^{-1}, 6a_1^1\rangle$ and $|1b_1^{-1}, 3b_2^1\rangle$ states. Finally, at $R_{S-H} = 2.84$ a.u. there is a conical intersection in the PESs of the triplet $|3a_1^{-1}, 6a_1^1\rangle$ and $|3a_1^{-1}, 3b_2^1\rangle$ states. The conical intersections in the SOC states are more challenging to identify, due to the dense manifold of these states. One approach to correctly assign the character of the SOC PESs in future studies would be to analyse the transition dipole moments.

The $K_\alpha$ RIXS spectra and the $L$-edge XA spectrum generated from the discrete RASPT2 spectra at equilibrium geometry are displayed.
Figure 5.13: Theoretical $K_\alpha$ RIXS spectra of the $S_{2p}^{-1}$ core-excited states and $L$-edge XA spectrum generated from discrete RASPT2 spectra at equilibrium geometry. The spectra of the SOU states are displayed by solid lines. Vertical bars display the energies and the relative $L$-edge XA / $K_\alpha$ RIXS intensities of the discrete spectra (in the RIXS spectra the red bars mark states that can be reached for both resonances). In (a) the spectrum shows transition from the $|S1s^{-1},3b_1^-\rangle$ core-excited RIXS intermediate state to the $S_{2p}^{-1}$ core-excited RIXS final states and in (b) the transitions from $|S1s^{-1},6a_1^+\rangle$ core-excited RIXS intermediate state to the $S_{2p}^{-1}$ core-excited RIXS final states are displayed. (c) Theoretical $L$-edge XA spectrum. (d) Comparison of the theoretical $L$-edge XA spectrum to the experimental $D_{2s}$ spectrum from Ref. [57]. Figure is reproduced from Paper IV.

In Fig. 5.13. From the convoluted $K_\alpha$ spectra, shown in Fig. 5.13(a-b), we obtain the following transition energies for $K_\alpha$ RIXS: 165.4 eV ($|S2p_{3/2}^{-1},3b_1^-\rangle$), 163.6 eV ($|S2p_{1/2}^{-1},3b_2^-\rangle$), 165.8 eV ($|S2p_{3/2}^{-1},6a_1^+\rangle$), and 166.9 eV ($|S2p_{1/2}^{-1},6a_1^+\rangle$). From the $K_\alpha$ RIXS we also obtain a spin-orbit splitting of 1.2 eV, which is in excellent agreement with the experimentally obtained splitting of 1.2 eV [58–60]. The theoretical $L$-edge XA spectrum is displayed in Fig. 5.13(c). The $L$-edge absorption energies we obtain from our calculations are the same as the $K_\alpha$ RIXS energy loss.
$L$-edge transition energies are determined from the experiment to [58]: 164.4 eV ($|S2p_{3/2}^{-1}, 6a_1^1\rangle$), 165.6 eV ($|S2p_{1/2}^{-1}, 6a_1^1\rangle$), 165.1 eV ($|S2p_{1/2}^{-1}, 3b_2^1\rangle$), and 166.3 eV ($|S2p_{1/2}^{-1}, 3b_2^1\rangle$). Our calculations predict the reversed order of the $|S2p_{1/2}^{-1}, 6a_1^1\rangle$ and the $|S2p_{1/2}^{-1}, 3b_2^1\rangle$ states with respect to the experimental $L$-edge spectrum [58]. However, in agreement with our results, a previous theoretical study [61] predicts the $|S2p_{1/2}^{-1}, 6a_1^1\rangle$ states to have higher energy than the $|S2p_{1/2}^{-1}, 3b_2^1\rangle$ states.

