Quantum Nuclear Dynamics in Resonant X-ray Scattering of Gas-Phase and Liquid Systems

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Abstract

This thesis focuses on the role of the nuclear degrees of freedom in X-ray induced molecular processes. An important part of it is devoted to establishing theoretical principles to model and interpret high-resolution resonant X-ray scattering experiments in gases and liquids. Our investigations address the resonant inelastic x-ray scattering (RIXS) of H$_2$O(g), H$_2$O(l) and CH$_3$OH(g) and Auger emission induced by hard X-rays in CO(g). The simulations for gas-phase systems are based on a multi-mode wave packet formalism and on potential energy surfaces computed with multi-configurational approaches.

For liquid systems, we propose a classical/quantum formalism for simulating RIXS based on a combination of 
*ab initio* molecular dynamics, density functional theory calculations and quantum nuclear wave packet propagation. The developed model is able to reproduce the experimental observation of shortening of the vibrational progression in H$_2$O(l).

We show that electronically-elastic RIXS has an intrinsic capability to map the potential energy surface and to carry out vibrational analysis of the electronic ground state in free molecules as well as liquids. For gas-phase water, we see that the landscape of different core-excited states cause the nuclear wave packet to be localized along specific directions thus allowing to reconstruct one-dimensional potential energy curves. For liquid water, we propose a model for deriving, from experiment, confidence intervals for the molecular potential energy curves along the OH bonds, which are determined by the local arrangement of the hydrogen bond network.

We also investigate the role of ultra-fast rotations induced by photoionization by hard X-rays. In this case, the ejection of a fast photoelectron results in an ultra-fast rotational motion of the molecule, which combined with the anisotropy of the Auger process causes the spectral profile to be split due to a dynamical Doppler effect.
List of papers included in this Thesis


**Paper IV**  V. Vaz da Cruz, E. Ertan, N. Ignatova, R. C. Couto, S. Polyutov, M. Odelius, V. Kimberg, and F. Gel’mukhanov, *Anomalous polarization dependence in vibrationally resolved RIXS of H_2O* (manuscript).


Additional papers not included in this Thesis


Comments on my contributions to the papers included in this thesis

- I was responsible for developing the code used for simulating the nuclear dynamics and computing the RIXS and XAS spectra in Papers I, II, III, IV, V and VI.
- I participated in the theoretical analysis, discussion of the results, nuclear dynamics calculations and writing of the manuscript in Papers I and II.
- I was responsible for the theoretical analysis and fitting the potentials, contributed to figure production and writing the manuscript of Paper III.
- I was responsible for all quantum nuclear dynamics and spectra calculations, results discussion, production of all figures and writing of the manuscript of Papers IV and V.
I was responsible for part of the nuclear dynamics calculations, participated in the discussion of the results, figure production and writing of the manuscript of Paper VI.

I participated in the theoretical modelling, writing of the manuscript and figure production of Paper VII.
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List of abbreviations

RIXS - Resonant inelastic X-ray scattering
PES - Potential energy surface
PEC - Potential energy curve
GS - Ground state
CE - Core-excited
FC - Franck-Condon
BO - Born-Oppenheimer
XAS - X-ray absorption spectroscopy
NEXAFS - Near-edge X-ray absorption fine structure
XES - X-ray emission spectroscopy
DFT - Density functional theory
XCH - Excited core-hole
FCH - Full core-hole
HCH - Half core-hole
CASSCF - Complete-active-space self-consistent field
RASPT2 - Restricted active-space second-order perturbation theory
MD - Molecular dynamics
AIMD - *ab initio* molecular dynamics
HB - hydrogen bond
D₁ - Single donor
D₂ - Double donor
RMSD - Root mean square deviation
**RMSF** - Root mean square fluctuation

**GA** - Genetic algorithm

**nD** - n-dimensional
Chapter 1

Introduction

Molecules may be regarded as a set of atoms which are held together by chemical bonds. According to non-relativistic quantum mechanics, these infinitely minuscule (length scale $\sim \AA = 10^{-10} \text{ m}$) objects obey the Schrödinger equation and have particle and wave-like properties [1]. Molecules are, for evident reasons, not observable to the naked eye, and at the macroscopic level at which humans go about their lives (length scale $\sim \text{ m}$), they are only perceived in terms of their collective properties such as color, smell, temperature, density among others. Although, at first, this information may seem satisfying, soon one is taken by a wish to understand the root of the observed macroscopic properties, which means addressing the molecular and quantum mechanical nature of matter.

Molecular systems may be more closely examined when one exposes them to external perturbations, which cause them to react to it, thus giving away some bit of information about the system. The most common type of external perturbation constitutes electromagnetic waves. When a molecule is exposed to such a wave the most obvious outcomes are: It may absorb the wave, thus promoting the system to an excited state; the wave may be scattered, either elastically or inelastically. The body of such techniques for measuring molecular properties through the use of electromagnetic waves are commonly denoted Spectroscopy.

This thesis deals with spectroscopic techniques in the realm of X-ray physics, which we shall introduce now. X-ray electromagnetic waves are unique in the sense that their wavelength is comparable to the interatomic distances in molecules and crystals. Therefore, it comes at no surprise that the discovery of X-rays by Röntgen [2] led to a revolution in physics, chemistry and biology, since diffraction of elastically scattered X-rays [3, 4] could be used to determine the structure of crystalline samples, ranging from simple ionic solids to DNA [5].

Although structural information is vital, the short wavelength of X-rays provides them with another extraordinary property: The capability of probing element-specific core processes.
When two atoms form a chemical bond, the wavefunction of the so-called valence electrons (outermost electrons) overlap and therefore the concept of an electron belonging to a specific atom in the molecule is lost, to a large extent. However, the electrons that lie closest to the nucleus remain in very confined wavefunctions, which have very limited overlap with the wavefunctions of neighboring atoms. Since core-electrons are localized on the atom, X-ray spectroscopy is largely credited with providing element specific information, even in complex systems, through different processes, such as by causing the ejection the inner shell electrons [6] (XPS), promoting them to unoccupied molecular levels [7] (XAS or NEXAFS), recording the cascade emission, after core-ionization, of photons [8] (XES) or Auger electrons, or by observing the inelastically scattered X-ray photons [9].

Inelastic scattering of X-rays is typically very weak. However, its occurrence can be drastically enhanced if the energy of the incoming photons matches an absorption resonance. This fact makes it possible to observe coherently scattered light, in what is known as resonant inelastic X-ray scattering [9] (RIXS). Resonantly scattered radiation provides detailed information about the electronic structure and vibrations of molecules, liquids and solids. Also the fact that RIXS is very sensitive to the polarization of the X-ray photons [10] and to relatively small changes of the excitation energy [11, 12] adds extra controlability to the process enabling a very comprehensive analysis of the studied system. Another important feature of RIXS is the property that the final spectrum is not affected by the core-hole lifetime broadening but rather by that of the final-state. This is vital when considering the quasi-elastic (or participator) scattering channel where the system decays to the electronic ground state, since it implies that the spectral resolution of this channel is only limited by the experimental broadening [9].

The ever improving experimental resolution of RIXS measurements means that a higher level of accuracy is required from theoretical formulations, and their corresponding computational implementations. This is a key aspect in this thesis, as we direct our efforts into investigating the finer details provided by X-ray spectroscopy, which are highly affected by the nuclear motion. At the very foundation of this thesis we have the development of computational wave packet techniques for multi-modes systems, in the context of RIXS spectroscopy. Therefore, this thesis may be regarded as an effort towards accurate theoretical modeling of high-resolution X-ray spectroscopy.

Our investigations were carried out for four different molecular systems, namely H\textsubscript{2}O(g), CH\textsubscript{3}OH(g), CO(g) and H\textsubscript{2}O(l). The systems were chosen based on a compromise among three factors: general relevance, availability of experimental data and amenability to high-level theory. The investigations carried out for each mentioned system share the common theme of having pronounced dynamical effects caused by the nuclear degrees of freedom. These effects are manifested as vibrations, rotations, bond elongations and molecular frag-
mentations that take place within the lifetime of a short-lived (time scale $\sim 10^{-15}$ s) core-excited/ionized state and result in experimentally measurable features, as seen throughout this thesis.

Gas-phase water is a very interesting system and it is relevant for several reasons. It constitutes a natural starting point for understanding X-ray induced phenomena in the corresponding liquid phase. In addition, it possesses enough complexity to be a good benchmark system for high-level theory.

A large part of this thesis is devoted to the vibrationally resolved RIXS spectrum of liquid water. Liquid water is a system of inherent interest due its crucial role for biological systems. Furthermore, it poses a challenge to theory owing to its structure being made up of a fluctuating hydrogen bond network. Although a few experimental investigations of the vibrationally resolved RIXS spectrum of liquid water can be found in the literature [13–15], no detailed theoretical calculations have been carried out, this is likely related to the fact that the well resolved vibrational resonances seen in the spectrum are not accurately described by classical nuclear dynamics [16]. This observation is in contrast with the NEXAFS and XES spectra of liquid water which have been extensively studied both experimentally [17–21] and theoretically [22–27]. A comprehensive overview may be found in ref. [28].

Another interesting system considered in this thesis is the methanol molecule. It shares many similarities with water, in the sense that it may also form hydrogen bonds in the condensed phase. However, when considering the free molecule, it has twelve vibrational modes instead of three in water. Liquid methanol has been investigated by XES [29], XAS [30], and RIXS [31]. Concerning the gas-phase, the O 1s X-ray absorption spectra of gas phase methanol were investigated by different groups [32–34] where the spectrum is assigned based on semi-empirical calculations [32–34]. There is one exception [30] where the transition-potential density functional theory approach was employed. A shortcoming of most previous studies is the neglect of the nuclear motion, even though it was shown through RIXS measurements in $CH_3OH(g)$ [34] and $CH_3OH(l)$ [31] that there is a strong sensitivity of the high-energy RIXS peak to isotopic substitution ($CH_3OH \rightarrow CH_3OD$). These observations warrant a detailed investigation of this important system.

Although the importance of vibrations and molecular rearrangements during the short core-hole lifetime may be easier to grasp, it might not be so intuitive for the rotational motions that happen during X-ray induced processes. This is due to the very small spacing between the rotational levels of molecular systems, which usually are spaced only by a few meV and are virtually undetectable. However, the role of rotations may be crucial when considering Auger emission which is initiated by hard X-rays. In this case the ejected photoelectron transfers large recoil momentum and angular momentum to the molecule thus resulting in
Doppler splitting and shift of the spectral line. In this thesis we study this effect for the CO(g) molecule where we ionize the C1s electron and detect the subsequent non-resonant Auger emission.

This thesis is organized follows. Chapter 2 presents a brief review of a few key theoretical concepts, derivation of the general model utilized throughout the thesis, short description of the numerical techniques employed and a review of the classical theory of rotations during Auger emission. Chapter 3 collects the results devoted to the quasi-elastic RIXS of gas-phase water. Chapter 4 is devoted to the quasi-elastic RIXS process in liquid water. Chapter 5 is devoted to the analysis of the RIXS of the free methanol molecule. In chapter 6, we investigate the role of the rotational degrees of freedom during the non-resonant Auger process in the CO molecule initiated by hard X-rays. Finally, chapter 7 compiles a summary of the achievements of this thesis.
Chapter 2

Theoretical background

In this Chapter, we outline the basic theory necessary for investigating the resonant X-ray scattering process in molecules and liquids. We start from the general formalism, both in the frequency and time domains, followed by the proposed model for handling multi-mode systems. A brief description of how these equations were implemented is also given. In addition, we lay out the basic theory for the translational and rotational degrees of freedom in the course of photoionization and Auger decay.

2.1 The molecular problem and the Born-Oppenheimer approximation

Within non-relativistic quantum mechanics, molecular systems are described by the time independent Schrödinger equation

\[ \mathcal{H}|\Psi(R, r)\rangle = E|\Psi(R, r)\rangle, \quad (2.1) \]

where \( \Psi \) is the wavefunction, which depends on the coordinates of all electrons \( r \) and nuclei \( R \), and \( \mathcal{H} \) is the Hamiltonian operator of the system, which in atomic units reads

\[ \mathcal{H} = -\sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{A>\beta} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}. \quad (2.2) \]

Here, the first two terms are the kinetic energy operators of the nuclei and electrons, respectively. The third term describes the nucleus-electron attraction, while the last two terms are the nucleus-nucleus and electron-electron repulsion terms. A direct solution of this equation
for polyelectronic systems is impractical without approximations. Therefore, we consider
the following factorization of the wavefunction

$$\Psi(R, r) = \sum_k |\Phi_k(R)\rangle |\chi_k(r; R)\rangle$$

(2.3)

where $\Phi_k$ is a function of only the nuclear degrees of freedom and $\chi_k$ is a function of the
electronic coordinates, while depending parametrically on the nuclear coordinates, the index
$k$ denotes the electronic state of the system, described below. Similarly, we may rewrite the
total Hamiltonian (Eq. 2.2) as

$$H = T_{nu} + h^e, \quad T_{nu} = -\sum_A \frac{1}{2M_A} \nabla^2_A$$

$$h^e = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_iA} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i,j} \frac{1}{r_{ij}}.$$

(2.4)

The parametric dependence of $h^e$ and $\chi_k(r; R)$ means that a set of nuclear coordinates
$R$ define a potential for the electrons for which one must solve the electronic Schrödinger
equation

$$h^e |\chi_k(r; R)\rangle = \mathcal{E}_k(R) |\chi_k(r; R)\rangle.$$  

(2.5)

The solution of this equation is the objective of quantum chemistry and the so-called $ab$-initio
methods. Now, we may write the equation that describe the nuclear degrees of freedom by
substituting Eq. 2.3 into Eq. 2.2 and multiplying, on the left side, by $|\chi_j(r; R)\rangle$

$$\sum_k (\chi_j(r; R) |T_{nu} |\Phi_k(R)\rangle |\chi_k(r; R)\rangle + \mathcal{E}_k(R) |\Phi_j(R)\rangle) = E |\Phi_j(R)\rangle.$$  

(2.6)

Here, the only complication resides in the first term, which coupled the nuclear and electronic
wavefunctions. However, this term is usually small, provided the potential energy surfaces
of different electronic states are well separated in energy. Therefore, we assume

$$T_{nu} [\Phi_k(R) |\chi_k(r; R)\rangle \approx [T_{nu} \Phi_k(R)] |\chi_k(r; R)\rangle,$$

(2.7)

now the nuclear motion is decoupled from the electronic degree of freedom, and the electrons
take on the role of a potential energy surface (PES) which guides the nuclear dynamics.
Therefore, we rename $V_k(R) \equiv \mathcal{E}_k(R)$ and write the final equations as

$$h^e \chi_k(r; R) = V_k(R) \chi_k(r; R),$$

$$[T_{nu} + V_k(R)] \Phi_k(R) = E \Phi_k(R).$$

(2.8)

The solution of the electronic problem is the main subject of quantum chemistry, the review
of these techniques is beyond this thesis, but may be found in the following references [35–
39].
2.2 Resonant X-ray scattering

RIXS may be understood as a two-step process and it is commonly depicted by the diagram shown in Fig. 2.1 (a) where in a first step a molecule absorbs an X-ray photon, being promoted from the ground state $|0\rangle$ to a set of intermediate states $|c\rangle$ while emitting a new X-ray photon upon decay to one of the many possible valence states $|f\rangle$ or even back to the ground state. The decay is caused by the lifetime of the core-excited state which is determined by zero-point vacuum fluctuations and electron-electron Coulomb interactions in the molecule [9].

![Figure 2.1: a) RIXS diagram in terms of electronic states. b) RIXS diagram in terms of illustrative one-dimensional potential energy curves.](image)

Within the Born-Oppenheimer approximation, the RIXS diagram for the nuclear motion may be illustrated by Fig. 2.1 (b) in terms of one-dimensional potential energy curves (PECs). In this case the ground state nuclear wavefunction is promoted to the potential energy curve of an intermediate electronic state $|c\rangle$. The ground state nuclear wave function is, in general, not an eigenfunction of the intermediate state potential energy curve and therefore it evolves in time. We denote this intermediate nuclear wavefunction by the general term wave packet. A nuclear wave packet is a coherent superposition of eigenstates of the system, which may be discrete (as for bound PECs) or a continuum wave functions (as for dissociative PECs). The intermediate wave packet continuously decays to the PEC of the many possible final states populating the respective excited vibrational levels of each PEC.

Now that we have a good qualitative description of RIXS it is time to outline the theory necessary for describing it. RIXS is a coherent scattering process, where the absorption and emission steps are linked, and it is formulated in terms of the Kramers-Heinsenberg (KH)
dependent picture: The RIXS cross section for a multi-mode molecule is given by the KH equation [9]

\[ \sigma(\omega', \omega) = \sum_{\nu_f} |F_{\nu_f}|^2 \Delta(\omega - \omega' - \omega_f0 - \epsilon_{\nu_f} + \epsilon_{\nu_0}, \Gamma_f), \]  

(2.10)

\[ F_{\nu_f} = \sum_{\nu_c} \langle \nu_f | D_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | \nu_0 \rangle (\omega - \omega_c0 + \epsilon_{\nu_0} - \epsilon_{\nu_c} + i\Gamma), \]

Here and below, unless stated otherwise, the ket and bra vectors denote nuclear wavefunctions within a single scattering channel which starts from the ground state vibrational wavefunction

\[ |\nu_0\rangle. \]  

(2.9)

**Time-independent picture:** Using the time-dependent representation for the Lorentzian

\[ \frac{1}{(x + i\Gamma)} = -\int_0^\infty e^{i(x + i\Gamma)t} dt, \quad \Delta(x, \Gamma) = -\text{Im} \frac{1}{x + i\Gamma} = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i(x + i\Gamma)t} dt \]

(2.12)

the KH scattering amplitude and the cross section (2.10) can be rewritten in the time-dependent picture [9]

\[ F_{\nu_f} = -i \sum_{\nu_c} \langle \nu_f | \Psi(0) \rangle, \]

(2.13)

\[ |\Psi(0)\rangle = \sum_{\nu_c} \frac{D_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | \nu_0 \rangle}{\omega - \omega_c0 + \epsilon_{\nu_0} - \epsilon_{\nu_c} + i\Gamma} = D_{fc} \int_0^\infty e^{i(\omega - \omega_c0 + \epsilon_{\nu_0} + i\Gamma)t} |\psi_c(t)\rangle dt, \]

\[ \sigma(\omega', \omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i(\omega - \omega' - \omega_f0 + \epsilon_{\nu_0} + i\Gamma)f} \sigma(t) dt, \quad \sigma(t) = (\Psi(0)|\Psi(t)). \]
The RIXS process is affected by nuclear dynamics in the core-excited and final (ground) states via the nuclear wave packets

\[ |\psi_c(t)\rangle = e^{-i\hbar c t} D_0 |\nu_0\rangle, \quad |\Psi(t)\rangle = e^{-i\hbar f t} |\Psi(0)\rangle. \tag{2.14} \]

### 2.2.1 Mixed representation: mD+nD model

In this thesis, we are interested in modeling multi-mode systems in which at least one coordinate is highly excited. For instance, the system dissociates along a given reaction path while the remaining degrees of freedom are only modestly active. For this purpose, we propose a model which we denominate “mixed-representation”, which involves partitioning the degrees of freedom into two sets. One which is to be treated in the time domain and another which is treated in the energy domain.