The energies we obtain from our calculations underestimate the splitting between the $|S2p_{3/2}^{-1}, 6a_1^1\rangle$ and $|S2p_{3/2}^{-1}, 3b_2^1\rangle$ states, and the $|S2p_{1/2}^{-1}, 6a_1^1\rangle$ and $|S2p_{1/2}^{-1}, 3b_2^1\rangle$ states. Also, for the $S1s^{-1}$ core-excited states, the splitting between the $|S1s^{-1}, 3b_2^1\rangle$, $|S1s^{-1}, 6a_1^1\rangle$ might be underestimated in comparison with experiment [62]. A reason for the underestimation of the $6a_1^1/3b_2^1$ splitting could be limitations in the active space used, where the $3d$ orbitals were excluded. However, calculations where the $3d$ orbitals are included also results in an underestimation of the splitting. The most probable cause of the underestimation at the $L$-edge is the $S2p$ orbitals, which are frozen from a previous RASSCF calculation. This results in the effect of the orbital relaxation not being reflected in the transition energies, which may be the reason for the discrepancy in the $3b_2^1/6a_1^1$ splitting between our result and the experiment. The valence response to the core-hole is, however, included in the full wave function.

5.2.3 Concluding remarks on XA and RIXS processes in H$_2$S and H$_2$O

![Figure 5.14: Representation of $K$-edge and $L$-edge XA and RIXS processes available for the H$_2$S molecule.](image)
For seemingly simple systems such as the H\(_2\)O molecule and the H\(_2\)S molecule we can actually study a variety of physical processes with RIXS (schematically displayed in Fig. 5.14). In the results of Papers I-III we have investigated the quasi-elastic and inelastic decay channels of RIXS of the H\(_2\)O molecule. We see how K-edge RIXS through the quasi-elastic decay channels can be used to obtain a detailed mapping of the ground state PES in the H\(_2\)O molecule.

RIXS in the H\(_2\)S molecules provides us with the possibility to investigate both K-edge and L-edge RIXS processes. Following excitation into the S\(_1\)s\(^{-1}\) core-excited state, decay can occur through the K\(_\alpha\) channel, where the final states are S2p\(^{-1}\) core-excited states (that is reached in L-edge XAS). Another possibility is decay through the K\(_\beta\) channel, where the final states are valence-excited states. The final states of the K\(_\beta\) RIXS process are also reached by the L-edge RIXS. The S2p\(^{-1}\) core-excited states provided us with the opportunity to investigate the effect of SOC and lifetime in final state and intermediate state.
5.3 Hydrogen bonding orbitals of aqueous NH$_3$

In this paper we have investigated both gas phase ammonia and ammonia in aqueous solution to investigate effects of hydrogen bonding. XES and RIXS spectra were calculated using periodic DFT and compared with experimental results. The emission energies of particular RIXS resonances in the gas phase NH$_3$ molecule were calculated using RASPT2. The core-excited state dynamics was simulated using classical dynamics, as opposed to quantum dynamics approach used for the water molecule (Section 5.1).

5.3.1 XES of NH$_3$(aq) and NH$_3$(g)

The effect of the hydrogen bonding is analysed by the N K-edge XES spectra of NH$_3$(aq) and NH$_3$(g). The N K-edge XES spectra of NH$_3$(g) and NH$_3$(aq) excited at 405 eV are displayed in Fig. 5.15, and the corresponding simulated spectra (with and without broadening of the line widths). The simulations do not include dynamic effects of the core-excited state. Both experimental and calculated spectra have contribution from the 3a$_1^{-1}$, 1e$^{-1}$, and 2a$_1^{-1}$ valence excited states. However, 2a$_1^{-1}$ is largely dipole forbidden, as is reflected by the small intensity.

When comparing the measured NH$_3$(g) spectrum to the measured NH$_3$(aq) spectrum, we find that for the 3a$_1^{-1}$ final state, the gas phase spectra exhibit a distinct vibrational fine structure whereas for the aqueous solution the same emission line is without these features and exhibits and asymmetric broadening to low emission energies. The smearing of the vibrational fine structure in NH$_3$(aq) is likely due to configurational broadening. The vibrational fine structure in the gas phase corresponds well with the vibrational fine structure from ab initio calculations [63] and the inset in Fig. 5.15 shows the comparison of these calculations (blue) and the spectra measured in this study. The intensities of the individual vibrations from Ref. [63] are shown by blue vertical bars, and their sum after broadening is represented by the blue spectrum.

The 1e$^{-1}$ and the 2a$_1^{-1}$ N K-edge XES exhibit blueshift upon hydration, reproduced in the simulated spectra, and which is a result of the hydrogen bonding environment. Both the experimental and simulated spectra exhibit additional intensity in the energy region between the 1e$^{-1}$ and the 3a$_1^{-1}$ emission lines (as indicated by the shaded regions in Fig. 5.15). This intensity is attributed to orbital mixing with the valence states of the solvent water resulting from the covalent contribution to the hydrogen bonding.
Figure 5.15: Left panel shows (a) the non-resonant ($h\nu_{\text{exc.}} = 405\text{ eV}$) N K-edge XES spectra of aqueous NH$_3$ (black line) and gas phase NH$_3$ (red line). The spectra are normalised to the peak maximum. The corresponding final states are given for each emission feature. The spectral region of the 2a$^{-1}$ feature is magnified by a factor of 100. (b-c): The theoretical N K-edge XES spectra for aqueous NH$_3$ (black line) and NH$_3$ in gas phase (red line), not including core-excited state dynamics. The theoretical spectra are sampled over 180 configurations derived from a molecular dynamics trajectory of aqueous NH$_3$. (b) Spectra broadened to reflect the line widths observed in the experiment, and (c) spectra without broadening. The theoretical spectra were shifted in energy to align the 3a$^{-1}$ line with the experiment. Inset: the 3a$^{-1}$ lines on an expanded scale in comparison to calculations (blue). The right-hand panels shows the iso-density surfaces of the molecular orbitals corresponding to emission at the energies marked by by Roman numerals in (c). The figure is reproduced from Ref. [10] with permission from the PCCP Owner Societies.

The right side of Fig. 5.15 shows the iso-density surfaces of characteristic orbitals corresponding to the emission energies marked by (I-IV) in the N K-edge XES spectra at the left in the same figure. The molecular orbitals (I) and (II) get the main character from the NH$_3$ 1e (I) and 3a$^{-1}$ (II) orbitals, with some additional contribution from the valence orbitals of the liquid water, which leads to the shifts in emission energies due to
the changes in the local environment. The molecular orbitals (III) and (IV) on the other hand, get their main character from the surrounding water molecules and have energies located in-between the NH$_3$ 1e and 3a$_1$ orbitals, hence resulting in the additional intensity in-between these emission lines in the N K-edge XES spectra. The calculated spectrum does not reproduce the correct energy splitting of the emission lines, which is attributed to the neglect of the final state relaxation effects in the modelling.

The energies of 3a$_1^{-1}$ and 1e$_1^{-1}$ emission in NH$_3$(g) are investigated in more detail by comparison of the experimental values with RASPT2 calculations. These calculated emission energies for NH$_3$(g) are displayed in Table (5.1). Here we have included excitation into the 4a$_1$, 2e, and 5a$_1$ resonances and non-resonant excitation. The line positions shift as a function of excitation energy (spectator shifts), and the shifts are within 0.6 eV for NH$_3$(g). The energies obtained using state-specific calculations reproduce the experimental spectator shifts, while the values obtained using state-averaging (where several states are described by the same set of orbitals) display a small shift in the opposite direction. Also displayed in Table (5.1) are also the corresponding experimental emission lines for NH$_3$(aq), and here we see shifts of the line positions within 0.4 eV. Shifts of the line positions is an effect of the interactions, or lack of interactions, of the excited electron with the electronic system.