Let us consider a molecular system with \(m+n\) degrees of freedom. In this case, \(m\) modes will be described using the time-dependent wave packet technique while the rest \(n\) modes using the stationary Franck-Condon (FC) method. Such a combined approach is convenient when we have dissociative states, which are easily handled by the wave packet technique.

Let us write the total nuclear Hamiltonian as the sum of two independent parts

\[ h_i = h_i^{(m)} + h_i^{(n)}, \quad i = 0, c, f \tag{2.15} \]

and will search for solutions of this equation in the mixed (time-energy) representation by writing the total wavefunction as a product of the wave packet \(\psi(t)\) and the eigenfunction \(|\nu_i\rangle\)

\[ |\psi(t)\rangle|\nu\rangle, \quad i \frac{\partial}{\partial t} |\psi\rangle = h_i^{(m)} |\psi\rangle, \quad h_i^{(n)} |\nu\rangle = \epsilon_{\nu} |\nu_i\rangle. \tag{2.16} \]

Now, the total initial vibrational state, in the general Eq.(2.14), should be replaced as follows

\[ |\nu_0\rangle \rightarrow |\nu_0\rangle|\mu_0\rangle, \quad \epsilon_{\nu_0} \rightarrow \epsilon_{\nu_0} + \epsilon_{\mu_0}. \tag{2.17} \]

Here \((|\nu_0\rangle, \epsilon_{\nu_0})\) and \((|\mu_0\rangle, \epsilon_{\mu_0})\) are the eigenfunctions and eigenvalues of the ground state Hamiltonians \(h_0^{(n)}\) and \(h_0^{(m)}\), respectively. Using this, the condition of completeness \(1 = \sum |\nu_c\rangle\langle\nu_c|\) and \(\exp(-i\hbar c t) \rightarrow \exp(-i\hbar^{(n)} c t) \exp(-i\hbar^{(m)} c t)\) one can do the following substitutions

\[ |\psi_c(t)\rangle = e^{-i\hbar c t} D_0 |\nu_0\rangle \tag{2.18} \]

\[ \rightarrow e^{-i\hbar^{(n)} c t} |\nu_0\rangle e^{-i\hbar^{(m)} c t} D_0 |\mu_0\rangle = e^{-i\hbar^{(n)} c t} |\nu_0\rangle |\psi_c(t)\rangle \]

\[ = \sum_{\nu_c} e^{-i\epsilon_{\nu_c} c t} |\nu_c\rangle \langle\nu_c|\nu_0\rangle |\psi_c(t)\rangle, \]
Chapter 2 Theoretical background

where

\[ |\psi_c(t)\rangle = e^{-i\hbar c t} D_{c0}|\mu_0\rangle. \] (2.19)

Now, we have all ingredients necessary to rewrite the expression for the wave packet \( |\Psi(0)\rangle \) (2.13)

\[ |\Psi(0)\rangle = D_{fc} \int_0^\infty e^{i(\omega - \omega_c + \epsilon_{\nu_0} + \epsilon_{\nu} + i\Gamma)t} |\psi_c(t)\rangle dt \] (2.20)

\[ \rightarrow \sum |\nu_c\rangle \langle \nu_0 | \psi_c(0)\rangle, \]

\[ |\Psi_{\nu_c}(0)\rangle = D_{fc} \int_0^\infty e^{i(\omega - \omega_c + \epsilon_{\nu_0} + \epsilon_{\nu} + i\Gamma)t} |\psi_c(t)\rangle dt \]

and for the wave packet \( |\Psi(t)\rangle \) (2.14)

\[ |\Psi(t)\rangle = e^{-i\hbar f t}|\Psi(0)\rangle \] (2.21)

\[ \rightarrow e^{-i\hbar f t} e^{-i\hbar c t} \sum |\nu_c\rangle \langle \nu_0 | \psi_c(0)\rangle \]

\[ \rightarrow \sum \sum e^{-i\epsilon_{\nu} t} |\nu_f\rangle \langle \nu_f | \psi_f(0)\rangle \]

\[ \Psi_{\nu_c}(t) = e^{-i\hbar f t}|\Psi_{\nu_c}(0)\rangle. \]

Where we used expression (2.20) for \( |\Psi(0)\rangle \) and the condition of completeness of the final vibrational states \( 1 = \sum |\nu_f\rangle \langle \nu_f | \). Further, using the orthonormality of the vibrational states \( \langle \nu_f | \nu'_f \rangle = \delta_{\nu_f, \nu'_f} \) and Eqs. (2.20) and (2.21), one is able to compute the auto-correlation function \( \sigma(t) \) (2.13) and find the final expression for the RIXS cross-section in the mixed representation

\[ \sigma(\omega', \omega) = \frac{1}{\pi} \text{Re} \sum_{\nu_f' \nu_c} \int_0^\infty e^{i(\omega - \omega' - \omega_{\nu_f'} + \omega_{\nu_f} + i\Gamma_{\nu_f'}t)\tau_{\nu_f'\nu_c}(t)} dt, \]

\[ \sigma_{\nu_f'\nu_c}(t) = (|\Psi_{\nu_f'}(0)\rangle |\Psi_{\nu_c}(t)\rangle). \] (2.22)

2.2.2 Numerical implementation: the eSPec-RAMAN code

The code developed in this thesis builds upon a wave packet propagation program named eSPec written by F. F. Guimarães [40], extensively used for X-ray absorption and IR-X-ray pump-probe simulations [41–45]. In this thesis, we have extended the original code to
be able to simulate RIXS and implemented the described \( nD + mD \) formalism for treating systems with several vibrational modes.

The basic algorithm for computing the RIXS cross-section is very intuitive and it is made of 5 major steps: 1) Find the initial state \( |\nu_0\rangle \); 2) Propagate \( |\nu_0\rangle \) on the intermediate state PES (Eq. 2.14); 3) Compute \( |\Psi(0)\rangle \) (Eq. 2.13); 4) Propagate \( |\Psi(0)\rangle \) on the final state PES and finally 5) Compute \( \sigma(\omega', \omega) \) as the half-Fourier transform of \( \sigma(t) \). We shall briefly go over the implementation of these steps.

All nuclear wave functions are represented by the discrete variable representation (DVR) in both time (time step \( \Delta t \)) and space (coordinate step \( \Delta R \)). The operators are expressed in the position space, and the second-order derivatives required for the kinetic energy operators are implemented by a fourth-order \( O(\Delta R^4) \) difference formula. All wave packet propagations were carried out by a simple second order difference scheme [40] with a time step of \( \Delta t = 5 \times 10^{-4} \) fs and using absorbing boundary conditions, in the calculations involving dissociative states, to avoid non-physical reflections at the edges of the grid. The time-independent Schrödinger equation was solved by direct diagonalization, when feasible, otherwise the iterative Lanczos diagonalization method was used.

A key ingredient of our implementation is the usage of the fast Fourier transform [46] in order to compute the intermediate wave packet \( |\Psi(0)\rangle \) (Eq. (2.20)), instead of direct integration [47]. This allows us to drastically reduce the total number of integrals required for the \( nD + mD \) implementation by taking advantage of the shift theorem of the Fourier transform.

The developed code was used in papers I through VI included in this thesis and also in papers 2, 3 and 4 which are not included in this thesis.

### 2.3 Rotations and translations induced by photoionization

In the previous sections we outlined the theory of RIXS taking into account electronic and vibrational degrees of freedom. Modern X-ray spectroscopy can easily resolve electronic and vibrational states due to the rather large spacing between electronic states (\( \sim 1-10 \) eV) and vibrational levels (\( \sim 0.1-0.5 \) eV). The situation is qualitatively different for rotational levels which in traditional X-ray spectroscopy, with resolution of 0.05-0.1 eV, are not resolved due to the small spacing between these levels \( \leq 0.01 - 0.001 \) eV. However, the rotational degrees of freedom can be seen in photoelectron spectroscopy. The main reason for this is the large momentum of the photoelectron which results in a rather large rotational recoil.
and rotational Doppler shift of spectral lines. Contrary to previous studies, in my thesis I will study the role of rotational and translational degrees of freedom in Auger spectroscopy, following recent experiments of core-ionization of the carbon atom followed by Auger decay in the CO molecule. Let us remind ourselves that the conventional shape of the Auger line is described by the amplitude of the studied non-resonant Auger process

\[ F \propto \frac{1}{\Delta E + i\Gamma}, \quad \Delta E = E_p - E_{res}, \quad E_{res} = E(1s^{-1}) - E_f \]  

(2.23)

which shows that the amplitude of process takes maximum when the energy of Auger electron \( E_p = p^2/2 \) is equal to the resonant energy \( E_{res} \) of the Auger decay.

Now, we would like to understand how the momenta of photon, fast photoelectron and Auger electron

\[ k_{ph}, \quad k, \quad p, \]  

(2.24)

\( k_{ph} \approx 2.7 \) a.u., \( k \approx 27 \) a.u., \( p \approx 4.5 \) a.u.

effect the resonant condition in Auger amplitude (Eq. 2.23). To this end, we should write the energy, momentum and angular momentum conservation laws for the photoionization

\[ \omega + E_0 + \frac{Mv^2}{2} + \frac{Iw^2}{2} = E_k + \frac{Mv_1^2}{2} + \frac{Iw_1^2}{2} + E(1s^{-1}), \quad E_k = \frac{k^2}{2}, \]  

(2.25)

\[ k_{ph} + Mv = Mv_1 + k, \]

\[ j_{ph} + Ib = j_{w1} + j_k, \]

and for the whole Auger process

\[ \omega + E_0 + \frac{Mv^2}{2} + \frac{Iw^2}{2} + \frac{Iw'^2}{2} + \frac{Iw''^2}{2} + \frac{E_f}{2}, \quad E_p = \frac{p^2}{2}, \]  

(2.26)

\[ k_{ph} + Mv = Mv' + k + p, \]

\[ j_{ph} + Ib = j_{w'} + j_k + j_p, \]

where \( E_0, E(1s^{-1}) \) and \( E_f \) are the energies of the ground, core-ionized and final states, respectively; \( E_k \) and \( E_p \) are the kinetic energies of photoelectron and Auger electron, respectively; \( M \) and \( I = \mu R^2 \) are the mass and moment of inertia of the molecule; \( \mu \) is the reduced mass of the studied diatomic molecule; \( v, v_1, v' \) and \( w, w_1, w' \) are the translational and angular velocities of the molecule in the initial, core-ionized and final states respectively.

Here

\[ j_{ph} = -[R_n \times k_{ph}], \quad j_k = [R_n \times k], \quad j_p = [R_n \times p] \]  

(2.27)

are the recoil angular momenta that the molecule gets in the course of absorption of a photon, ejection of a photoelectron, and ejection of an Auger electron, respectively; \( R_n \) is the radius vector of core-ionized atom \( n \) with respect to the molecular center of gravity.
From Eq. 2.25, we find the kinetic energy of the photoelectron

\[ E_k = \omega + E_0 - E(1s^{-1}) \]

\[ - \left[ (v \cdot (k_{ph} - k)) + \frac{(k_{ph} - k)^2}{2M} + w \cdot (j_{ph} - j) + \frac{(j_{ph} - j)^2}{2I} \right]. \]

This equation, together with Eq. (2.26), results in the resonant condition for the Auger electron energy

\[ E_p - E_{res} - p \cdot \left( v + \frac{k_{ph}}{M} - \frac{k}{M} \right) - j_p \cdot \left( w + \frac{j_{ph}}{I} - \frac{j}{I} \right) + \frac{p^2}{2M} + \frac{j^2}{2I} = 0. \] (2.29)

Now, we are in position to modify the Auger amplitude Eq. (2.23)

\[ F \propto \frac{1}{\Delta E + D_{tr} + D_{rot} + \Delta_{rec} + i\Gamma} = -i \int_0^\infty e^{i(\Delta E + D_{tr} + D_{rot} + \Delta_{rec} + i\Gamma)t} dt, \] (2.30)

\[ D_{tr} = p \cdot v_{eff}, \quad D_{rot} = j_p \cdot w_{eff}, \quad \Delta_{rec} = \frac{p^2}{2M} + \frac{j^2}{2I}. \]

We see that the Auger line is shifted by the translational \( D_{tr} \) and rotational Doppler shifts \( D_{rot} \) and by the recoil shifts \( \Delta_{rec} \). The recoil energy is caused by translational and angular recoil effects, related to the ejection of an Auger electron. The total recoil shift, being much smaller than the Doppler shifts, is neglected below. The effective translational velocity \( v_{eff} \) and angular velocity \( w_{eff} \) consist of three qualitatively different terms

\[ v_{eff} = -v - \frac{k_{ph}}{M} + \frac{k}{M}, \quad w_{eff} = -w - \frac{j_{ph}}{I} + \frac{j}{I}. \] (2.31)

The first terms, \( v \) and \( w \), come from the thermal motion

\[ v \sim \frac{p}{Mk_bT}, \quad w \sim \frac{w}{Mk_bT} = \sqrt{\frac{2k_bT}{I}}. \] (2.32)

The second terms \( k_{ph}/M \) and \( j_{ph}/M \) are the translational and angular velocities gained by the molecule in the course of photoabsorption, while the last terms \( k/M \) and \( j_k/M \) are caused by momentum and angular momentum transferred to the molecule by the ejected photoelectron. We can safely neglect the photon momentum according to the estimation given in Eq. 2.24. The situation is not so trivial for the thermal motion term because

\[ \frac{p\bar{v}}{p\nu_k} = \frac{\bar{v}}{\nu_k} = \sqrt{\frac{Mk_bT}{E_k}} \approx 0.36, \quad v_k = \frac{k}{M}. \] (2.33)
In spite of the fact that the thermal Doppler broadening is only three times smaller than $pv_k$, the contribution of the thermal Doppler broadening in total Doppler broadening

\[ D = \sqrt{(pv_k)^2 + (p\bar{v})^2} \approx pv_k \left[ 1 + \frac{1}{2} \left( \frac{\bar{v}}{v_k} \right)^2 \right] \approx pv_k (1 + 0.08) \]  

(2.34)

is one order of magnitude smaller than $pv_k$. This justifies the neglect of the thermal translational and rotational Doppler broadenings. So finally, we will use the following expression for the Doppler broadening

\[ D_{tr} = \frac{p \cdot k}{M}, \quad D_{rot} = \frac{\mathbf{j}_p \cdot \mathbf{j}_k}{I}. \]  

(2.35)

In previous studies, devoted to photoelectron spectroscopy, the initial speed $v$ and angular velocity $w$ were given by the thermal velocity and angular velocity

\[ \bar{v} = \sqrt{\frac{2k_BT}{M}}, \quad \bar{w} = \sqrt{\frac{2k_BT}{I}}, \]  

(2.36)

according to Boltzmann distributions

\[ W(v_x) = \frac{1}{\sqrt{\pi \bar{v}^3}} e^{-\frac{v^2}{\bar{v}^2}}, \quad W(w_x) = \frac{1}{\sqrt{\pi \bar{w}^3}} e^{-\frac{w^2}{\bar{w}^2}}. \]  

(2.37)

In ambient conditions, the thermal translational and rotational velocities are small. Therefore, the translational and rotational Doppler effects are also small ($\lesssim 0.1$ eV).

### 2.3.1 Enhancement of the Doppler effect in Auger spectra initiated by hard X-rays

The picture changes drastically in Auger process, which is initiated by hard X-rays. This process consists of two steps. In the first step of ejection of a fast photoelectron, a non-equilibrium distribution over the translational and angular velocities is created due to the recoil effect (see chapter 6). Now, the initial translational and angular velocities are much bigger than the thermal ones (see Eq. 2.24)

\[ v \sim \frac{k}{M} \gg \bar{v}, \quad w \sim \frac{R_n k}{I} = v \frac{M R_n}{\mu R^2} \gg \bar{w}, \]  

(2.38)

this leads to much larger Doppler shifts in comparison with the thermal counterpart

\[ D_{tr} \sim \frac{p k}{M} \gg p \bar{v}, \]  

(2.39)

\[ D_{rot} \sim D_{tr} \left( \frac{M}{\mu} \right) \left( \frac{R_n}{R} \right)^2. \]  

(2.40)
One should also notice that the rotational Doppler effect is strongly anisotropic. It depends on the angle between the molecular axis and momenta k and p

\[ D_{\text{rot}} \sim [R \times k][R \times p], \]

(2.41)

where the last one strongly affects the spectral shape of Auger line as we will show in Chapter 6.
Chapter 3

RIXS of gas-phase water

This chapter is devoted to the RIXS process in a gaseous water sample which ends up in the ground state. It constitutes the most natural starting point for understanding the same process in water in the liquid phase while at the same time being a system amenable to highly accurate theory. It is also an interesting showcase for demonstrating how site selective and state-specific RIXS excitation can be used for probing the ground state potential energy surface of molecular systems with several vibrational modes. We start by outlining some basic properties of X-ray spectroscopy of H$_2$O(g), followed by a strict analysis of the reconstruction of 1D cuts of the ground state PES. Finally, in the last section, we present a prediction of an anomalous polarization dependence of the vibrationally resolved RIXS spectrum in water caused by a break-down of the Franck-Condon approximation. Note that, in this chapter, the term “RIXS” will be used to denote specifically the quasi-elastic channels (scattering back to the ground state).

3.1 General properties of RIXS in gas-phase water

Let us start by a brief analysis of the main resonances seen in X-ray absorption spectrum of gas-phase water near the edge and the respective RIXS channels. In Fig. 3.1 a) we see the three lowest core-excited states alongside the theoretical XAS from Paper I, while in panel b) we see the analogous assignment made within a one-electron picture, displayed by the computed natural orbitals. Excitation to the $|O1s^{-1}4a_1^b\rangle$ state leads to a broad band, as shall be discussed in detail, this is due to the dissociative character of this state. Excitation to $|O1s^{-1}2b_1^a\rangle$ state leads to the appearance of fine structure reflecting the vibrational levels of the core-excited state, evidencing the bound character of this state. The third peak corresponds to excitation to the $|O1s^{-1}2b_1^a\rangle$ state, which has Rydberg character (Fig. 3.1b))
and this absorption band is considerably narrower, showing a asymmetric profile, which as we shall see, arises from the bending motion in the core-excited state.

As shown in the figure, we consider here the quasi-elastic channels. Also called “participator” channels. In this case the system is core-excited to the intermediate state, and continuously decays, according to \( \exp(-\Gamma t) \) to the ground state. Conversely, a core-electron is promoted from the 1\( a_1 \equiv O1s \) orbital to one of the unoccupied molecular orbitals, followed by continuous decay of this same electron filling the original core-hole. This process causes a sudden, and often severe, change on the forces acting on the nuclei of the molecule, therefore it is natural to expect that vibrational excitations occur.

### 3.2 Nuclear degrees of freedom and core-excited PESs

The water molecule has three vibrational modes, symmetric and anti-symmetric stretching of the OH bonds, and bending deformation of the \( \angle \) HOH angle. In Papers I and II, we model the RIXS and XAS of water within the 2D+1D model (according to the framework presented in Chapter 2). This is motivated by the fact that in H\(_2\)O the two stretching modes are strongly coupled [48, 49] whereas the bending mode couples weakly to the stretching motion. This observation leads us to treat the stretching motion by 2D wave packet calculations, while considering the uncoupled bending mode by FC amplitudes.
The first step towards including nuclear dynamics in the RIXS and XAS calculations is computing the molecular PES. All *ab-initio* PES, displayed in Fig. 3.2, were obtained with the RASPT2 method [50–52] and the details of the calculations may be found within Paper II. The 2D stretching PES were computed in valence coordinates [53], considering the bending angle frozen at the equilibrium value $\theta = 104.2^\circ$ while the 1D potentials were computed according to the bending mode coordinate obtained from frequency analysis. From the computed 2D stretching PES (Fig. 3.2) we notice the highly anharmonic GS surface of the stretching motion, which reflects the strong coupling between the symmetric and anti-symmetric stretching modes. The landscape of the dissociative $|01s^{-1}4a_1^1\rangle$ state is in obvious contrast with the GS PES, and its main features are the dissociative valleys along the OH bonds. The surface of the $|01s^{-1}2b_2^1\rangle$ state is bound, and has a valley lying along the symmetric stretching line. Meanwhile, the PES of $|01s^{-1}2b_1^1\rangle$ state has the same equilibrium geometry as the GS, and is fairly similar to it also. As for the bending mode

Figure 3.2: (a) 2D maps of the potential energy surfaces representing the two stretching vibrational modes in valence coordinates $(R_1, R_2)$ of the ground and core-excited $(4a_1, 2b_2$ and $2b_1)$ states of gas-phase water. The straight lines at the PESs show the direction of symmetric $(Q_s \sim R_1 + R_2)$ and anti-symmetric $(Q_a \sim R_2 - R_1)$ vibrational normal modes. (b) Potential energy curves along the bending coordinates. Reproduced from Paper I with permission from the PCCP Owner Societies.
PECs we see that the $|O1s^{-1}a_1\rangle$ state minimum position matches that of the GS, while both $|O1s^{-1}b_2\rangle$ and $|O1s^{-1}2b_1\rangle$ are shifted with respect to it.

### 3.3 Gating to different vibrational modes

In Papers I and II we describe how the excitation energy allows to excite the system to a state specific PES which yields selective vibrational excitation in gas-phase water. This property is enabled by the very distinct character of the multidimensional core-excited PES of different core-excited states, this leads to confinement of the nuclear wave packet along only a spatially selective coordinate which leads to different excitations upon decay to the ground state. Namely, in the showcase $H_2O(g)$, the different intermediate states act as "gates" to different vibrational modes (Fig. 3.3). At the $|O1s^{-1}a_1\rangle$ resonance we observe a long vibrational progression associated with the OH stretching and a nearly complete suppression of the bending mode (Fig. 3.3a). At the $|O1s^{-1}b_2\rangle$ resonance, we see the excitation of the symmetric stretching mode, dressed by one bending mode overtone (Fig. 3.3b). In

![Experimental and theoretical RIXS spectra](image)
contrast, at the $|O1s^{-1}2b_i\rangle$ resonance, the stretching mode is not excited at all (due to the fact that the stretching PES has the same minimum as the GS PES) and we observe a progression of the bending motion, exclusively (Fig. 3.3c). The interpretation of this facts allows one to reconstruct the molecular potentials selectively along these vibrational modes, and this will be thoroughly discussed in Sec. 3.5.

### 3.4 Ultra-fast dissociation at the $|1a_1^{-1}4a_1^1\rangle$ state

In this section we give a extra details about the nuclear dynamics during RIXS through the dissociative $|O1s^{-1}4a_1^1\rangle$ state. We do this because of the crucial importance of this electronic state as building block for analyzing water in the liquid phase, since the so-called pre-edge feature in the XAS spectrum of $H_2O(l)$ has the same character as the $|O1s^{-1}4a_1^1\rangle$ state in $H_2O(g)$.

Upon excitation to the $|O1s^{-1}4a_1^1\rangle$ state, the water molecule undergoes an ultra-fast fragmentation along the OH bonds. This is due to the fact that the PES of this state is dissociative with respect to these bonds. Due to the symmetry of the molecule both bonds have equal probability of dissociating, therefore, the nuclear wave packet describes the coherent superposition of these two processes. These is seen in the probability density of the time-dependent core-excited wave packet $\psi_c(t)$ in Fig. 3.4. It is striking to notice that within 7 fs the H atom is already 4.0 a.u. apart from the $^*OH$ fragment (bear in mind that $\psi_c(t)$ decays according to $\exp(-\Gamma t)$).

The dynamics along the OH bond leads, when decaying back to the ground state, to a long vibrational progression in the RIXS spectrum at this resonance. This will be discussed in
the next section. Here we briefly would like to point out some details about the decay in the fragment of dissociation (*OH). This leads to the formation of a quasi-atomic peak. Since the origin of this peak is dynamic, it is natural to expect that this feature will be sensitive on the isotopic substitution effect, as shown in Fig. 3.5. The presence of this peak is direct evidence of the ultra-fast dissociation in the core-excited state and, furthermore, it overlaps with the lowest electronic inelastic band, thus playing a role in the splitting of the so called 1b1 peak RIXS band. This discussion is beyond this thesis, but it is presented in reference [54].

Figure 3.5: Effect of isotopic substitution in the vibrationally resolved RIXS spectrum of water. Differences are seen in the vibrational frequency and specially for the intensity of the quasi-atomic peak. Reproduced from Paper I with permission from the PCCP Owner Societies.
3.5 Extraction of 1D cuts of multidimensional potentials

In Paper III, it was demonstrated how it is possible to use RIXS as a tool for extracting one dimensional cuts through potential energy surfaces. The realization of this idea is based on a strict link between the eigenvalues of an effective Hamiltonian, defined along the propagation coordinate of the core-excited wave packet, and the centers of gravity of the vibrational peaks in the RIXS spectrum.

![Figure 3.6: Squared core-excited state nuclear wave packets $|\Psi|^2$ as function of (a) OH bond lengths $R_1$ and $R_2$ and (b) bending normal coordinate $Q_b$. The projection $\langle \psi_{n_1n_2} | \Psi \rangle$ of the core-excited wave packet onto the ground state allows to reconstruct 1D cuts of the ground state potential $V_{GS}$ along different directions. Figure taken from Paper III.](image)

In Fig. 3.6, we may analyze the physical picture for the 1D cut reconstruction. The three distinct core-excited states, each with a state-specific landscape, lead to the formation of highly
confined core-excited wave packets $\Psi$, which upon decay reveal unique 1D cuts through the multidimensional potential energy surface.

### 3.5.1 1D cut of the PES and the pseudospectrum

In this section, we derive the expressions necessary to justify the 1D potential extraction. In the process it will become evident the role of highly confined core-excited wave packets in allowing this extraction to be carried out. For the purpose of this text it will be enough to consider the coupled 2D stretching, this, however, does not affect the generality of the results.

The RIXS amplitude [9, 55]

$$ F_{n_1n_2} = -i (\langle \psi_{n_1n_2} | \Psi \rangle), $$

$$ \Psi = \int_0^\infty e^{i(\omega - \omega_{c0} + \epsilon_0 + \Gamma)t} \psi(t) \, dt, \quad \psi(t) = e^{-i\hbar/2} \psi(t) $$

is given by the projection of $\Psi$ onto the vibrational eigenfunctions $\psi_{n_1n_2}$ of the ground state. Here, $\omega_{c0}$ is the energy of the vertical transition $0 \to c$, $\hbar/2$ and $\Gamma = 0.08$ eV are the 2D Hamiltonian and the lifetime broadening of the core-excited state, respectively. The general form of the 2D Hamiltonian of the coupled stretching motion in the ground state is

$$ h_2 = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial Q_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial Q_2^2} - \zeta \frac{\partial^2}{\partial Q_1 Q_2} + V(i)(Q_1, Q_2), $$

where $\mu_1$ and $\mu_2$ are the reduced masses. The choice of the general coordinates $Q_1$ and $Q_2$, as we will see below, depends on the direction of the propagation of the nuclear wave packet $\Psi$ in the PES of core-excited state. This Hamiltonian has eigenfunctions $\psi_{n_1n_2}(Q_1, Q_2)$ and eigenvalues $\epsilon_{n_1n_2}$. Note that $\psi_{n_1n_2}(Q_1, Q_2) \neq \psi_{n_1}(Q_1)\psi_{n_2}(Q_2)$ since the stretching modes are strongly coupled [55–57]. Therefore, we carry out a numerical solution of the time-dependent Schrödinger equation by direct diagonalization of the Hamiltonian matrix [58]. The eigenvalues $\epsilon_{n_1n_2}$ are clustered into groups [55–57], characterized by the group number

$$ n = n_1 + n_2, \quad n = 0, 1, 2, \ldots $$

Each $n$-th group is made up of $n + 1$ close-lying vibrational sub-levels, as may be seen in Fig. 3.7, and the fine-structure of these levels remain unresolved in the RIXS spectra. The intensity of each $n$-th peak, in the RIXS spectrum, is given by the state-specific Franck-Condon distribution. In the considered case, this is reflected on the different peak positions.
seen in the RIXS through the $|O1s^{-1}a_1^1\rangle$ and $|O1s^{-1}b_2^1\rangle$ states (Fig. 3.8). Let us define the center of gravity of the $n$-th RIXS peak

$$
\epsilon_n^{cg} = \sum_{n_1+n_2=n} P_{n_1n_2}^{(n)} \epsilon_{n_1n_2},
$$

$$
P_{n_1n_2}^{(n)} = \frac{|\langle \Psi | \psi_{n_1n_2}^{\phi} \rangle|^2}{\sum_{n_1+n_2=n} |\langle \Psi | \psi_{n_1n_2}^{\phi} \rangle|^2}.
$$

(3.4)

Here $P_{n_1n_2}^{(n)}$ probability of the transition (normalized to unity) to the $\epsilon_{n_1n_2}$ level within the $n$-th group (Eq. (3.1)).

Now, we should make use of the fact that the core-excited wave packet $\Psi$ is confined along one dynamical coordinate. Namely, it extends along the reaction path $Q_1$, oriented along the valleys of the PES, while being narrow in the orthogonal coordinate $Q_2$. For instance, at the $|O1s^{-1}a_1^1\rangle$ resonance, the wave packet is extended along one OH bond ($Q_1 = R_1$ or $R_2$) while for $|O1s^{-1}b_2^1\rangle$ the wave packet is lies between the OH bonds, along the symmetric stretching coordinate ($Q_1 = Q_s$). The confinement of the wave packet is described by factorizing the core-excited wave packet through the introduction of a sharp, normalized, function $\Delta(Q_2)$

$$
\Psi(Q_1, Q_2) = \phi(Q_1) \Delta(Q_2 - Q_{2e}),
$$

(3.5)

where $\Delta(Q_2 - Q_{2e})$ has its maximum at $Q_2 = Q_{2e}$.

In order to establish a link between the projection (on the ground state PES) of the narrow wave packet (Eq. 3.5) and a 1D cut of the $V(Q_1, Q_{2e})$ PES along the confinement coordinate $Q_1$, we investigate the relationship between the center of gravity $\epsilon_n^{cg}$ (3.4) and the eigenvalues $\epsilon_n$ of an 1D Hamiltonian defined along $Q_1$.

$$
h_1 \psi_n(Q_1) = \epsilon_n \psi_n(Q_1),
$$

$$
h_1 \equiv (\Delta| h_2 |\Delta) = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial Q_1^2} + V(Q_1, Q_{2e}) + C.
$$

(3.6)

The constant offset $C = (\Delta|\kappa (Q_2-Q_{2e})^2/2+T(Q_2)|\Delta)$ (see Paper III) of the 1D Hamiltonian $h_1$ is not important because we define the potential with respect to the bottom of the well. Apparently, the spectrum of the 1D Hamiltonian $\epsilon_n$ depends on the state sensitive propagation direction of $\phi(Q_1)$ in full agreement with experiment and simulations (Fig.3.7).

Let us write the normalized wave packet $\phi(Q_1)$ in terms of eigen functions $\psi_n(Q_1)$

$$
|\phi\rangle = |\psi_n\rangle \langle \psi_n|\phi\rangle + \sum_{m(\neq n)} |\psi_m\rangle \langle \psi_m|\phi\rangle,
$$

$$
\langle \Psi| \psi_{n_1n_2} \rangle = \langle \phi \Delta| \psi_{n_1n_2} \rangle = \langle \phi| \psi_n \rangle \langle \psi_n \Delta| \psi_{n_1n_2} \rangle + \sum_{m(\neq n)} \langle \phi| \psi_m \rangle \langle \psi_m \Delta| \psi_{n_1n_2} \rangle.
$$

(3.7)
Figure 3.7: (a) White curves show the crossings of the stretching isoenergetic surfaces $\epsilon_{n_1n_2}$ with the ground state PES $V(R_1,R_2) = \epsilon_{n_1n_2}$. Circles along the coordinates $R_1$ (green line) and $Q_s$ (blue line) are the centers of gravity $\epsilon_{n}^{cg}$ of the n-th group of the $|1s^{-1}4a_1^1\rangle$ and $|1s^{-1}2b_2^1\rangle$. The curves show the theoretical RIXS profile computed at the (a) $|1s^{-1}4a_1^1\rangle$ and (b) $|1s^{-1}2b_2^1\rangle$ resonances. The bars above show the pseudospectra $\epsilon_n = \epsilon_{n}^{cg}$ which can be extracted along different coordinates from the $|1s^{-1}4a_1^1\rangle$ (b) and $|1s^{-1}2b_2^1\rangle$ (c) RIXS due to different Franck-Condon factors (shown by black vertical lines). Figure taken from Paper III.

As it is shown in Paper III, the overlap between $|\psi_m\Delta\rangle$ and $|\psi_{n_1n_2}\rangle$ which belong to different groups is negligible due to small spacing $\delta\epsilon_{n_1n_2}$ between the levels inside of the same group ($n_1 + n_2 = n$) in comparison with the spacing $\epsilon_n - \epsilon_m$ between the levels from different groups ($n \neq m$) [55, 57]

$$\langle \psi_m\Delta|\psi_{n_1n_2}\rangle \approx 0, \quad n_1 + n_2 = n \neq m. \quad (3.8)$$

This together with the identity $\langle \psi_m|\psi_n\rangle = 0$ allows to write Eq. (3.4) as follows

$$P_{n_1n_2} = \frac{|\langle \psi_n\Delta|\psi_{n_1n_2}\rangle|^2}{\sum_{n_1+n_2=n} \langle \psi_n\Delta|\psi_{n_1n_2}\rangle \langle \psi_{n_1n_2}|\psi_n\Delta\rangle} = \frac{|\langle \psi_\Delta|h_2|\psi_n\Delta\rangle|^2}{\langle \psi_n|h_1|\psi_n\rangle} = \frac{|\langle \psi_\Delta|\psi_n\Delta\rangle|^2}{\langle \psi_n|\psi_n\rangle} = \epsilon_n. \quad (3.9)$$

Thus eqs.(3.4) and (3.9) lead to the main result of this section

$$\epsilon_{n}^{cg} = \sum_{n_1+n_2=n} \langle \psi_n\Delta|\psi_{n_1n_2}\rangle \epsilon_{n_1n_2} \langle \psi_{n_1n_2}|\psi_n\Delta\rangle = \langle \psi_n\Delta|h_2|\psi_n\Delta\rangle = \langle \psi_n|h_1|\psi_n\rangle = \epsilon_n. \quad (3.10)$$

Namely, the center of gravity of the n-th group coincides with the eigen value $\epsilon_n$ of the 1D Hamiltonian along the $Q_1$ coordinate. As one can see from Fig. 3.7 and Fig. 3.8 this center
of gravity depends on the direction of the one-dimensional cut which in turn depends on the core-excited state. Thus, the extraction of the pseudospectrum $\epsilon_n$ from the experimental data gives a unique opportunity to reconstruct the potential along $Q_1$.

3.5.2 Extracted potentials

4$a_1$ RIXS. First, we consider the reconstruction of the potential from experimental RIXS spectrum for the scattering through the dissociative $|O1s^{-1}4a_1^1\rangle$ core-excited state. The long stretching vibrational progression (see Figs. 3.3 and 3.7), which allows to reconstruct the 1D potential in the direction of the OH bond $Q_1 = R_1$ in wide range of $R_1$ (Fig.3.6). The RIXS spectrum at the $|O1s^{-1}4a_1^1\rangle$ resonance (see Fig.3.8a) exhibits exclusively stretching excitations. The fit of the pseudospectrum $\epsilon_n = \epsilon_n^{cg}$ from the vibrationally resolved experimental RIXS spectrum (Fig.3.8a) by the eigenstates of the Morse potential

$$V_M(Q - Q_e) = D (1 - \exp(-\alpha(Q - Q_e)))^2$$

(3.11)

with $R_e = 1.81$ a.u. provides us the vibrational frequency $\omega_e = (475.4 \pm 1.1)$ meV and the anharmonicity constant $\omega_{e\omega_e} = (9.99 \pm 0.14)$ meV (where we used $D = \omega_e^2/(4\omega_{e\omega_e})$ and $\alpha = \sqrt{2\mu\omega_{e\omega_e}}$). Using these constants, and the reduced mass $\mu = m_Hm_O/(m_H + m_O) = 0.94$ a.m.u., we obtained the following parameters of the Morse potential $\alpha = 1.122 \pm 0.008$ a.u., $D = 5.66 \pm 0.09$ eV. The reconstructed potential is in nice agreement with the calculated 1D potential along the OH bond as shown in Fig. 3.8a.

2$b_2$ RIXS. When the photon energy in tuned in resonance with the $|O1s^{-1}2b_1^1\rangle$ core-excited state, the wave packet $\Psi$ is confined within the narrow potential well located between the bonds (Fig.3.6). Now, we are able to extract a cut of the ground state PES in a different direction, along the symmetric stretching coordinate $Q_1 = Q_s$ (see Fig.3.6). The fit of the pseudospectrum $\epsilon_n = \epsilon_n^{cg}$ from the experimental RIXS channel results in the following Morse parameters(Eq. 3.11) $\omega_e = (457.65 \pm 0.70)$ meV, $\omega_{e\omega_e} = (4.76 \pm 0.13)$ meV, $\alpha = 0.82 \pm 0.02$ a.u. and $D = 11.0 \pm 0.3$ eV. Here, we used following value for the reduced mass of the symmetric stretching mode $\mu = 1.044$ a.m.u. The difference between the obtained value of $D$ and the thermochemical dissociation energy of 9.5 eV [59] is due to the fact that the vibrational progression is not long enough, for the studied state, to accurately predict the dissociation limit. The comparison the reconstructed and ab initio potentials, shown in Fig. 3.8b, displays nearly perfect agreement in the probed range.