<table>
<thead>
<tr>
<th>Absorption Resonance</th>
<th>3a$_1^{-1}$ Energy (eV)</th>
<th>1e$_1^{-1}$ Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas exp. (calc.)</td>
<td>aq. exp.</td>
</tr>
<tr>
<td>Non-resonant</td>
<td>394.7 (394.74/75)</td>
<td>394.7</td>
</tr>
<tr>
<td>5a$_1$</td>
<td>394.6 (394.87/-)</td>
<td>-</td>
</tr>
<tr>
<td>2e</td>
<td>394.5 (394.69/39)</td>
<td>394.6</td>
</tr>
<tr>
<td>4a$_1$</td>
<td>394.1 (394.84/24)</td>
<td>394.3</td>
</tr>
</tbody>
</table>

**Table 5.1:** NH$_3$(g) and NH$_3$(aq) line positions of the 3a$_1^{-1}$ and 1e$_1^{-1}$ emission lines for excitation into the three lowest absorption resonances and non-resonant excitation. Calculated state-averaged/state-specific RASPT2 energies are included in the parentheses when available. Table is reproduced from Ref. [10] with permission from the PCCP Owner Societies.
5.3.2 Core-excited state dynamics of RIXS in NH$_3$(g)

We will start the investigation of the core-excited state dynamics by looking at the N K-edge RIXS spectra of NH$_3$(g) at 4a$_1$ excitation (400.5 eV), at 2e excitation (402.1 eV), and non-resonant excitation (405.0 eV) displayed in Fig. 5.16(a). We see that the spectra for excitation into 2e and non-resonant excitation only exhibit slight differences due to the vibration fine structure changes and differences in spectator shifts. An interesting feature is the broad loss structure in the region of 395-399 eV (labeled D$_2$) in the spectrum at the 4a$_1$ resonance, as well as the shoulder at 392.5 eV in the same spectra, labeled by D$_1$, both of which are indicative of nuclear dynamics on the timescale of the core-hole lifetime leading to dissociation. Upon inspection of the energy
regions of features $D_1$ and $D_2$, we find that the intensity is the greatest for excitation into $4a_1$. Hence, we see that the $|N_{1s}^{-1}, 4a_1^1\rangle$ core-excited state of the NH$_3$ molecule is dissociative, just like the $|O_{1s}^{-1}, 4a_1^1\rangle$ core-excited state in the H$_2$O molecule studied in Papers I-III.

5.3.3 Core-excited state dynamics of RIXS into $4a_1$ of NH$_3$(g), NH$_3$(aq) and ND$_3$(aq)

![Figure 5.17](image.png)

Figure 5.17: N K RIXS spectra snapshots as a function of time delay after the core-excitation, as calculated by dynamical DFT. The time evolution of gas phase and aqueous NH$_3$ is compared for excitation into the $4a_1$ resonance and non-resonant excitation. The figure is reproduced from Ref. [10] with permission from the PCCP Owner Societies.

We continue by studying the N K-edge RIXS spectra at $4a_1$ excitation for NH$_3$(g), NH$_3$(aq), and ND$_3$(aq), which are shown in Fig. 5.16(b). The spectra in the left panel are normalised to the $3a_1^{-1}$ peak maximum and in the right panel, the spectra are normalised to the elastic peak. The features at the low energy side of the elastic peak (labeled with $V$ in the right panel), at 400 eV corresponds to vibrationally excited final states. In the normalised spectra aqueous NH$_3$(aq) exhibits the strongest intensity at energy regions attributed to dissociation, $D_1$ (left panel) and $D_2$ (right panel), which is an indication that the dissociation effects are stronger on aqueous NH$_3$ than on ND$_3$(aq) and gas phase NH$_3$. The increased dissociation for NH$_3$(aq) is attributed to the hydrogen bonding environment in aqueous solution. The dissociation in ND$_3$(aq) is slower than in NH$_3$(aq) due to the mass difference of H and D.

Fig. 5.17 displays calculated N K-edge RIXS spectra for excitation to the $4a_1$ resonance and non-resonant excitation for snapshots of con-
figurations of NH$_3$(g) and NH$_3$(aq) corresponding to the evolution of the core-excited state at different time instances after core-excitation.