2$b_1$ RIXS. Let us reconstruct the potential along the bending mode by tuning the photon frequency to the $|O1s^{-1}2b_1^1\rangle$ core-excited state (see Fig.3.8c), where the RIXS spectrum exhibits only bending excitations (see Sec. 3.3). Now, the wave packet $\Psi$ propagates only along the bending coordinate $Q_b$ (Fig 3.6b). The projection of $\Psi$, confined in the valley of
Figure 3.8: (left) The centers of gravity of each vibrational peak form the pseudospectrum (colored horizontal lines) of the ground-state 1D potential along the coordinates $R_1$, $Q_s$ and $Q_b$. (right) The reconstructed potentials (colored) are in a good agreement with the \textit{ab initio} potentials (black) in the energy range of available vibrational states. Figure taken from \textbf{Paper III}.

the bending potential, onto ground state enables to get the 1D cut of the ground state PES along $Q_b$. Contrary to the previous cases, the bending potential of H$_2$O has two minima ($Q_{e1} = 0$ and $Q_{e2} = 3.891$ a.u.) symmetric around the angle $\theta = \angle (HOH)=180^\circ$, which corresponds to the top of barrier at $Q_e = 1.632$ a.u. This motivates us to use a piece-wise defined potential function $V_b$ formed by two non-overlapping Morse potentials $V_M(Q)$ and $V_M(-(Q - Q_{e2}))$ connected by a parabolic barrier $U(Q - Q_e) = U_{\text{max}} - \eta(Q - Q_e)^2$

$$V_b(Q) = \begin{cases} V_M(Q), & Q \leq -\Delta + Q_e \\ U(Q - Q_e), & -\Delta + Q_e \leq Q \leq \Delta + Q_e \\ V_M(-(Q - 2Q_e)), & Q \geq \Delta + Q_e. \end{cases}$$

(3.12)
3.6 Role of geometry dependence of transition dipole moment

The origin of this potential is located in the bottom of left well. The requirement of continuity of the potential and its derivative at the points $Q = Q_e \pm \Delta$ defines $U_{\text{max}} = D(1 - e^{-\alpha(Q_e - \Delta)})^2 + \eta \Delta^2$ and $\eta = (\alpha D/\Delta)e^{-\alpha(Q_e - \Delta)}(1 - e^{-\alpha(Q_e - \Delta)})$. The parameters $\omega_e = (201 \pm 2)\text{meV}$, $\omega_e x_e = (1.9 \pm 0.4)\text{meV}$ and $\Delta > Q_e$ were determined by a fit of the eigenvalues of $V_b$ to the experimental data, using the reduced mass $\mu = \mu_b = 1.083\text{a.m.u}$. The reconstructed potential along the bending coordinate $Q_b$ is compared to the $ab\text{ initio}$ simulation in Fig. 3.8c. We are unable to accurately define the height $U_{\text{max}}$ of the barrier $U(Q - Q_e)$ due to the limited number of vibrational states seen in the experimental spectrum. However, the least square method used yields a confidence interval of $1.09\text{eV} < U_{\text{max}} < 1.70\text{eV}$ (see Fig.3.8c).

3.6 Role of geometry dependence of transition dipole moment

Above, we have used the FC approximation, neglecting the dependence of the transition dipole moment of core-excitation $d_{c0}(R)$ on the nuclear coordinates $R$. However, this dependence can be significant as one can see from Fig. 3.9. This figure shows the $y$ and $z$ components of $d_{c0}(R)$ where the $y$-axis lies along the anti-symmetric coordinate and the $z$-axis is oriented along the symmetric line. The strongest dependence is observed for $d_{c0}^{(y)}(R)$ which contrary to $d_{c0}^{(z)}(R)$ is an anti-symmetrical function of $y$. This anti-symmetric dependence is important because it opens the symmetry forbidden RIXS channel to anti-symmetric vibrational states with odd quantum numbers $|00\rangle \rightarrow |n_a n_a\rangle$, $n_a = 2m + 1$. The $R$ dependence of the transition dipole moment brings another non-FC effect related to the scattering anisotropy. Because the $y$ and $z$ components of $d_{c0}(R)$ are responsible for the RIXS transitions, respectively, to odd ($n_a = 2m + 1$) and even ($n_a = 2m$) anti-symmetric states one can expect different polarization dependencies of even and odd RIXS resonances. Lastly, as shown from Fig. 3.10, the antisymmetry of the $y$ component of the transition dipole moment, means that we have opposite rotation of the transition dipole moment vector during the coherent dissociation along the two pathways $H^{(1)}O - - - - H^{(2)}$ and $H^{(2)}O - - - - H^{(1)}$ (see also sec. 3.4).
Figure 3.9: Components of the transition dipole moment \( \mathbf{d}_{\text{c}_0} \) as functions of \( R_1 \) and \( R_2 \). Panel a) displays the anti-symmetric \( y \) component while panel b) shows the symmetric \( z \) component. Figure taken from Paper IV.

### 3.6.1 Rotation of transition dipole moment in the course of dissociation

At the ground state equilibrium geometry the transition dipole moment has only \( z \)-component in the molecular frame, and \( y \)-component equals to zero. At the bond-length elongation however the \( y \)-component starts to grow. The physical reason for the rotation of the transition dipole moment \( \mathbf{d}_{\text{c}_g} \) is the symmetry breaking in the course of the elongation of one bond.

To shed light on the \( R \)-dependence of transition dipole moment of the decay \( \mathbf{d}_{\text{c}_g} \) in the cause of elongation of the \( OH_1 \) bond one should look on the asymptote of the wave functions at \( R_1 = \infty \). Let us start from the ground state singlet wave function which is at \( R_1 = \infty \)

\[
\Psi_{\text{GS}} = \frac{1}{\sqrt{2}} \left( ||3a_1^24a_1^0|| - ||3a_1^04a_1^2|| \right) = \frac{1}{\sqrt{2}} \left( 3a_1(1)3a_1(2) - 4a_1(1)4a_1(2) \right) \chi_S(1,2),
\]

\[
\chi_S = \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right].
\]

(3.13)

Here \( ||\cdot|| \) is the Slater determinant, \( \alpha \) and \( \beta \) are the spin functions. According to Figure 3.11 both degenerated at \( R_1 = \infty \) orbitals

\[
3a_1 = \frac{1}{\sqrt{2}} \left[ 2p_{z'}^{(O)} + 1s^{(H)} \right], \quad 4a_1 = \frac{1}{\sqrt{2}} \left[ 2p_{z'}^{(O)} - 1s^{(H)} \right].
\]

(3.14)

are equally contribute to \( \Psi_{\text{GS}} \). Here the \( z' \)-axis is perpendicular to the \( OH_2 \) bond (see Fig. 3.10). Substitution of this equation into (3.13) gives the following asymptote for \( \Psi_{\text{GS}} \)
at $R_1 = \infty$

$$\Psi_{\text{GS}} = \frac{1}{\sqrt{2}} \left( 2p_z^{(O)}(1)1s^{(H)}(2) + 2p_z^{(O)}(2)1s^{(H)}(1) \right) \chi_S(1, 2)$$

$$= \frac{1}{\sqrt{2}} \left( \|1s^{(O)}\alpha 1s^{(O)}\beta \cdots 2p_z^{(O)}\alpha 1s^{(H)}\beta\| - \|1s^{(O)}\alpha 1s^{(O)}\beta \cdots 2p_z^{(O)}\beta 1s^{(H)}\alpha\| \right).$$

Figure 3.10: Schematic depiction of the transition dipole moment rotation. The green colormap shows the potential energy surface of the dissociative $|O1s^{-1}4a_1^+\rangle$ core-excited state, as function of the bond lengths $R_1$ and $R_2$. The orientation of the transition dipole moment is depicted schematically by the arrows in the molecular frame. Figure taken from Paper IV.

Let us now look on asymptote of the wave function of the core-excited state at $R_1 = \infty$

$$\Psi_{\text{CE}} = \frac{1}{\sqrt{2}} \left( \|1s^{(O)}\alpha \cdots 3a_1 \alpha 3a_1 \beta 4a_1 \beta\| - \|1s^{(O)}\beta \cdots 3a_1 \alpha 3a_1 \beta 4a_1 \alpha\| \right)$$

$$= \frac{1}{\sqrt{2}} \left( \|1s^{(O)}\alpha \cdots 2p_z^{(O)}\alpha 2p_z^{(O)}\beta 1s^{(H)}(1)\beta\| - \|1s^{(O)}\beta \cdots 2p_z^{(O)}\alpha 2p_z^{(O)}\beta 1s^{(H)}(1)\alpha\| \right).$$

Indeed, according to our simulations at $R_1 = \infty$ (Figure 3.11)

$$3a_1 = 2p_z^{(O)}, \quad 4a_1 = 1s^{(H)}_1,$$

the LUMO $4a_1$ is localized on the dissociated hydrogen $H_1$. Thus the transition dipole moment $d_{cg} = \langle \Psi_{\text{CE}}|d|\Psi_{\text{GS}} \rangle$ at $R_1 = \infty$ has only the $z'$ component.
3.6.2 Theory of RIXS including dynamical rotation of dipole moment

To describe these effects, we should generalize the theory to account for $R$ dependence of the transition dipole moment. First of all, we need to perform the averaging of the RIXS cross-section (Eq. (2.10)) over molecular orientations taking into account the rotation of the transition dipole moments of core-excitation $d_{c0}(R)$ and decay transition $d_{fc}(R)$ in the course of nuclear dynamics. Substituting the scalar products

$$D_{c0} = (\mathbf{e} \cdot \mathbf{d}_{c0}) = \sum_i e_i d_{c0}^{(i)} , \quad D_{fc} = (\mathbf{e}' \cdot \mathbf{d}_{fc}) = \sum_k e'_k d_{fc}^{(k)}$$

into Eq. (2.10) one can get the following expression for the cross-section

$$\sigma(\omega', \omega) = \sum_{ijkl} e_i e_j e'_k e'_l \sigma_{jikl} ,$$

$$\sigma_{jikl} = \sum_{\nu_f} (F_{ij}^{\nu_f})^\dagger F_{kj}^{\nu_f} \Delta \left( \omega - \omega' - \omega_{f0} - \epsilon_{\nu_f} + \epsilon_{\nu_0} , \Gamma_f \right)$$

$$= \sum_{\nu_f} \langle \Psi_{ij}(0) | \nu_f \rangle \langle \nu_f | \Psi_{kj}(0) \rangle \Delta \left( \omega - \omega' - \omega_{f0} - \epsilon_{\nu_f} + \epsilon_{\nu_0} , \Gamma_f \right) ,$$

$$F_{ij}^{\nu_f} = -i \langle \nu_f | \Psi_{ki}(0) \rangle , \quad | \Psi_{ki}(0) \rangle = i \sum_{\nu_c} \frac{d_{fc}^{(k)} | \nu_c \rangle \langle \nu_c | d_{c0}^{(i)} | \nu_0 \rangle}{\omega - \omega_{c0} + \epsilon_{\nu_c} - \epsilon_{\nu_0} + i\Gamma} .$$
Figure 3.12: Panels a) and b) show the effect of the transition dipole moment operator during the excitation step. Panels c)-f) show the real part of the components of the nuclear wave packet tensor. The insert in panel a) show the molecular frame. Figure taken from Paper IV.

Here, we averaged over the polarization vectors while keeping the molecule fixed. Using the following equation [9]

\[
e_j e_j e'_k e'_l = \frac{1}{6} \left[ \delta_{ij} \delta_{kl} \left( 1 - \cos^2 \theta \right) + \frac{1}{3} \sum_{ijkl} \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right] \left( 3 \cos^2 \theta - 1 \right),
\]

\[
\cos \theta = (e' \cdot e).
\]  

one can get

\[
\sigma[\theta] \equiv \sigma(\omega', \omega) = \frac{1}{15} \left[ (1 + 2 \cos^2 \theta) \left( \sigma_{zzzz} + \sigma_{yyyy} \right) + (2 - \cos^2 \theta) \left( \sigma_{zyzz} + \sigma_{yzzy} \right) \right] + \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \left( \sigma_{yzzy} + \sigma_{zyzz} \right) + \left( \sigma_{yyzz} + \sigma_{zzyy} \right),
\]

\[
\theta = \angle (e', e), \quad \chi = \angle (k', e).
\]

Typically, the X-ray spectrometer collects the signal from the scattered photons of all polarizations $e'$. Therefore, we need to average over $e'$ around momentum of scattered photon $k$ with $(e \cdot e')^2 = (1 - \cos^2 \chi)/2$.
Figure 3.13: Full cross-section $\sigma$ and partial cross-sections $\sigma_{\text{odd}}$ and $\sigma_{\text{even}}$ (Eq. 3.24) for $\chi = 0^\circ$ (upper panel) and $\chi = 90^\circ$ (lower panel). The inserts in both panels show the strict cross-section compared with the one computed within the FC approximation. The spectra were normalized so that the peak $n = 1$ in $\sigma$ equals 1. Figure taken from Paper IV.

\[
\sigma[\chi] \equiv \sigma(\omega', \omega) = \frac{1}{30} \left[ 2(2 - \cos^2 \chi) \left( \sigma_{zzzz} + \sigma_{yyyy} \right) + (3 + \cos^2 \chi) \left( \sigma_{zyyz} + \sigma_{yzyz} \right) 
+ \frac{1}{2} (1 - 3 \cos^2 \chi) \left[ \sigma_{yyzz} + \sigma_{zzyy} \right] + \left[ \sigma_{zyzy} + \sigma_{yzyz} \right] \right].
\]

Similarly to Eq. (2.13) one can write the partial cross-section in time-dependent representation.

\[
\sigma_{ijkl}(\omega', \omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i(\omega - \omega' + \epsilon_{q0} + \Gamma_f) t} \sigma_{ijkl}(t) dt,
\]

\[
\sigma_{jkl}(\omega', \omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{i(\omega - \omega' + \epsilon_{q0} + \Gamma_f) t} \left( \sigma_{jkl}(t) + \sigma_{iklj}(t) \right) dt,
\]

\[
\sigma_{ji}(t) = (\Psi_j(t)|\Psi_i(t)) \quad \text{and} \quad \psi_c^{(i)}(t) = e^{-i\hbar c t} d_{ic0}^{(i)}(t),
\]

\[
|\Psi_i(0)\rangle = d_{fc}^{(k)} \int_0^\infty e^{i(\omega - \omega_c + \epsilon_{q0} + \Gamma_f) t} \psi_c^{(i)}(t) dt.
\]
Let us consider now conventional RIXS which starts from the lowest vibrational level 
\[ \nu_0 = (0, 0). \]

In order to show the breakdown of the selection rules caused by \( \mathbf{R} \) dependence of the transition dipole moment, let us write the cross-section as a sum of two contributions. The first one corresponding to transitions to odd anti-symmetric levels \( (\nu_f = (n_s, 2m + 1)) \) while the second term corresponds to transitions to odd final states, which are forbidden when \( \mathbf{d}_{i0}(\mathbf{R}) \equiv \text{const.} \)

\[
\sigma_{\text{even}}[\chi] \equiv \sigma_{\text{even}}(\omega', \omega) = \frac{1}{30} \left[ 2(2 - \cos^2 \chi) (\sigma_{zzzz} + \sigma_{yyyy}) + \frac{1}{2} (1 - 3 \cos^2 \chi) [\sigma_{yyzz} + \sigma_{zzyy}] \right],
\]

\[
\sigma_{\text{odd}}[\chi] \equiv \sigma_{\text{odd}}(\omega', \omega) = \frac{1}{30} \left[ (3 + \cos^2 \chi) (\sigma_{zyyz} + \sigma_{yzzy}) + \frac{1}{2} (1 - 3 \cos^2 \chi) [\sigma_{zyzy} + \sigma_{yzyz}] \right].
\]

Figure 3.14: Polarization dependence of the ratio of the area of the \( n \)-th peak to the first peak in the RIXS spectrum. Figure taken from Paper IV.

The intensity of the RIXS transition to the final state \( |\nu_f \rangle = |n_s, n_a \rangle \) is defined by the overlap \( \langle n_s, n_a | \Psi_{k1}(0) \rangle \) (see Eq. (3.21)) which can only be non-zero if the parities (related to reflection \( y \rightarrow -y \)) of \( |n_s, n_a \rangle \) and \( |\Psi_{k1}(0) \rangle \) are the same. Conversely

\[
\langle n_s, 2m | \Psi_{yz}(0) \rangle = \langle n_s, 2m | \Psi_{zy}(0) \rangle = 0,
\]

\[
\langle n_s, 2m + 1 | \Psi_{kk}(0) \rangle = 0
\]

because \( \Psi_{yz}(0) \) and \( \Psi_{zy}(0) \) are anti-symmetric functions of \( y \) (see Eq. (3.23) and Fig. 3.12).
The total $\sigma$ and corresponding partial ($\sigma_{\text{even}}$, $\sigma_{\text{odd}}$) cross-sections are collected in Fig. 3.13, for two different angles. Naturally, $\sigma_{\text{odd}}$ has no contribution to elastic peak ($n = 0$). Our calculations do not account for the Thomson scattering term [9]. Due to this, the elastic line is not correctly described for $\chi = 90^\circ$, this does not affect the calculations for $\chi = 0^\circ$, because the Thomson term is absent at this angle.

The inserts in Fig. 3.13 show the comparison between the computed total RIXS cross-sections and one computed within the FC approximation (which is not sensitive to polarization). We can see that going beyond the FC approximation brings an enhancement of the higher vibrational peaks. In addition, the relative intensity of the atomic-like peak, originating from decay of the OH fragment [54], increases.

![Image](image.png)

**Figure 3.15:** a) Polarization dependence of the ratio $\rho^{(1)}$ of the cross-sections for the vibrational levels $\epsilon_{1,0}$ and $\epsilon_{0,1}$ in the RIXS spectrum of H$_2$O. Panel b) displays the cross-section within the FC approximation where $d_{\epsilon_{0}}$ is constant. Panels c) and d) show the RIXS cross-section bars for levels $\epsilon_{1,0}$ and $\epsilon_{0,1}$ for $\chi = 0^\circ$ and $90^\circ$ respectively. The full profile shown considers a Gaussian experimental broadening of 0.02 eV half-width at half maximum. Figure taken from **Paper IV**.

Current experimental RIXS setups allow only to resolve vibrational peaks belonging to different groups characterized by group number $n = n_s + n_o$. Therefore, this effect could be observed by considering the angular dependence of the ratio of the areas of the 6-th peak to the first peak, for example. Unfortunately, according to our calculations (Fig. 3.14), this
dependence is weak. This is because an unresolved RIXS resonance contains intensities of both even and odd vibrational sub-levels which counteract each other leading to strong suppression of the angular dependence.

Eq. (3.24) show that even and odd anti-symmetric vibrational states have qualitatively different polarization dependence. This becomes evident when we consider the ratio

$$\rho^{(1)}[\chi] = \frac{\sigma^{(1,0)}[\chi]}{\sigma^{(0,1)}[\chi]} = \frac{\sigma_{\text{even}}^{(1,0)}[\chi]}{\sigma_{\text{odd}}^{(0,1)}[\chi]}$$

(3.25)

of the peak intensities for “symmetry allowed” $|0,0\rangle \rightarrow |1,0\rangle$ and “symmetry forbidden” $|0,0\rangle \rightarrow |0,1\rangle$ RIXS transitions (see Fig. 3.15).

One should notice that the observation of such an anomalously strong polarization dependence requires RIXS spectroscopy of super-high resolution to resolve the $(1,0)$ and $(0,1)$ levels with a spacing of about 9 meV. The latest experimental developments indicate that such resolution should be possible in the near future [60–63].
Chapter 4

RIXS of liquid water

Let us turn our attention to RIXS of liquid water. Now we face very different scenario of formation of the X-ray spectra. The main reason for this is the strong interaction between water molecules in the liquid phase through the formation a hydrogen bond (HB) network. Although hydrogen bonds are weaker than the chemical bonds of a water molecule, these interactions effects drastically the physical-chemical properties of liquid water and it is usually attributed as the cause of the anomalies of liquid water [64, 65]. A diverse array of different experimental techniques are used to investigate different aspects of this unusual liquid. Here, we will focus only on RIXS spectra at the pre-edge peak in the NEXAFS of liquid water which is attributed to core-excitation to a dissociative state. Moreover, we will study the special case of RIXS which ends up in the ground electronic state, in line with previous chapters. All cross-sections are given in arbitrary units and are normalized to the intensity of the first peak after the elastic line. All potential energy curves are given in eV and all equations are expressed in atomic units.

4.1 Theoretical tools for modeling the RIXS of liquid water

Liquid water is comprised of a fluctuating hydrogen bond network, hence it is necessary to account for all possible geometry configurations. This can be done using classical mechanics for the nuclei, namely molecular dynamics (MD) simulations. However, experimental RIXS spectra display a nicely resolved vibrational progression which cannot be described by Newton’s equations of motion. This motivates us to develop a hybrid quantum-classical approach by combining ab-initio molecular dynamics (AIMD) [23] and quantum wave packet tech-
Figure 4.1: Schematic depiction of the proposed quantum-classical model: From a 64-molecule cluster simulated with AIMD we take a snapshot. For each molecule in the snapshot the molecular potential is computed, considering the remaining environment frozen. Finally, the RIXS spectrum is computed by the quantum wave packet technique for each molecule in the cluster and the total cross-section taken as the ensemble average of all molecules.

Techniques (outlined in previous chapters). Liquid Water in ambient conditions \( (T = 298 \text{ K}) \) was simulated using AIMD simulations of a 64-molecule cluster (Fig. 4.1), considering periodic boundary conditions. The forces on the nuclei were derived from DFT/BLYP calculations. The dissociative \( 4a_1 \) band was approximated by taking the lowest lying core-excited level, yielded by the “excited core-hole” XCH technique, for each one of the 64 molecule cluster. This level of theory has already been shown to accurately reproduce the pre-edge feature of the XAS spectrum [23, 25] of liquid water. The molecular potentials of and transition dipole moment between the ground state and the lowest O1s core-excited state (XCH) were computed from unrestricted all-electron Kohn-Sham density functional calculations using the GAPW method in CP2K [66–68], the gradient-corrected BLYP functional [69, 70] and the Ahlrichs-def2-QZVP basis sets [71] and a plane wave cut-off of 300 Ry for the soft part of the density. For comparison, we also calculated transition dipole moments using the half-core-hole (HCH) and full-core-hole (FCH) methods [23].

Finally, the differential RIXS cross-section for the liquid phase was calculated as the sum over the partial contributions for each \( k \)-th molecule in the cluster

\[
\sigma(\omega', \omega) = \sum_{k=1}^{64} \sigma_k(\omega, \omega').
\]  

(4.1)
In order to compute the vibrationally resolved quasi-elastic RIXS, we need a quantum description of the OH vibrations in liquid water, therefore we scanned the molecular potential along the length of each OH bond for all molecules in the cluster. The Hamiltonian, in valence coordinates, on the electronic state $|i\rangle$ for each molecule is constructed by assuming an independent bond approximation with a frozen local environment

$$H^i_k = -\frac{1}{2\mu} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial R_2^2} - \frac{\cos\theta_0}{m_O} \frac{\partial^2}{\partial R_1 R_2} + V^i_k(R_1) + V^i_k(R_2),$$  \(4.2\)

where $R_1$ and $R_2$ are the OH bond lengths of the $k$-th molecule; $\mu = m_H m_O / (m_H + m_O)$ where $m_H$ and $m_O$ are the masses of the hydrogen and oxygen atoms; $\theta_0$ is the equilibrium $\angle$ HOH angle; and $V^i_k$ is the molecular potential along an OH bond of the $k$-th molecule in the cluster on the electronic state $|i\rangle$. The ground state vibrational spectrum of molecule $k$ is then given by the time independent Schrödinger equation

$$h_0^k |\phi_{n_1, n_2}\rangle = \epsilon_{n_1, n_2} |\phi_{n_1, n_2}\rangle,$$

where $\phi_{n_1, n_2}$ is the 2D vibrational eigenstate with the respective energy $\epsilon_{n_1, n_2}$.

The single molecule cross-sections were computed using the wave packet formalism [55, 57], as the half-Fourier transform of the auto-correlation function

$$\sigma_k(\omega, \omega') = \frac{|d^k_{t,0}|^4}{\pi} \text{Re} \int_0^\infty dt \ e^{i(\omega - \omega' - \epsilon_{00}^k + \Gamma_t)t} \langle \Psi_k(0) | \Psi_k(t) \rangle,$$  \(4.3\)

where $d^k_{t,0}$ is the transition dipole moment, at the equilibrium geometry, between the ground state and the core-excited state for the $k$-th molecule, and where we introduced the integrated core-excited wave packet

$$|\Psi_k(0)\rangle = \int_0^\infty dt \ e^{i(\omega - \omega_0^k + \epsilon_{00}^k + \Gamma t)t} |\phi_{k0}\rangle,$$

$$|\psi_k(t)\rangle = e^{-ih_0^k t} |\phi_{00}\rangle, \quad |\Psi_k(t)\rangle = e^{-ih_0^k t} |\Psi_k(0)\rangle.$$  \(4.4\)

In liquid phase, the scattered X-ray photons are very likely to be reabsorbed by nearby molecules, we account for this effect by carrying out a self-absorption correction in the same fashion as previous works [55, 72].

## 4.2 Local structure classification convention

A water molecule in liquid phase generally has two non-equivalent OH bonds, which are affected by their local surroundings. For example, one OH bond may not participate in hydrogen bonding (often called a “broken” HB) while another one may be strongly bound to a neighbor water molecule. There are also many water molecules in which both OH bonds are involved in HBs. The first case is broadly called “single-donor” structure (D1) while the...
second one is referred to as a “double-donor” structure (D₂). Both D₁ and D₂ structures are commonly defined based on geometrical criteria [19, 73]. There is also an alternative “high-density” and “low-density” definition [74, 75] based on the local structure index. Although HB definitions give valuable insight, they suffer from a fundamental problem in that hydrogen bonding is not universally defined [73, 76, 77]. This fact may lead to ambiguous statements in many structural studies due to lack of a strict boundary between D₁ and D₂ structures [77].

Figure 4.2: a) schematic depiction of the local HB classification employed. Illustration of possible D₂ (b) and (c) D₁ structures. Figure taken from Paper V.

In this thesis, we have opted for using the following geometrical definition for the HB formation, which is similar to the one used in reference [19], as $R_{OO} < 3.3\text{Å}$ and $\theta < 30^\circ$ (see Fig. 4.2). This very simple definition is used in this thesis only to provide qualitative insight into the partial contributions to the RIXS spectrum and also to put our results in perspective with previous X-ray investigations in the literature.

4.3 X-ray-induced dynamics at the pre-edge: Insights from AIMD

As thoroughly discussed in Chapter 3, for the gas-phase, excitation to the lowest core-excited state leads to an ultra-fast dissociation process. In the liquid, however, one would expect that the molecule cannot dissociate, since there are neighboring molecules around which cause the potential energy curve to become bound in the core-excited state. This
expectation is indeed true, however, on average, the core-excited energy landscape is quasi- dissociative in the liquid phase, conversely, there is a strong gradient acting on the hydrogen atoms of a given core-excited H₂O molecule thus leading to an ultra-fast elongation of these bonds. The physical picture described may be verified through analysis of AIMD trajectories

\begin{equation}
RMSD(t) = \sqrt{\frac{1}{N} \sum_k \Delta R_k^2(t)}, \quad RMSF_k = \sqrt{\frac{1}{N_T} \sum_{t_i} \Delta R_k^2(t_i)},
\end{equation}

where \(\Delta R_k(t) = R_k(t) - R_k(0)\) is the deviation of the \(k\)-th OH bond length from its initial value, \(N\) is the total number of OH bonds, \(t_i\) is the time at the \(i\)-th step and \(N_T\) is the total number of steps in the time interval considered (\(T = 10\) fs). Both these quantities allow us to access the role of OH motion after core-excitation.
The time interval considered for analyzing the AIMD trajectories deserves a special comment. The first impression is that this time interval should be defined by the lifetime of the core-excited state $1/2\Gamma \approx 4$ fs. However, the RIXS process is coherent and its dynamics is defined by the decay of the wave packet in the core-excited state ($\psi_c(t) \propto \exp(-\Gamma t)$). This motivates us to consider a longer time interval around $1/\Gamma \approx 8$ fs.

We have a very interesting observation that the time dependence of the RMSD(t) is qualitatively different for ground and core-excited states. The main reason for this is that the ground state is bound contrary to the core-excited state which has quasi-dissociative character. Fig. 4.3 shows the OH bond lengths as a function of time for the ground state, which have sinus-squared-like behavior. A closer look shows that $|\Delta R_k(t)| \approx 0.2 \times |\sin(2\pi t/T_{vib} + \delta_k)|$ a.u. with the period of stretching mode vibrations $T_{vib} \sim 9$ fs near the bottom of the well. Averaging over different bonds results in a curve with a single maximum instead of two as follows from the previous equation. Due to pre-edge core-excitation to a quasi-dissociative state this behavior changes drastically, and shows both breaking of the OH bond as well as quasi-bound motion. This information is complemented by the RMSF distribution plots (Fig. 4.3) which shows the very weak fluctuation of $\Delta R_k$ for the ground state and rather large variation for the core-excited state. This is evident from the small width of the blue distribution when compared with the much broader red one.

The reason for the observed maximum in the RMSF histogram (around 1 a.u.) for the core-excited state is the finite lifetime of the core-excited state (more precisely the chosen time interval $T = 10$ fs). One can see this clearly from the time-dependent $\Delta R_k(t)$ (left panel of Fig. 4.3) that shows the mean value of $\Delta R_k(t)$ in the time interval of 10 fs is smaller than 1.5 a.u.

To conclude, the large mean value and width of the RMSF distribution (Fig. 4.3) of core-excited state is direct evidence of the site-sensitive quasi-dissociative character of the nuclear motion during lifetime of this state. In contrast, the small values of both these quantities for the ground state is due to very small fluctuations of $\Delta R_k(t)$ near the bottom of the GS PES.

### 4.4 Liquid vs Gas-phase: Randomization of RIXS profile caused by fluctuation of the HB network

In this section, we have computed the RIXS spectrum of liquid water (Fig. 4.4) following the procedure outlined in Sec. 4.1 and compare it to the measurements performed at the ADRESS beamline at Swiss Light Source (see Paper V). To see clearer the effects of the
4.4 Liquid vs Gas-phase: Randomization of RIXS profile caused by fluctuation of the HB network

In the free water molecule, this leads to an ultra-fast dissociation of the OH bonds (see Sec. 3.4). Upon decay to the ground state, this results in a long vibrational progression seen in upper plots of Fig. 4.4. The picture changes for the liquid. Both experiment and theory, see Fig. 4.4, demonstrate a clear trend of shortening of the vibrational progression of the RIXS profile comparing to the gas-phase. The length of vibrational progression is determined by the wave packet propagation on the core-excited state PES. This can bring an erroneous conclusion that the nuclear core-excited wave packet in liquid water propagates a much shorter distance than in the gas-phase. This naive interpretation is not fully correct, because this shortening is caused by the strong fluctuation of the potential of the OH bond due to interactions with the HB network (See Fig. 4.5a). These fluctuations affect mainly the long-range part of the potential thus resulting in variation in the position of the high-energy

![Figure 4.4: Theoretical and experimental RIXS spectra for gas-phase and liquid water at the top of resonance of the 4a₁ state and the pre-edge (as shown in the insert). Figure taken from Paper V.](image)
4.5 Role of inequivalent OH bonds

Due to the similarity of the RIXS spectra of gas-phase and liquid water, the assignment of the liquid RIXS has been considered to be gas-phase-like [13] or to be given in terms of normal modes [14]. However, the presented analysis of the fluctuation of the \textit{ab initio} potentials and the partial density of states shows clear violations of these simple assignment. Furthermore, a H$_2$O molecule in liquid phase may often be in a situation where its OH bonds

\[ \rho_m(\epsilon) = \sum_{k=1}^{64} \sum_{n_1+n_2=m} \Phi(\epsilon - \epsilon_{n_1,n_2}^k + \epsilon_{0,0}^k). \]  

Here $\Phi(x) = \exp(-x^2/\Delta^2)/\Delta\sqrt{\pi}$, $\Delta = 0.01$ eV, $n_1$ and $n_2$ are the vibrational quantum numbers for each OH bond in the $k$-th water molecule in the cluster (see Sec. 4.1). One can see that there is strong overlap of the partial density of states belonging to different groups characterized by group number $m = n_1 + n_2$ (Fig. 4.5 b). This explains the transformation of the high-energy part of the RIXS spectrum ($> 3.5$ eV) into a smooth background. This idea is supported also by the increasing width of the vibrational peaks with increase of the energy, as shown in the insert of Fig. 4.5 a. Thus, the shortening of the progression is closely linked to the fluctuations of the hydrogen bond network.
are inequivalent, due to the immediate local environment. In this case, each of the bonds will have qualitatively distinct potentials and, consequently, different energy eigenvalues. Also, contrary to free water molecules (see Chapter 3), in liquid water the vibrational modes become localized on the OH bonds due to the asymmetry of the local environment.

To shed light on the role of inequivalent OH bonds in the formation of the RIXS profile, it is instructive to examine the simulated RIXS spectrum of an individual molecule. Therefore, we choose from the cluster, a molecule in which the local environment of each OH bond is highly asymmetric ($D_1$). As expected, we see a long progression (Fig. 4.6 a) but, however, this spectrum differs very much from the gas-phase one (Fig. 4.4).

The underlying reason is that both OH bonds are coherently excited in the RIXS process, with the same transition dipole moment, and this is seen clearly in the square of the time-integrated core-excited wave packet shown in Fig. 4.6 b. More precisely, the co-existence of two bonds, with qualitatively different potentials, in the same molecule leads to an intricate spectrum formed by single bond excitations ($\epsilon_{n_1,0}$ ($0,0,n_2$)) and mixed excitations ($\epsilon_{n_1,n_2}$) associated with simultaneous excitation of both bonds (Fig. 4.6a).

![Figure 4.6](image_url)

Figure 4.6: a) The filled blue profile shows the total theoretical spectrum while the filled orange profile show the RIXS profile for chosen asymmetric molecule. The green bars correspond to the eigenstates $\epsilon_{n_1,0}$ of the shallow potential, the magenta ones to the eigenvalues $\epsilon_{0,n_2}$ of the steep potential, while the blue ones correspond to the overtones $\epsilon_{n_1,n_2}$ ($n_1,n_2 \neq 0$). The shaded area display all potential curves in the studied cluster (same as in Fig. 4.5d)). The green and magenta curves correspond to the shallow and steep OH potentials. b) Square of a representative core-excited nuclear wave packet in liquid water.

It is important to notice that the eigenvalues which correspond to the shallow, hydrogen bonded, potential do not match the gas-phase assignment, while the eigenvalues of the steep potential approximately match the peak positions of the total spectrum (Fig. 4.6a).
example, in the peak \( n = 3 \), there is contribution from eigenvalues with quantum number \( n_2 = 4 \) and \( 5 \). Also, the eigenvalue \( n_2 = 9 \) of the shallow potential contributes to the peak \( n = 6 \). The complexity increases further due to peaks arising from simultaneous excitation of vibrations in the both shallow and steep potentials (see Fig.4.5c).

Thus, there is considerable violation of the eigenvalue group rule, for example, eigenvalues which one would expect to contribute to fifth peak end up contributing to the fourth peak in RIXS spectrum. This means that there is not necessarily a one-to-one correspondence between the number of vibrational peak in the RIXS which coincide with the naive gas-phase-like assignment of the RIXS spectrum of liquid water, and actual quantum number of vibrational level.

The observation of this effect provides a unique opportunity to estimate, from the experimental data, the confidence intervals for steep and shallow OH potentials in liquid water.

\[ \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \] (4.8)

where the upper row enumerates the vibrational peaks starting from peak \( n = 1 \), while the bottom row shows the number of vibrational states for a single OH bond which lie within

4.6 Confidence intervals for the molecular potentials from liquid RIXS

As it was shown in Paper III, RIXS may be used to selectively extract the potential along different vibrational modes. However, due to the inherent chaotic nature of liquid water, one cannot expect to obtain well defined potential energy curves from RIXS. Indeed, Fig. 4.6 a) display almost continuous distribution of the potential energy curves. Thus, the maximum information available from the experimental spectrum is the confidence interval for the OH bond potential across the full distribution of HB environments, namely ranging from a non-bonded steep boundary to a strongly bonded shallow one. In order to extract the confidence intervals we designed a computational procedure based on the genetic algorithm [78] (GA) (the detailed algorithm is outlined in Paper V) using various constraints of number of vibrational levels which are can belong to a given RIXS peak, as it will be detailed below.

To exploit the fact that a steep and a shallow potential have eigenvalues that contribute different to the RIXS spectrum, we introduce a key idea which characterizes the number of vibrational eigenvalues which are allowed to be located within the energy interval designated by a given \( n \)-th peak of the spectrum. This is done by introducing an eigenvalue distribution as a function of peak number

\[ \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \] (4.8)
that peak. The shown case corresponds to a steep potential along the OH bond which is related with a weak or broken HB. In this case for each peak we have one respective eigenvalue 4.6. On the other hand, OH bonds which are engaged in HB lead to shallow potential energy curves, which can have more than one eigenvalue per peak, for example (112222) or (112122) (see Fig. 4.6). For brevity, we will skip the upper row and use only the number of eigenvalues per peak, keeping in mind the correspondence peak-number of eigenstates in Eq. (4.8). This may be summarized as follows

\[
\begin{align*}
\text{weak or no-} & \quad \text{HB} \quad (111111), \quad (111112) \quad (4.9) \\
& \quad \text{HB} \quad (112212), \quad (112222), ... \quad (4.10)
\end{align*}
\]

According to our simulations, at most two eigenstates belong to a given \( n \)-th peak in the spectrum. The variation of the local environment leads to a variation in the eigenvalue distribution, which depends on the steepness of the potential curve along the OH bond. The calculations reveal the following patterns: first, for the eigenvalues of the steep potentials the \( n \)-th vibrational level lies in the region of the \( n \)-th peak, the only exception being peak \( n = 6 \) (see Eq. (4.9)). Secondly, in contrast, two vibrational levels (for example \( n_2 = n + 1 \) and \( n_2 = n \)) of a shallow potential can lie within the \( n \)-th peak (see Eq. (4.10)). The only exception is the vibrational peak \( n = 1 \). That is because this level lies very close to the bottom of the potential energy curve, which is only weakly affected by HBs.