For excitation to 4a$_1$, the spectral evolution of both gas phase and aqueous NH$_3$ exhibit an oscillatory energy shift of the 3a$_1^{-1}$ and 1e$_1^{-1}$ emission lines as a function of time delay after excitation, a behaviour which is the result of the molecular vibrations. The 1e$_1^{-1}$ emission line is split into two separate lines after 7 fs in aqueous solution and 20 fs in gas phase. For NH$_3$(aq), one of the lines is blueshifted so that it merges into a low energy shoulder of the 3a$_1^{-1}$ emission line. As was seen in the experimental RIXS spectra (Fig. 5.16), the dynamics is considerably faster in solution than in gas phase.

As a comparison to excitation into 4a$_1$, we also investigate non-resonant excitation. The non-resonant spectra as a function of time delay exhibits oscillatory energy shifts but the overall changes are not as significant as in 4a$_1$ excitation. The splitting of the 1e$_1^{-1}$ emission line is not as clearly visible in the non-resonant case.
5.4 Local vibrations of the hydroxyl groups in kaolinite

In this paper O K-edge XAS and quasi-elastic RIXS is used to probe the local vibrations of the hydroxyl groups in the kaolinite clay crystal. XAS spectra are simulated with DFT employing the half-core-hole (HCH) transition potential method. PESs of ground state and the lowest core-excited state along the different vibration modes are calculated using periodic plane wave DFT. The core-excited state dynamics of the quasi-elastic decay channels is simulated using 1D quantum dynamics (see chapter 4).

5.4.1 Kaolinite structure and vibration modes

The kaolinite clay crystal is organised in a layer-wise structure of alumina and silica sheets connected covalently to each other by sets of three spectroscopically inequivalent hydroxyl groups, OH(2-4), Fig. 5.18. A fourth spectroscopically inequivalent OH-group, OH(1), is found in-between the silica-alumina layers. By tuning the incoming photon frequency in quasi-elastic O K-edge RIXS, we seek to selectively probe vibrational excitations of specific hydroxyl oxygen atoms in the crystal.

![Figure 5.18: Confinement of the OH-groups in the kaolinite clay crystal.](image)

The 1D cuts in the multidimensional PESs of the ground state and the lowest core-excited state of the OH-group are calculated along the degrees of freedom relating to the six OH normal modes, which are likely to be excited by RIXS (plotted in Fig. 5.19). To reduce the complexity and multi-dimensionality of the RIXS dynamics, we employ a computational scheme of isotopic substitution to disentangle the vibrations of the hydroxyl group from the environment. These schemes are referred to as Scheme II-III and more details are given in Ref. [11].

5.4.2 Dominance of OH(1) at the pre-edge region

The experimental O K-edge XAS spectrum is displayed in Fig. 5.20. In addition to the main resonance the spectra contain signals at lower
Figure 5.19: Visualisation of the normal modes in kaolinite, represented by the OH(1) group. Top row displays from left to right OH-stretching mode, rotation mode I and rotation mode II. Bottom row displays from left to right translation mode I, translation mode II and translation mode III. Figure is reproduced from Ref. [11] with permission from American Physical Society ©American Physical Society.

photon energies, denoted by the letters A-D. Feature A and B result from the signal of defect states and radiation induced production of quasi-molecular oxygen [64]. The pre-edge feature at 534.3 eV, D, on the other hand, is the result of absorption into resonances related to the OH-groups. Adjacent to this feature, at the absorption energy denoted C (532.9 eV), we should be able to see effects of detuning from the OH-resonance. However, there is also possibility to see some effects also from B at this energy.