Lastly, let us clarify the notion “region of the \( n \)-th peak”. We define this region as the energy interval \( \Delta \varepsilon_n \) enclosed by the minima between of the peaks adjacent to the \( n \)-th peak, based on a gaussian fit of the experimental spectrum. When we say, for example, that two eigenvalues belong to the \( n \)-th peak, it means that this eigenvalues can be located anywhere within the \( \Delta \varepsilon_n \) interval.

Apparently, the distribution of eigenvalues per RIXS peak gives information about the potential energy curve along the OH bond in the ground state. However, many potentials can satisfy the constraint defined by eqs. (4.9) and (4.10). This means that eigenvalue distributions (4.9) and (4.10) allow to extract only confidence intervals for the potential energy curves for the weak- or non-hydrogen-bonded and hydrogen-bonded cases, respectively.

To obtain the confidence interval for the OH potentials, from the experimental RIXS data, we fitted the parameters of the modified Morse potential

\[
V(R) = V_M(R) + B e^{\beta R}, \quad V_M(R) = D \left(1 - e^{\alpha R}\right)^2, \quad (4.11)
\]

using the GA [78] to search for potentials that satisfy the constraints defined by Eqs. (4.9) and (4.10). As it was expected, the constraint (4.9) yields a narrow confidence interval which correspond to the steep potentials. In contrast, the constraint (4.10) results in a
Figure 4.7: Potentials reconstructed from the experimental RIXS spectrum using the GA technique. (1) Displays the confidence interval for OH bonds involved in weak hydrogen bonding; (b) shows the confidence interval for hydrogen bonds with medium strength; and (c) shows the confidence interval obtained for OH bonds involved in strong hydrogen bonds. Figure taken from Paper V.

much wider distribution. Such a wide distribution of the molecular potentials is, of course, a direct consequence of the continuous distribution of possible local HB arrangements. The total reconstructed confidence interval (Fig. 4.7) is given by the sum of the confidence intervals of all eigenvalue constraints, and we see that it is in agreement with the ab initio distribution computed for the OH potential (Fig. 4.5).

4.7 Local Structure Analysis

In this section, we briefly address the discussion surrounding the local structure of liquid water, based on the information provided by our simulations of the RIXS spectrum.

Several previous investigations have pointed out that excitation at the pre-edge region of liquid water leads to the selection of OH bonds with a broken HB [15, 17, 19, 28], this drives us to understand whether this subset of structures plays any special role in the formation of the RIXS spectrum of liquid water. Let us start by looking at the single bond approximation. In reference [13] it is suggested that the vibrational progression seen in RIXS may be understood simply in terms of a Morse potential along a single OH bond, namely the
Figure 4.8: Upper panel: comparison of total theoretical RIXS spectrum $\sigma$ (dark blue) and the RIXS composed only the non-hydrogen bonded potentials $\sigma_{D_1}^{sb}$ (red) for all $D_1$ structures (single bond calculations). Middle panel: RIXS spectra considering a single bond model for all OH bonds in the cluster $\sigma_{D_1}^{sb}$ (green) alongside $\sigma_{D_1}^{sb}$. Lower panel: Partial RIXS spectra for $D_1$ structures $\sigma_{D_1}$ (purple) and $D_2$ structures $\sigma_{D_2}$ (pink) considering the coherent excitation of both OH bonds. Figure taken from Paper V.

one with a broken HB. As one can see from Fig. 4.8 this approximation does not match with the strict theoretical RIXS profile and it is much too narrow to explain the experimental data, which shows linearly increasing peak width (Fig. 4.5). Furthermore, this spectrum does not display background until $n = 6$. The reason for this is that the fluctuation of steep potentials (weak/broken HB), and hence the fluctuation of the corresponding eigenvalues are relatively small.

The agreement with experiment is even worse for the partial cross-section within the single bond approximation which include all OH bonds (still considering the respective transition dipole moments), as shown by the green curve in Fig. 4.8. This is because $\sigma_{D_1}^{sb}$ neglects the coherent excitation of both OH bonds during the scattering process (see Sec. 4.5).
We have also computed the partial RIXS cross sections for the D_1 and D_2 subset of structures. We see a red shift of the vibrational peaks of \( \sigma_{D2} \) with respect to \( \sigma_{D1} \), which seems natural because of the larger average number of HB for D_2 structures. It is important to note that the although the number of water molecules classified as D_1 structures constitute only 20% of all structures in our MD simulations of 64 water molecule cell. In spite of this the D_1 and D_2 structures contribute almost equally to the total RIXS profile (Fig. 4.8) due to larger transitions dipole moments for the D_1 structures yielded by the XCH method.

There is an intrinsic obstacle with trying to derive relative concentrations of hypothesized local structures from RIXS data in the ground state. To elaborate on this point, let us imagine that the transition dipole moment associated with D_1 structures is excessively larger than the ones for D_2 structures. In this case, one would arise to an erroneous conclusion that D_1 structures dominate liquid water, when in fact it would only mean that RIXS would not detect D_2 structures. One should mention that similar questions have been raised in XAS studies of liquid water [17, 19, 23, 79].

Fig. 4.9 displays this point more accurately. We have used three different techniques of calculation. One exaggerates the transition dipole moment at the pre-edge of D_1 structures (the HCH method [23, 26]), and two other that give a more balanced distribution (the FCH and XCH methods [25]). These techniques give the following relative contribution (computed for the areas of the spectra) D_1-D_2 to the total RIXS profile: HCH 86%-14%, FCH 53%-47%, and XCH 57%-43%. Evidently, none of these values reflect the true relative concentrations of D_1 and D_2 molecules in the actual snapshot used to compute the RIXS spectrum. They instead reflect the slight bias of the different techniques. Moreover, Fig. 4.9
4.8 On the Role of Soft-Modes

shows that the RIXS spectra calculated with transition dipoles from these three DFT-based techniques have very similar profiles.

In summary, it would seem ill-advised to draw definite conclusions about the local structure configuration of liquid water from RIXS data without carrying out far more accurate \textit{ab initio} calculations.

4.8 On the Role of Soft-Modes

In our quantum calculations for liquid water we were forced to carry out a number of approximations. Among them, the neglect of the so called soft-modes needs to be addressed. In our theory, we neglect the bending mode, hindered rotations and translations, as well as intermolecular vibrations. Apparently, this approximation leads to a lack of intensity on the blue side of each RIXS peak (Fig. 4.10). To verify this, we included the bending mode, using a 2D+1D model (Sec 2.2.1). We see that the bending mode results in a peak on the blue side of each main peak of the spectrum (Fig. 4.11). This indicates that the neglected softer modes, which would fill the region between the main peak and the bending peak,
create a blue tail seen in the experiment.

![Theoretical RIXS spectra computed including only the OH intramolecular stretches (shaded red) and considering both stretching and bending modes (solid black line).](image)

**Figure 4.11:** Theoretical RIXS spectra computed including only the OH intramolecular stretches (shaded red) and considering both stretching and bending modes (solid black line). Figure taken from Paper V.

### 4.9 Origin of the shift between the IR absorption and the $\nu_f = 1$ peak of RIXS of liquid water

Fig. 4.12 shows the IR absorption and the $\nu_f = 1$ peak of RIXS of water in liquid and gas-phase. One can see that the liquid-gas shift in IR absorption ($\approx 280$ cm$^{-1}$) is significantly larger than in RIXS ($\approx 93$ cm$^{-1}$). The aim of this section to understand the origin of this effect.

#### 4.9.1 Shift of RIXS first peak vs collective vibrations

As mentioned in Chapter 3, the two degenerated OH bonds are strongly coupled in the free water molecule. This leads to nearly degenerated symmetric and anti-symmetric stretching modes. In the liquid, different symmetry breaking local environments diminish this coupling and localizes the vibrational modes on the OH bonds. On the other hand, the OH stretches on different molecules are coupled in the liquid leading to the formation of collective vibrational states delocalized over ten or more molecules [81, 82]. Here, we would like to
4.9 Origin of the shift between the IR absorption and the $\nu_f = 1$ peak of RIXS of liquid water

Figure 4.12: Experimental IR absorption [80] for liquid water and RIXS profiles for liquid and gas-phase water. The green dashed lines show the experimental peak position of the symmetric and anti-symmetric stretching modes in gas-phase water.

shed light on the role of collective vibrational modes on the different peak positions of IR absorption and RIXS (Fig. 4.12).

The electronic transitions of core-excitation and de-excitation, in the RIXS process, happen on the same site $\ell$. We focus in this section on the quasi-elastic RIXS channel to the manifold of the final vibrational states

$$|\nu_f\rangle = |1\rangle.$$

To give fast insight in the main physics we consider the ensemble of $N$ coupled oscillators (OH stretching mode) localized on different sites $\ell$. Following previous investigations of the IR absorption [81], we will take into account this coupling only in the first excited vibrational state. We label localized vibrational states by $\ell$ and use the following notations for localized lowest vibrational ground state, localized final and core-excited states

$$|0\rangle = |0_1\rangle\cdots|0_N\rangle, \quad |\ell\rangle = |0_1\rangle\cdots|1_{\ell}\rangle\cdots|0_N\rangle, \quad |\Phi_{\ell}(0)\rangle = |0_1\rangle\cdots|\Psi_{\ell}(0)\rangle\cdots|0_N\rangle.$$ (4.12)

The use of localized vibrations, in the core-excited state, may be motivated as follows. The hopping time $\tau_h = 1/|V_{\ell\ell'}|$ of the vibrational transfer from one site to another one is the
inverse coupling parameter $|V_{\ell\ell}| \approx 25 \text{ cm}^{-1} = 3 \times 10^{-3}$ \[81\]

$$
\tau_h \approx \frac{1}{0.003 \text{eV}} = 219 \text{ fs} \gg \tau = \frac{1}{\Gamma} \approx 8 \text{ fs}.
$$ (4.13)

This together with our RIXS simulation (which includes the coupling $V_{ij}$) indicate that vibrational excitations localized on the OH bond "have no time" to be transferred to the OH bond of a nearby water molecule during the lifetime of core-excited state $\tau$. Thus, we may write the multisite nuclear Hamiltonians in ground, core-excited and final states

$$
H_0 = \sum_{\ell=1}^{N} h_0^{(\ell)}, \quad H_c^{(\ell)} = h_c^{(\ell)} + \sum_{\ell' \neq \ell}^{N} h_0^{(\ell')}, \quad H_f = \sum_{\ell=1}^{N} h_0^{(\ell)} + \sum_{\ell \neq \ell'} V_{\ell\ell'} Q_{\ell} Q_{\ell'}
$$ (4.14)

in terms of single site Hamiltonians $h_0^{(\ell)}$ and $h_c^{(\ell)}$ in the ground and core-excited states, respectively. It is important to notice that according to the IR studies the first excited vibrational state is delocalized over around 10-12 water molecules (chromofores)\[81\]. Therefore, we should use for the final state a delocalized (collective) vibrational state $|i\rangle$ instead of a localized one $|\ell\rangle$

$$
|i\rangle = \sum_{\ell=1}^{N} c_{i\ell} |\ell\rangle, \quad H_f |i\rangle = \epsilon_i |i\rangle, \quad i = 1, \ldots, N
$$ (4.15)

with eigenvalue $\epsilon_i$.

Similar to Sec. 4.1, the cross section for multisite RIXS can be written as follows:

$$
\sigma(\varepsilon, \omega) = \sum_{\ell=1}^{N} \frac{1}{\pi} \text{Re} \int_{0}^{\infty} e^{i(\varepsilon + \varepsilon_0 + i\Gamma_\ell)t} \sigma_\ell(t) dt,
$$

$$
\sigma_\ell(t) = \kappa_\ell \sum_{i=1}^{N} (\Phi_\ell(0)|i\rangle \langle i| e^{-iH_f t} |\Phi_\ell(0)\rangle), \quad \sigma_\ell(0) = \kappa_\ell \sum_{i=1}^{N} |(\Phi_\ell(0)|i\rangle|^2,
$$ (4.16)

$$
|\Phi_\ell(0)\rangle = \int_{0}^{\infty} e^{i(\omega - \omega' + \epsilon_0 + i\Gamma)t} |\psi_c^{(\ell)}(t)\rangle dt, \quad |\psi_c^{(\ell)}(t)\rangle = e^{-iH_c^{(\ell)} t} |0\rangle,
$$

where $\varepsilon \equiv \omega - \omega'$, $\epsilon_0 = \sum_{\ell=1}^{N} \epsilon_0^{(\ell)}$, $\kappa_\ell = (D_{f_c}^{(\ell)} D_{c_0}^{(\ell)})^2$, $D_{f_c}^{(\ell)} = (e' \cdot d_{f_c}^{(\ell)})$ and $D_{c_0}^{(\ell)} = (e \cdot d_{c_0}^{(\ell)})$. To characterize the effect of the collective vibrations on RIXS, we compute the center of gravity
or the first moment of the studied RIXS profile

\[
\Delta = \frac{\int_{-\infty}^{\infty} \varepsilon \sigma(\varepsilon, \omega) d\varepsilon}{\int_{-\infty}^{\infty} \sigma(\varepsilon, \omega) d\varepsilon} = \frac{\sum \text{Re} \left\{ \int_{-\infty}^{\infty} d\varepsilon \int_{-\infty}^{\infty} e^{i(\varepsilon_0 + \Gamma_f)t} \sigma(\varepsilon_0) dt \right\}}{\sum \text{Re} \left\{ \int_{-\infty}^{\infty} d\varepsilon \int_{-\infty}^{\infty} e^{i(\varepsilon + \varepsilon_0 + \Gamma_f)t} \sigma(\varepsilon) dt \right\}}
\]

\[
\Delta = \frac{\sum \text{Re} \left\{ i \int_{-\infty}^{\infty} d\varepsilon \left[ \sigma(t) + \int_{0}^{\infty} e^{i \left( \varepsilon(\varepsilon_0 + \Gamma_f) + \varepsilon_0 \right) t} dt \right] \right\}}{\sum \text{Re} \left\{ \int_{-\infty}^{\infty} d\varepsilon \left[ \sigma(\varepsilon) \right] \right\}}
\]

\[
\Delta = \frac{\sum \text{Re} \left\{ \int_{-\infty}^{\infty} d\varepsilon \sigma(t) \right\}}{\sum \text{Re} \sigma(t)}
\]

Since \( \text{Im} \sigma(0) = 0 \) we get

\[
\Delta = -\frac{\sum \text{Re} \sigma(t) \left| \right. t=0}{\sum \sigma(t) \left. \right|}
\]

(4.17)

Using Eq. (4.16) one can write the derivative of the auto-correlation function at the instant \( t = 0 \) as follows

\[
\frac{d\sigma(t)}{dt} \bigg|_{t=0} = \kappa_{\ell} \sum_{i=1}^{N} d\langle \Phi_{\ell}(0) | i \rangle \langle i | e^{-iH_f t} \Phi_{\ell}(0) \rangle \bigg|_{t=0} = -i\kappa_{\ell} \sum_{i=1}^{N} \langle \Phi_{\ell}(0) | i \rangle \langle i | H_f | \Phi_{\ell}(0) \rangle.
\]

(4.18)

This gives

\[
\Delta = -\varepsilon_0 + \frac{\sum \kappa_{\ell} \langle \Phi_{\ell}(0) | i \rangle \langle i | H_f | \Phi_{\ell}(0) \rangle}{\sum \sigma_{\ell}(0)}.
\]

(4.19)

Since the localized and delocalized states are connected by the unitary transformation one can go the localized states representation using

\[
\sum_{i=1}^{N} | i \rangle \langle i | = \sum_{\ell=1}^{N} | \ell \rangle \langle \ell |.
\]

(4.20)
This and \( \langle \Phi_\ell(0)|\ell'\rangle = \delta_{\ell\ell'} \langle \Phi_\ell(0)|\ell \rangle \) allow to rewrite the center of gravity as

\[
\Delta = -\epsilon_0 + \frac{\sum_{\ell_1} \sum_{\ell_1} \kappa_{\ell}(\Phi_\ell(0)|\ell')(\ell'|H_f|\Phi_\ell(0))}{\sum_{\ell_1} \sigma_{\ell}(0)},
\]

(4.21)

\[
\sigma_{\ell}(0) = \sum_{\ell_1} \kappa_{\ell}(\Phi_\ell(0)|\ell')(\ell'|\Phi_\ell(0)) = \kappa_{\ell}|\langle \Phi_\ell(0)|\ell \rangle|^2.
\]

(4.22)

Taking into account equation

\[
\langle \ell'|H_f = \langle 0_1|\cdots|1_{\ell'}|\cdots|0_N \rangle \left[ \sum_{\ell_1} h_{\ell_1}(\ell) + \sum_{\ell'_{\neq \ell}'} V_{\ell_1\ell''}Q_{\ell_1}Q_{\ell''} \right]
\]

(4.23)

\[
= \langle \ell'| \left[ \epsilon_0 + \epsilon_{1}(\ell') - \epsilon_{0}(\ell') + \sum_{\ell'_{\neq \ell}'} V_{\ell_1\ell''}Q_{\ell_1}Q_{\ell''} \right] \]

one can obtain

\[
\Delta = -\epsilon_0 + \frac{\sum_{\ell_1} \kappa_{\ell}(\Phi_\ell(0)|\ell)(\ell| \epsilon_0 + \epsilon_{1}(\ell) - \epsilon_{0}(\ell) + \sum_{\ell'_{\neq \ell}''} V_{\ell_1\ell''}Q_{\ell_1}Q_{\ell''}|\Phi_\ell(0))}{\sum_{\ell_1} \sigma_{\ell}(0)}.
\]

(4.24)

\[
= \frac{\sum_{\ell_1} \sigma_{\ell}(0)(\epsilon_{1}\ell - \epsilon_{0}\ell)}{\sum_{\ell_1} \sigma_{\ell}(0)} + \frac{\sum_{\ell_1} \kappa_{\ell}(\Phi_\ell(0)|\ell)(\ell| \sum_{\ell'_{\neq \ell}''} V_{\ell_1\ell''}Q_{\ell_1}Q_{\ell''}|\Phi_\ell(0))}{\sum_{\ell_1} \sigma_{\ell}(0)}.
\]

Since \( \ell' \neq \ell'' \) and \( \langle 0_\ell|Q_{\ell'}0_\ell \rangle = 0 \), the last term \( \propto V_{\ell_1\ell''} \) on the right-hand side of Eq. (4.24), related to the collective modes, is equal to zero

\[
\sum_{\ell'_{\neq \ell}''} V_{\ell_1\ell''}(\ell'|Q_{\ell'}Q_{\ell''}|\Phi_\ell(0)) = 0.
\]

(4.25)

For example, \( \langle \ell|Q_{\ell'}Q_{\ell''}|\Phi_\ell(0) \rangle = \langle 0_\ell|Q_{\ell'}0_\ell' \rangle \langle 0_{\ell''}|Q_{\ell''}'0_{\ell''} \rangle \langle 1_\ell|\Psi_i(0) \rangle = 0 \) when \( \ell' \neq \ell, \ell'' \neq \ell \). Thus, the center of gravity of the RIXS spectrum

\[
\Delta = \frac{\sum_{\ell_1} \sigma_{\ell}(0)(\epsilon_{1}\ell - \epsilon_{0}\ell)}{\sum_{\ell_1} \sigma_{\ell}(0)}
\]

(4.26)

is given by localized vibrational states and is not affected by the shift caused by the collective states (described by \( V_{\ell_1\ell''} \)) which are lying in the low energy side of the density of the states.

To conclude, the center of gravity \( \Delta \) (4.26) depends on the spectral distributions of the transition dipole moments \( \kappa_{\ell} \propto (d_{\ell}^{(\ell)})^2 \) and FC factors \( |\langle \Psi_i(0)|\ell \rangle|^2 \), and it is not affected by intermolecular coupling \( V_{\ell_1\ell''} \).
4.9 Origin of the shift between the IR absorption and the $\nu_f = 1$ peak of RIXS of liquid water

4.9.2 Enhancement of the rate of hopping of vibration in core-excited state

In the previous section, we investigated the coupling of $\nu_f = 1$ states near the bottom of the PES well. One can expect that this coupling should be enhanced in the core-excited state, when the size of the wave packet is large. To check this idea, let us consider a linear model where two coupled OH bonds are aligned along the OO direction

$$O_1^* - H_1 - - - - - - - - - O_2 - H_2.$$  \hfill (4.27)

Here, the core excited oxygen atom is denoted as $O^*$. We freeze the positions of the heavy oxygen atoms and allow only the hydrogen atoms to move: $R_{O_1O_2} = R_0 = \text{const}$. We denote the coordinate of the $n$-th hydrogen atom with respect to the $n$-th oxygen atom as $Q_n$.

Figure 4.13: The comparison of the RIXS profiles for two coupled ($\zeta = 0.01$) and uncoupled ($\zeta = 0$) OH bonds shows that vibrational energy transfer in the core-excited state affects mainly the high energy part of the spectrum, which is smeared out in the liquid phase (see Sec. 4.4). Here $\zeta = e_1e_2/R_0^3$.

Using the Born-Oppenheimer approximation $\Psi = \psi^{el}\chi$ we can write the Schrödinger equation
for the nuclear wave function $\chi(Q_1, Q_2)$ of the coupled oscillators

$$\dot{\chi} = h\chi, \quad h = h_1 + h_2 + V(Q_1, Q_2),$$

$$h_n = -\frac{1}{2m_H} \frac{\partial^2}{\partial Q_n^2} + U_n(Q_n)$$

with initial condition

$$t = 0: \quad \chi(Q_1, Q_2) = \chi_0^{(1)}(Q_1)\chi_0^{(2)}(Q_2),$$

where $\chi_0^{(n)}(Q_n)$ is the zero-point vibrational wave function is the $n$th well of the ground state. The interaction between OH stretches localized on different sites is modeled within a point-charge model

$$V(Q_1, Q_2) = V_{O_1O_2} + V_{O_1H_2} + V_{H_1O_2} + V_{H_1H_2}$$

$$= -e_1e_2Q_1Q_2R_0(R_0 + Q_2)(R_0 - Q_1)(R_0 + Q_2 - Q_1)$$

(4.28)

with the charges on the $n$-th oxygen and hydrogen atoms equal to $e_n$ and $-e_n$, respectively. For example $V_{O_1O_2} = e_1e_2/R_0$. In the simulations, we used the parameter $\zeta = e_1e_2/R_0^3 = 0.08 \times e_1e_2$, for $R_0 = 5$ a.u. The potentials for each OH bond $U_n(Q_n)$ were computed with the DFT method, as described in Sec. 4.1.

The results of the simulations, using the described model, show that the inclusion of the intermolecular coupling affects strongly the high-energy part of the RIXS spectrum, as seen in Fig. 4.13. This is clearly seen in the lower intensity of the high energy peaks, when compared with the uncoupled case, and also in the appearance of extra peaks in the spectrum, related to excitation of the neighboring O$_2$H$_2$ bond. In agreement with Sec. 4.9.1, we see that the first peak ($\nu_f = 1$) is not affected by the coupling $V(Q_1, Q_2)$. One should notice that the enhancement of the coupling effect for high vibrational states is difficult to observe in RIXS measurements because the fine structure of the high energy part is smeared out due to formation of the quasi-continuum (Sec. 4.4).

It is interesting to notice that enhancement of the vibrational energy transfer for high vibrational levels is confirmed by classical AIMD calculations as can be seen from Fig. 4.14.

### 4.9.3 Liquid-gas shift of RIXS first peak vs spectral distribution of the transition dipole moments

At the beginning of the discussion one should emphasize that non-hydrogen-bonded OH stretch modes have have higher $\nu_f = 1$ vibrational frequencies than those of hydrogen-bonded OH stretch modes. Conversely, the potential along a OH bond affected by hydrogen
4.9 Origin of the shift between the IR absorption and the $\nu_f = 1$ peak of RIXS of liquid water

Figure 4.14: Vibrational energy transfer in the core-excited state (hoping mechanism) results in an enlargement of the amplitude of the vibrations in the neighbor molecule with oxygen atom O$_2$. The left panel shows the increase of the O$_1$H$_1$ bond lengths in the core-excited state (solid lines) in comparison with the ground (dashed lines) due to the quasi-dissociation of O$_1^*$H$_1$. In the right panel we see the enhancement of the amplitude of vibrations in the O$_2$H$_2$ neighbor when O$_1$H$_1$ is core-excited (solid lines). Here the dashed lines show the variation of the O$_2$H$_2$ bond when O$_1$H$_1$ is not core-excited. The dynamics is illustrated by the snapshots along the trajectory on the left-hand side of the figure.

bonds is more shallow in comparison with the steep OH potential of non-hydrogen-bonded OH stretches, because the hydrogen bond weakens the chemical OH bond.

The simulations show that the dipole moments of the IR transitions and of RIXS have very different spectral distributions. The IR transition dipoles of non-hydrogen-bonded OH stretch modes (spectrally located in the high-frequency region) are significantly smaller than those of hydrogen-bonded OH modes (spectrally located in the low-frequency region). This is the cause of the red shift of the maximum of the IR absorption with respect to the maximum of the density of the states, and with respect to the gas-phase value [82]. The
situation is reversed in RIXS. According to our simulations the transition dipole moments of core-excitation $d_{co}$ are larger for non-hydrogen-bonded OH stretch modes. This results in a blue shift of the RIXS peak in liquid water with respect to the maximum of the density states. And namely this is the reason why the peak position of the $\nu_f = 1$ peak in RIXS of liquid water is so close to the gas-phase value, as one can see from Fig. 4.12. To make the picture clear, we would like to compare the theoretical simulations of IR absorption by Skinner’s group [81] and our RIXS simulations. Our calculations have lower accuracy than that of Skinner’s group, as they have nearly complete agreement with the experimental IR absorption. Indeed, our $\nu_f = 1$ peak position is red-shifted with respect to the experimental RIXS by 250 cm$^{-1}$, this is a well known deficiency of the BLYP functional [83] employed. This motivates us to calibrate our calculations with those of Skinner’s group’s by matching

![Figure 4.15: Theoretical IR absorption [81] and RIXS profiles along with the respective densities of states $\rho_1^{(0)}$ and $\rho_1$ used in the calculations. The RIXS spectrum and density of states were red shifted by 265 cm$^{-1}$ (see text). The vertical dashed lines show the experimental symmetric and anti-symmetric stretching frequencies of the free water molecule. The vertical black line shows the theoretical peak position of the RIXS in gas-phase.]
4.9 Origin of the shift between the IR absorption and the \( \nu_f = 1 \) peak of RIXS of liquid water

the peak position of our density of states with theirs, for better comparison (see Fig. 4.15). The reference density of states \( \rho_1^{(0)} \) [81] is based on a mixed classical-quantum model of a 128-molecule cluster with better sampling than the one used in our calculations. The differences seen in the shapes of \( \rho_1 \) and \( \rho_1^{(0)} \) (Fig. 4.15) may be attributed to this fact.

As already mentioned above, the reason for the red and blue shifts of IR absorption and RIXS profiles, respectively, is the opposite spectral distributions of IR and RIXS transition dipole moments. The red shift of the RIXS profile, with respect to the gas-phase, is of about 93 cm\(^{-1}\) which is nearly three times smaller than the corresponding shift in IR absorption (\( \approx 280 \) cm\(^{-1}\)).

![Figure 4.16: Partial cross-sections \( \sigma_{D_1} \) and \( \sigma_{D_2} \) together with the total profile \( \sigma \) for the final state \( \nu_f = 1 \). The vertical green solid line shows the peak position for the gas-phase RIXS computed at the same level as the liquid using DFT and the XCH method (see Sec. 4.1). The black dashed line shows the RIXS profile \( \sigma_{D_1}^{sb} \) (normalized to peak intensity of \( \sigma \)) simulated including only the single OH stretches with a broken hydrogen bond (single bond per molecule).](image)

Now, we turn our attention to analysis of the role of the local hydrogen bond environment on
the spectral shape of the $\nu_f = 1$ resonance, based on the HB definition in Sec. 4.2. Fig. 4.16 shows that in spite that $D_2$ structures have smaller transition dipole moment, in comparison with the $D_1$ structures, both class of structures contribute almost equally. The reason for this is the larger number of $D_2$ structures ($\approx 80\%$) in our simulated cluster (see Sec. 4.7). The partial profile for the $D_1$ structures deserves a special comment. Here we see that the idea that only the OH stretch with a broken HB contributes to the RIXS profile [13, 15] is not strictly correct. As discussed in Sec. 4.5 and shown in Fig. 4.6, a water molecule with an OH bond with a broken or weak HB ($D_1$ structure) has also a strong hydrogen bonded OH stretch associated with it. Here it is important to stress that both bonds are excited coherently with the same probability (transition dipole moment) in the course of RIXS.

The main peak in $\sigma_{D_1}$ is associated with the OH stretch with a weak or broken HB. Notice that this peak lies close to the reference gas-phase RIXS peak. However, we clearly see an extensive low energy tail originated from the hydrogen-bonded OH stretch. This low energy tail has smaller intensity but comparable area with the main peak. The profile yielded by taking into account only the broken hydrogen bonds, within a single bond per molecule approximation, is too narrow to explain the wide total profile (Fig. 4.16). Thus we cannot claim that only broken HB contribute to the spectrum. This becomes evident, also, when looking at $\sigma_{D_2}$ which has comparable contribution.

In conclusion, the physical reason for experimental shift between the infrared absorption and RIXS of liquid water is caused by opposite spectral distribution of the IR and RIXS transition dipole moments. This means that RIXS and IR measurements emphasize different regions of the density of vibrational states of liquid water. The analysis of the IR and RIXS profiles reveals that these techniques allows to probe OH bonds with different hydrogen bonding only approximately. However, they are unable to give definite answers about relative fractions of different local structures of the liquid in its ground state.
Chapter 5

RIXS of gas-phase methanol

Methanol is a molecule which is rather similar to water where one of the hydrogen atoms is replaced by a methyl group. Not surprisingly, in the liquid phase, methanol also displays the formation of a hydrogen bond network [84–87]. Contrary to H\textsubscript{2}O, methanol belongs to the Cs point group and has 12 vibrational modes instead of 3 for the water molecule.

![Methanol molecule with orbitals](image)

**Figure 5.1:** Occupied natural orbitals are extracted from the ground state multi-electron wavefunction. Unoccupied natural orbitals are extracted from the corresponding core-excited state. Figure taken from Paper VI.

In the ground state of methanol, 9 molecular orbitals are doubly occupied (see Fig. 5.1). The resonant X-ray scattering in methanol goes through the intermediate core-excited states related to the promotion of the 1s electron of Oxygen to the unoccupied orbitals shown in Fig. 5.1. We will study here the RIXS through the lowest core-excited state \([1s^{-1}_O 8a']\).
Table 5.1: Vibrational modes of methanol active in the \( |1s_{o}^{-1}8a'\) RIXS.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Frequency Exp, cm(^{-1}) (eV)</th>
<th>Frequency Theor (DFT), cm(^{-1}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO stretching</td>
<td>( \nu_8 ) 1033 (0.128)</td>
<td>1039 (0.129)</td>
</tr>
<tr>
<td>OH bending</td>
<td>( \nu_6 ) 1345 (0.167)</td>
<td>1365 (0.169)</td>
</tr>
<tr>
<td>CH(_3) s-deform.</td>
<td>( \nu_5 ) 1455 (0.180)</td>
<td>1477 (0.183)</td>
</tr>
<tr>
<td>OH stretching</td>
<td>( \nu_1 ) 3681 (0.456)</td>
<td>3829 (0.475)</td>
</tr>
</tbody>
</table>

One should mention that only four modes (\( \nu_1, \nu_5, \nu_6, \nu_8 \)) are active in the studied RIXS channel. The theoretical harmonic frequencies, and corresponding experimental values, for these modes are collected in Tab. 5.1. The potential energy curves of these active modes are depicted in Fig. 5.2. The major role in the formation of the RIXS profile is played by \( \nu_1 \) mode, which is dissociative in the core-excited state and related to the breaking of the OH bond. Due to this, the nuclear wave packet propagates a long distance in the studied core-excited state, in close analogy with water (see section 3.4), leading to a long vibrational progression of quasi-elastic RIXS and the formation of an atomic-like feature.

![Potential energy curves](image)

Figure 5.2: Potentials along most active vibrational modes of ground and 8\( A' \) core-excited state.

## 5.1 Quasi-elastic RIXS of methanol

First of all, let us study the quasi-elastic RIXS, which ends up in the ground state. Our simulations are based on a 1D+3D model, as described in sec. 2.2.1. Within this framework,
the mode $\nu_1$ is treated time-dependently while the remaining modes are treated using FC amplitudes. The results of our simulations of the RIXS, strictly in resonance with the vertical transition, are shown in Fig. 5.3. The skeleton of the spectrum is formed by the high-frequency OH stretching mode ($\omega_1 = 0.456 \text{ eV}$) which is the main reason for the long vibrational progression. The broad band at $\omega - \omega' \approx 8 \text{ eV}$ is an atomic-like resonance \cite{9, 88–90}. 

Figure 5.3: Cross-section of quasi-elastic RIXS. The energy of the incoming photon $\omega$ is tuned in resonance with dissociative $|1s_{O}^{-1/8}\alpha/\rangle$ core-excited state. The yellow bars display the most intense transitions while the black bars show all overtones. Figure taken from Paper VI.

$\omega + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^* + \text{H} \rightarrow \text{CH}_3\text{O} + \text{H} + \omega'$.

It is important to notice that this radical belongs to the $C_3v$ symmetry and its lowest state is a doubly degenerated state with E symmetry. This implies that another electronic state should have the same asymptotic limit as the ground state of methanol.
5.2 The $|1s^{-1}8a'|$ RIXS channel which ends up in the final state $|2a''^{-1}8a'|$

In the previous section, we described how the fragment of dissociation gives rise to an atomic-like peak in the quasi-elastic RIXS channel. However, that analysis is incomplete without taking into account the lowest inelastic channel, which also contributes to this feature. The methoxy radical ($C_{3v}$ point group) has a doubly degenerate $X^2E$ ground state [91]. Therefore, there are two electronic states of methanol with the same dissociation limit. They are the ground state $|GS\rangle$ and the dissociative $|2a''^{-1}8a'|$ state (see Fig. 5.4). Therefore, there are two channels that contribute to the formation of the quasi-atomic peak: The one which ends up in the ground state (see previous section) and the one which ends up in the dissociative valence excited state $|2a''^{-1}8a'|$. The RIXS profile arising from these two distinct channels will be qualitatively different, as can be expected by investigating the difference of the PECs $\Delta U_{cf}(Q) = U_c(Q) - U_f(Q)$ for final states $|f\rangle = |GS\rangle$ and $|f\rangle = |2a''^{-1}8a'|$ (Fig. 5.4).

Figure 5.4: Potential energy curves for the ground, core-excited $|1a''^{-1}8a'|$ and valence-excited $|2a''^{-1}8a'|$ states. The upper panel shows the difference between potentials of core-excited (black) and ground states (green) and core-excited and valence excited states (red). Figure taken from Paper VI.

Here, we analyse the RIXS in terms of a simple 1D model, by including only the $\nu_1$ mode
5.2 The $|1s_O^{-1}8a'\rangle$ RIXS channel which ends up in the final state $|2a''^{-1}8a'\rangle$ in the calculations. We do so because this is the most active mode and captures the main physical phenomena of the problem. It is known that, when the PECs of the intermediate and final states are exactly parallel, the molecular band and the atomic peak coincide with each other [9]. As we can see from Fig. 5.4, the PEC of the valence state is nearly parallel to that of the core-excited state, while the ground state one differs very much from it. This will lead to strong differences in the molecular band formed in each of these channels.

The formation of the atomic-like feature is given by the condition $\Delta U_{cf}(Q) = \text{const}$. In Fig. 5.4 we see that this is satisfied for the valence final state $|2a''^{-1}8a'\rangle$ at $Q \approx 1$ a.u. while for the ground state it happens at longer distances $Q \geq 3$ a.u. Note that it only takes about 5 fs for the wave packet to reach $Q \approx 1$ a.u. while it takes 10 fs to reach $Q \approx 3$ a.u. this plays a sufficient role in the intensity of the atomic-like peak of each channel. From Fig.

![Figure 5.5: Isotopic substitution effect on the quasi-elastic and lowest inelastic RIXS bands simulated at the top of $|1s_O^{-1}8a'\rangle$ XAS resonance. The insert shows the experimental data taken from ref. [34]. Figure taken from Paper VI.](image)

5.4 we may also estimate the relative position of the molecular bands and atomic peaks for each channel. For the ground-state channel, the separation between the maxima of the atomic-like peak and the molecular band is given by $\omega^{\prime}_{\text{mol}} - \omega^{\prime}_{\text{at}} \approx \Delta U_{c0}(0) - U_{c0}(\infty) = 8$ eV. The situation differs for decay to the dissociative $|2a''^{-1}8a'\rangle$ state, since now the atomic and molecular bands are expected to be close-lying in energy, since $\omega^{\prime}_{\text{mol}} - \omega^{\prime}_{\text{at}} \approx \Delta U_{cf}(0) - U_{cf}(1 \text{ a.u.}) = 0.76$ eV (Fig. 5.4). The results of our calculations nicely confirm these estimations.
based on the potential curves, as shown by the simulated RIXS profile in Fig. 5.5. Attention should be paid to the fact that the nature of the atomic-like peak formed in the RIXS that ends up in the valence-excited state is very different from the one formed in the ground-state channel. When the system decays to the GS, the atomic-like peak is formed by decay of the core-excited methoxy radical CH$_3$O*, while the origin of this peak in the inelastic channel happens in the CH$_3$OH, close to the equilibrium. As we will see below (Fig. 5.7) the double-peak structure formed near the atomic-like feature arises mainly due to the valence RIXS channel. According to the previous discussion, this profile is formed mainly by decay near the equilibrium. This leads to an important conclusion regarding the origin of the splitting of the 2$a''$ RIXS resonance in liquid phase [31]: The dynamical origin of this splitting in gas-phase will be preserved also in liquid methanol, at pre-edge excitation, because the region near equilibrium is affected very little by the hydrogen bond network.