Figure 5.20: Experimental oxygen K-edge XAS spectrum of kaolinite. Particular pre-edge features are marked (A-D) to facilitate discussion. Experimental data reproduced from Ref. [11]

To distinguish between the contribution of the four different hydroxyl groups to the XAS spectrum, we simulate the O K-edge XAS for all oxygen atoms individually, shown Fig. 5.21(a). By comparison of the
Figure 5.21: (a) The theoretical (DFT-HCH) XAS spectra displaying the contribution of the chemically inequivalent oxygen atom to the total absorption spectrum compared to the experimental oxygen K-edge XAS. For notation of the O atoms see Ref. [11]. The excitation energy of the pre-edge feature D is marked by a dashed vertical line. (b) The average of the individual theoretical spectra and the contribution of hydroxyl oxygen in OH(1) compared to the experimental XAS spectrum. Figure is reproduced from Ref. [11] with permission from American Physical Society ©American Physical Society.

When comparing the theoretical results to the experimental spectrum, we notice that only the spectrum of OH(1) has intensity at the pre-edge region. Hence, it is evident by exciting into the resonance at D, quasi-elastic RIXS probes the vibrational states of this hydroxyl group. The position of OH(1) in the layer, resulting in weak hydrogen bonding with its surroundings, is interpreted to be the reason for its dominance at the pre-edge, an effect that is previously established in liquid water [65].

In Fig. 5.21(b), the experimental spectrum is compared to the theoretical spectrum, derived by the average of the individual simulated spectra. The theoretical spectrum shows a qualitative agreement with the experimental spectrum. However, due to the limited accuracy of the HCH DFT method, the spectral profile of the experimental data is not faithfully reproduced. Nonetheless, based on the XAS results, we continue investigating RIXS for this particular hydroxyl group.
5.4.3 Character of the 1D cuts in the ground state and core-excited state potential energy surfaces

From an investigation of the XAS, we concluded that only the OH(1) group will be of interest for the simulation of the O K-edge RIXS in kaolinite. Therefore, we focus the discussion of the 1D PESs on this hydroxyl group. The PESs of the ground state and the lowest core-excited state for the six vibration modes of OH(1) are displayed in Fig. 5.22(a-f).

Evidently the PES cuts for the different degrees of freedom have distinct characters. This implies that the wave packet propagation, and, as such, the nuclear dynamics of the core-excited state is affected by the degree of freedom. Therefore, we will spend some time identifying the characters of the PESs of the ground state and the core-excited state and lay the foundation for the analysis of the RIXS spectra that is discussed in section 5.4.4.

The ground state PES of the OH-stretching mode, shown in Fig. 5.22(a), is bound and anharmonic for OH-bond length elongation, indicating a coupling of OH-stretching with other OH-vibration modes. The minimum of the core-excited state PES is displaced with regards to the ground state minimum, hence, the gradient for vertical excitation from the ground state is large. This implies that ultrafast bond elongation will result from core-excited state dynamics.

The change in the dipole moment of the hydroxyl group upon ex-
citation strongly influences the attractive (electrostatic) and repulsive (caging) interactions with the environment, resulting in the "double well" shape of the core-excited state PESs of the OH-rotation modes, as seen in Fig. 5.22(b-c).

The character PESs of the three translation modes, shown in Fig. 5.22(d-f), vary with the direction of the translation motion. For vertical excitation from the ground state, the gradient is small for all three modes.

5.4.4 O K-edge on-resonance RIXS along the six vibration modes

Figure 5.23: Experimental RIXS spectra for incoming radiation frequencies corresponding to C (532.9 eV) and D (534.3 eV). The spectra are normalised against the measurement time (20 min for feature C and 70 min for feature D). (a) Complete RIXS spectra at C and D. (b) Spectra zoomed in to the shaded region to display vibrational progression. Figure is reproduced from Ref. [11] with permission from American Physical Society ©American Physical Society.

The measured RIXS spectra are presented in Fig. 5.23. At 7-14 eV energy loss (Fig. 5.23(a)) we see a broad signal that disappears for the detuned spectra (C) corresponding to excitation into electronically excited states. The signal from vibrational excitations is visible in the 0-3 eV energy loss region, Fig. 5.23(b). Excitation into the D resonance, results in a vibrational progression consisting of four to five overtones, each of them consisting of a "double peak" with $\sim 0.1$ eV splitting. Exci-
tation into C shortens the vibrational progression and no "double peaks" are observed, which is an effect of the detuning from the D resonance.

The simulated RIXS spectrum for the OH-stretching mode is displayed in Fig. 5.24(g). The energy position of the stretching vibrational resonances of the simulated spectrum are in good agreement with the main resonances of the experimental spectrum. The fine structure, giving rise to the experimental "double peak", is not reproduced by the simulated spectrum for the OH-stretching mode.

To account for the fine structure in the experimental RIXS spectrum, we need to look at the spectra generated by the remaining five vibration modes, also plotted in Fig. 5.24(g). The OH-rotation modes, Fig. 5.24(b-c), have overlapping vibrational progressions. The lower vibrational frequency of the rotation modes compared to the OH-stretching mode results in a smaller energy spacing of the vibrational resonances. Hence, there is contribution of the rotation modes of OH to the fine structure of the RIXS vibrational resonances. The translation modes, Fig. 5.24(d-f), are not excited in RIXS, Fig. 5.24(g), mainly due to the small gradient in the core-excited PES at vertical excitation. Hence, we ascribe the origin of the experimental "double peak" to excitation of lower frequency OH-rotation modes.
Figure 5.24: Top two panels (a)-(f): 1D cuts in the ground state and lowest core-excited state PESs along six vibrational modes of OH(1) in kaolinite. Vertical lines show the vertical transition from the ground state minimum. (g) Theoretical on-resonance RIXS spectra of OH(1) simulated for cuts along each vibrational mode, respectively, compared to the experimental RIXS spectrum. Theoretical spectra are normalised internally against the elastic ($\nu_0 \rightarrow 0$) transition. Figure is reproduced from Ref. [11] with permission from American Physical Society. ©American Physical Society.
6. Summary and Outlook

In this thesis, results from RIXS investigations of multidimensional dynamical processes in molecules and molecular systems have been presented. Both small systems, such as the gas phase H$_2$O and H$_2$S molecules, and extended molecular systems, such as aqueous ammonia and kaolinite clay, were studied. These investigations were carried out using a computational approach, in which quantum chemistry calculation were used to generate the multidimensional PESs of states involved in the RIXS process. The motion of the nuclei were modelled with quantum nuclear wave packet simulations and occasionally classical dynamics. The theoretical results were compared against high-resolution experimental measurements.

Insight into the intramolecular and intermolecular interactions governing the dynamics have been gained. By simulation of the decay back to the electronic ground state, via the quasi-elastic RIXS decay channel, a detailed mapping of the ground state PES has been obtained. Particularly, this investigation have revealed effects on the dynamics that are related to anharmonicity of the ground state PES. Ultrafast dissociation, occurring on a similar timescale as the RIXS decay process, has been investigated and the contribution from decay in the slightly distorted core-excited molecule as well as in the core-excited dissociation fragments have been identified. A multidimensional treatment of dynamics in RIXS is important, which is seen in the investigation the RIXS process in kaolinite and in H$_2$O.

Future prospects include simulation of the quantum dynamics of the K-edge RIXS process of the H$_2$S molecule. There are similarities between the PES of the H$_2$O and the H$_2$S molecules but also important differences, so this investigation may yield new insights into dynamics of RIXS. A natural continuation would be to study the NH$_3$ molecule using a computational approach similar to the one used for the H$_2$O and H$_2$S molecules. The NH$_3$ molecule has an additional stretching degree of freedom that would need to be efficiently incorporated in the model. Another interesting future development would be to calculate RASPT2 PESs also for solvated systems. In this case the molecular
cluster needs to be embedded by, *e.g.* a QM/MM approach. When such a computational methodology is implemented, specific excited states can be targeted and a highly detailed description of the dynamics in solvated systems would be obtained.
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