![Theoretical RIXS map for scattering through the 8A' state of methanol. The position of the atomic-like peak (CH$_3$O$^-$) does not depend on excitation energy $\omega$ contrary to molecular band CH$_3$OH which follows the Raman law.](image.png)

Figure 5.6: Theoretical RIXS map for scattering through the 8A' state of methanol. The position of the atomic-like peak (CH$_3$O$^-$) does not depend on excitation energy $\omega$ contrary to molecular band CH$_3$OH which follows the Raman law. Figure taken from Paper VI.

The role of isotopic substitution is demonstrated by the results of the 1D simulations of the RIXS profile (Fig. 5.5). First, we observe that the vibrational progression is affected when we replace the hydrogen atom by deuterium. The difference arises due to different frequencies of the OH and OD groups. The second effect is related to the lower kinetic energy of the nuclear wave packet in the core-excited state of CH$_3$OD in comparison to the CH$_3$OH, due to the large mass difference. This leads a less intense atomic-like peak in the
5.2 The $|1s_O^{-1}8a'|$ RIXS channel which ends up in the final state $|2a''_{2}^{-1}8a'|$ RIXS of CH$_3$OD than that of CH$_3$OH, in agreement with experiment [34] (Fig. 5.5).

Isotopic substitution is not the only tool available for the identification of molecular and atomic peaks. The dispersion law of the scattering process also allows to tell them apart. This is because the emission energy of the atomic-like peak does not depend on the excitation energy (As it is well known [9, 89]). In contrast, the molecular band follows the so called Raman dispersion law (see Fig. 5.6).

Figure 5.7: Upper panel shows the polarization dependence of CH$_3$OH and CH$_3$OD. The lower panel displays the partial contributions related to decay to the ground (blue) and valence excited (orange) states. Figure taken from Paper VI.

Finally, let us consider the polarization dependence of studied RIXS profile. This is important since the transition dipole moments $d_{c0}$ and $d_{2a''}$ of the two channels are orthogonal to each other (see Table 5.2). The different orientations of the transition dipoles may be understood in terms of the molecular orbitals. The $8a'$ orbital lies in the molecular plane.

Table 5.2: Components of the transition dipole moments (in a.u.) from RASPT2 calculations in the frame shown in Fig. 5.1.

| Transition                      | $d_x$    | $d_y$    | $d_z$    | $d=|\mathbf{d}|$ |
|--------------------------------|----------|----------|----------|------------------|
| GS $\rightarrow |1s_O^{-1}8a'\rangle$ | -0.00817 | -0.03040 | 0.00000 | 0.03148          |
| $|1s_O^{-1}8a'\rangle$ $\rightarrow |2a''_{2}^{-1}8a'\rangle$ | 0.00000  | 0.00000  | -0.05519 | 0.05519          |
whereas the $2a''$ orbital is oriented orthogonally to this plane, because of its $\pi$ character (Fig. 5.1). Therefore, the total RIXS cross-section (2.22) within the $\omega - \omega' \leq 8eV$ region is made up by the sum of two contributions with distinct polarization dependence

$$\sigma(\omega', \omega) = \frac{d_2^2}{30} \left[ d_{2a}^2 (2 - \cos^2 \chi) \sigma_0 + d_{2a''}^2 (3 + \cos^2 \chi) \sigma_{2a''} \right].$$

(5.2)

Here, the partial cross-sections $\sigma_0$ and $\sigma_{2a''}$ correspond to the scattering channel the ground and $|2a''-18a''\rangle$ states, respectively are computed using Eq. (2.22) with $D_{c_0} = D_{f_c} = 1$ within the one-dimensional model (Fig. 5.4) described in this section. The RIXS profile (5.2), shown in Fig. 5.7, displays a strong polarization dependence for both CH$_3$OH and CH$_3$OD, as it was expected.
Chapter 6

Dynamical rotational Doppler effect

In this section, according to paper **Paper VII**, we discuss a novel effect that affects molecular Auger spectra and which increases with the photon energy. This is the rotational Doppler splitting caused by ultra-fast rotation induced by the ejection of a fast photoelectron. As a consequence of the ultra-fast rotation, the molecule changes its orientation during the lifetime of the core-hole state. The change in orientation coupled with the high anisotropy of the Auger process, leads to different intensities of the Doppler splitted peaks. The physical picture is illustrated in Fig. 6.1.

Here, we study the Doppler effect in non-resonant Auger process in the carbon monoxide molecule

\[
\omega + \text{CO}(X^1\Sigma^+) \rightarrow \text{CO}^+(C1s^{-1}\,^2\Sigma^+) + e^-_k \rightarrow \text{CO}^{++}(d\,^1\Sigma^+) + e^- + e^-_p
\]  

(6.1)

where the high energy X-ray photon (2.5 keV \(\leq \omega \leq 12\) keV) ionizes a 1s core electron of the carbon atom with radius vector

\[
\mathbf{R}_C = \alpha \mathbf{R}, \quad \alpha = \frac{m_O}{M}.
\]  

(6.2)

In Sec. 2.3, we got Eq. (2.30) and Eq. (2.35)

\[
F \propto \frac{1}{\Delta E + D_{tr} + D_{rot} + \Delta_{rec} + i\Gamma} = -i \int_0^\infty e^{i(\Delta E + D_{tr} + D_{rot} + \Delta_{rec} + i\Gamma)t} \, dt,
\]  

(6.3)

\[
D_{tr} = \frac{p \cdot k}{M}, \quad D_{rot} = \frac{j_p \cdot j_k}{I} = j_p \cdot w_k,
\]

\[
w_k = \frac{j_k}{I} = \alpha \frac{R \times k}{I}, \quad j_p = \alpha [R \times p].
\]

This equation is not strictly correct because it assumes that both the fast photoelectron and the Auger electron are ejected at the same instant, \(t = 0\). At this instant, the photoelectron
Figure 6.1: The physical picture of the asymmetry of the Auger profile caused by the rotational dynamics. At the bottom of the figure, a photoelectron with momentum $\mathbf{k}$ is at $t = 0$ ejected from the carbon atom (black dots) in the direction away from the detector. Induced by the recoil momentum the molecule translates with a speed $\mathbf{u} = \mathbf{k}/M$ and rotates with an angular velocity $\mathbf{w}_k$ towards the detector. As a result, an Auger electron with momentum $\mathbf{p}$ emitted at $t = \tau$ towards the detector is blueshifted as shown by the schematic spectrum displayed in the upper part. When the photoelectron is emitted in the opposite direction, the velocity $\mathbf{u}$ and angular velocity $\mathbf{w}_k$ are inverted (mid part). This results in a redshifted Auger electron. The shaded gray areas around the carbon atoms depict an Auger emission with anisotropic angular distribution in the molecular frame. This means that a molecule that rotates away from the detector will lead to smaller intensity, whereas a molecule that rotates towards the detector will emit more electrons. Figure taken from Paper VII.

transfers to the molecule angular momentum $\mathbf{j}_k$ and according to Eq. (2.26) the molecule starts to rotate with angular velocity $\mathbf{w}_k$. However, the Auger electron is ejected later at the instant $t > 0$. During this time delay, between the ejection of the fast photoelectron and emission of the Auger electron the molecular axis rotates according to Newton’s equation

$$\frac{d}{dt} \hat{\mathbf{R}}(t) = [\mathbf{w}_k \times \hat{\mathbf{R}}(t)] = w_k [\hat{\mathbf{w}}_k \times \hat{\mathbf{R}}(t)],$$

$$\hat{\mathbf{R}}(t) = \hat{\mathbf{R}}(0) + \int_0^t w_k [\hat{\mathbf{w}}_k \times \hat{\mathbf{R}}(t_1)] dt_1.$$
This makes the recoil angular momentum \( \mathbf{j}_p(t) = \alpha [\mathbf{R}(t) \times \mathbf{p}] \) due to ejection of the Auger electron time-dependent. Hence, the rotational Doppler shift is also time-dependent

\[
D_{\text{rot}}(t) = \mathbf{j}_p(t) \cdot \mathbf{w}_k, \quad \mathbf{j}_p(t) = \alpha [\mathbf{R}(t) \times \mathbf{p}].
\]

One should notice that Eq. (6.3) ignores the time-dependence of the rotational Doppler shift. In order to get the correct result we should start from the semi-classical expression for the scattering amplitude (see Paper VII)

\[
F = -\int_0^\infty e^{\imath \alpha (\mathbf{p} \cdot \mathbf{R}(t))} e^{\imath (\Delta E + D_{\text{tr}} + \imath \Gamma) t} dt.
\] (6.5)

This and the last equation in Eq. (6.4) modify the scattering amplitude (Eq. (6.3))

\[
F = -\int_0^\infty e^{\imath \alpha (\mathbf{p} \cdot \mathbf{R}(t_1)) dt_1} e^{\imath (\Delta E + D_{\text{tr}} + \imath \Gamma) t} dt.
\] (6.6)

where we omitted the unimportant prefactor \( \exp(\imath \alpha \mathbf{p} \cdot \mathbf{R}(0)) \)

To solve Eq. (6.4), we take into account the fact that the molecule rotates in a plane perpendicular to \( \mathbf{w}_k \), therefore we introduce two orthogonal vectors

\[
\hat{\mathbf{R}}(0), \quad \hat{\mathbf{R}}_\perp \equiv \hat{\mathbf{w}}_k \times \hat{\mathbf{R}}(0),
\] (6.7)

lying in this plane as a basis to describe this rotation

\[
\hat{\mathbf{R}}(t) = \cos(\theta(t))\hat{\mathbf{R}}(0) - \sin(\theta(t))\hat{\mathbf{R}}_\perp.
\] (6.8)

Substitution of this equation in the equation of rotational motion, Eq. (6.4), and taking into account \( \mathbf{w}_k \times \hat{\mathbf{R}} = w_k \hat{\mathbf{R}}_\perp \) and \( \mathbf{w}_k \times \hat{\mathbf{R}}_\perp = -w_k \hat{\mathbf{R}} \), give us the angle of rotation

\[
\dot{\theta}(t) = w_k, \quad \theta(t) = w_k t.
\] (6.9)

We use here a linear approximation over time

\[
\hat{\mathbf{R}}(t) = \hat{\mathbf{R}}(0) - \hat{\mathbf{R}}_\perp w_k t,
\] (6.10)

because the molecule has no time to perform a full rotation within the lifetime \( \tau \) of core-excited state

\[
w_k \tau \leq 0.2 \ll 1.
\] (6.11)

Within this approximation, we obtain the following dynamical rotational Doppler shift

\[
D_{\text{rot}}(t) = \alpha [\mathbf{R}(t) \times \mathbf{p}] \cdot \mathbf{w}_k = \alpha R([\hat{\mathbf{R}}(0) - \hat{\mathbf{R}}_\perp w_k t] \times \mathbf{p}) \cdot \mathbf{w}_k
\] (6.12)

\[
= D_{\text{rot},0} + \rho((\hat{\mathbf{R}}(0) \times \hat{\mathbf{k}})^2 (\mathbf{p} \cdot \hat{\mathbf{R}}(0))) t, \quad \rho = \frac{\alpha^3 R^3 k^2 p}{I^2}.
\]
Chapter 6 Dynamical rotational Doppler effect

where \( D_{\text{rot},0} = \alpha [\mathbf{R}(0) \times \mathbf{p}] \cdot \mathbf{w}_k \).

In the limit of the slow rotation (Eq. (6.11)), one can expand the exponent \( \exp(\imath \rho (\dot{\mathbf{R}}(0) \times \mathbf{k})^2 (\dot{\mathbf{p}} \cdot \mathbf{R}(0)) t^2) \) in Taylor series taking into account the first term. Hence the scattering amplitude

\[
F \approx -i \int_0^\infty dt e^{i[\Delta E + D_{\text{tr}} + D_{\text{rot},0} + \imath \Gamma]t} \left( 1 + i \rho (\dot{\mathbf{R}}(0) \times \mathbf{k})^2 (\dot{\mathbf{p}} \cdot \mathbf{R}(0)) t^2 \right)
\]

is divided into two qualitatively different parts, \( F_0 = -i \int_0^\infty dt \exp(i\phi(0)t) \) and \( F_d = \rho (\dot{\mathbf{R}}(0) \times \mathbf{k})^2 (\dot{\mathbf{p}} \cdot \mathbf{R}(0))^2 \int_0^\infty dt \exp(i\phi(0)t) t^2 \)

\[
F_0 = \frac{1}{\Delta E + D_{\text{tr}} + D_{\text{rot},0} + \imath \Gamma}, \quad F_d = \frac{-2i\rho (\dot{\mathbf{R}}(0) \times \mathbf{k})^2 (\dot{\mathbf{p}} \cdot \mathbf{R}(0))}{[\Delta E + D_{\text{tr}} + D_{\text{rot},0} + \imath \Gamma]^2},
\]

where \( \phi(0) = \Delta E + D_{\text{tr}} + D_{\text{rot},0} + \imath \Gamma \). The "instantaneous" term \( F_0 \) describes the Auger process when the molecule has no time to change the orientation. The recoil-induced rotation of the molecular axis is taken into account by the smaller dynamical term \( F_d \). The "instantaneous" scattering channel described by \( |F_0|^2 \) results in a Doppler broadening and splitting of the symmetric Auger profile [92–94] (see Paper VII)

\[
\sigma_0(\Delta E) = \langle (\mathbf{e} \cdot \dot{\mathbf{k}}) F_0^2 \rangle = \left\langle \frac{1 + \beta P_2(\dot{\mathbf{k}} \cdot \dot{\mathbf{p}})}{(\Delta E + D_{\text{tr}} + D_{\text{rot},0})^2 + \Gamma^2} \right\rangle.
\]  

(6.15)

Here and below the brackets denote an integration over \( \dot{\mathbf{k}} \) and \( \dot{\mathbf{R}}(0) \), \( P_2(x) \) is the Legendre polynomial. The splitting refers to the opposite translation and rotational Doppler shifts of two islands in the velocity and angular velocity distributions (Fig. 6.2c). The physical picture of this effect is rather similar to what was discussed in refs. [93, 94]. The simulations show that cross-section given by Eq. (6.15) is a symmetrical function of energy (see Fig. 6.3a). In spite of the fact that the rotational motion is treated classically, there is a pure quantum effect to consider: Owing to the well defined phase between the "instantaneous" and the time delayed parts of the rotational wave packet in the core-ionized state, there are interferences between these waves. The corresponding interference term \( \text{Re}(F_0 F_d^*) \) of "instantaneous" \( (F_0) \) and "time-delayed" \( (F_d) \) scattering amplitudes is equal to zero in the cross-section defined by Eq. (6.15)

\[
\left\langle \text{Re}(F_0 F_d^*) \right\rangle \propto \left\langle (\dot{\mathbf{p}} \cdot \dot{\mathbf{R}}(0)) \right\rangle = 0.
\]  

(6.16)

The cross-section \( \sigma_0 \) does not provide a full description of the studied process. There is a polar anisotropy in the ejection of the photoelectron and of the Auger electron, described by the terms \( (\dot{\mathbf{k}} \cdot \dot{\mathbf{R}}(0)) \) and \( (\dot{\mathbf{p}} \cdot \dot{\mathbf{R}}(0)) \), respectively. This polar anisotropy does not affect the
Figure 6.2: a) Scheme of the experiment with the polarization direction of the synchrotron radiation $\mathbf{e}$ and the momentum of the Auger electron, $\mathbf{p}$. b) In the quantum picture, the Auger process is strongly affected by the interference of the Auger channels going through different rotational levels of core-ionized state. c) Velocity distributions $W(u)$ and angular velocity distributions $W(w)$. The left panel shows the velocity $W_0(u)$ and angular velocity $W_0(w)$ distributions in the ground state at room temperature. The middle and the right panel display these distributions after the emission of a fast photoelectron. Figure taken from Paper VII.

Auger spectrum of randomly oriented molecules when the anisotropic rotational Doppler effect is neglected. As shown in Paper VII, the role of the polar anisotropy of the ejection of a fast photoelectron is negligibly small. However, this is not the case for the rather slow Auger electron. To account for this effect, we introduce the prefactor $1 + \eta(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))$ which describes the polar anisotropy of the Auger process

$$\sigma(\Delta E) = \langle |(\mathbf{e} \cdot \hat{\mathbf{k}})F|^2(1 + \eta(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))) \rangle. \quad (6.17)$$

Now, contrary to Eq. (6.16), the interference between "instantaneous" ($F_0$) and "time-delayed" ($F_d$) amplitudes is not equal to zero

$$\langle \text{Re}(F_0 F_d^*)(1 + \eta(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))) \rangle = \eta(\text{Re}(F_0 F_d^*)(\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))) \propto \langle (\hat{\mathbf{p}} \cdot \hat{\mathbf{R}}(0))^2 \cdots \rangle \neq 0. \quad (6.18)$$
Figure 6.3: a) The symmetrical profile of the calculated partial cross section $\sigma_0$, see Eq. (6.15), where the recoil-induced rotation of the molecular axis is neglected. The splitting of the Auger profile is caused by recoil induced deformation of the translational and rotational Maxwell-Boltzmann distributions $W(u)$ and $W(w)$, as it is sown in Fig. 6.2c. b) The theoretical total cross-section $\sigma$ of the Auger process is asymmetric due to the anti-symmetric dynamical contribution $\sigma_{\text{int}}$, see Eq. 6.17 and Fig. 6.4b. The asymmetry stems from the dynamical rotational Doppler effect. In the calculations we used the following parameters $\zeta = 1.78$, $\eta = 0.6$ and $\Gamma = 0.043$ eV. c) Experimental data, in agreement with the simulations, shows that the dynamical asymmetry grows with increasing $\omega$. Figure taken from Paper VII.

This interference results in an additional contribution to the cross-section (Eq. (6.15))

$$\sigma(\Delta E) = \sigma_0(\Delta E) + \eta \sigma_{\text{int}}(\Delta E), \quad (6.19)$$

$$\sigma_{\text{int}}(\Delta E) = 4\rho \Gamma \frac{f}{[(\Delta E + D_{\text{tr}} + D_{\text{rot,0}}) + \Gamma^2]^3},$$

where $f = [1 + \zeta P_2(\hat{k} \cdot \hat{p})]((\hat{R}(0) \times \hat{k})^2(\hat{R}(0) \cdot \hat{p})^2$. Contrary to $\sigma_0(\Delta E)$ the interference term $\sigma_{\text{int}}(\Delta E)$ depends anti-symmetrically on the energy $\Delta E$ (Fig. 6.4)

$$\sigma_{\text{int}}(\Delta E) = -\sigma_{\text{int}}(-\Delta E), \quad \sigma_0(\Delta E) = \sigma_0(-\Delta E). \quad (6.20)$$

This makes the total Auger profile $\sigma(\Delta E)$ asymmetric in full agreement with experiment (see Fig. 6.3 b and c).

To conclude, the time delayed Auger electron emission provides a unique opportunity to investigate the dynamics of ultra-fast molecular rotation, because a significant change of
Figure 6.4: a) The symmetric partial cross section \( \sigma_0 \) describes the translational and rotational Doppler broadening and the Doppler splitting. b) The interference of the "instantaneous" and "time-delayed" Auger channels results in an anti-symmetric contribution \( \sigma_{\text{int}} \). Simulations are performed for \( \omega = 12 \text{ keV} \), \( \zeta = 1.78 \), \( \eta = 0.6 \) and \( \Gamma = 0.043 \text{ eV} \). Figure taken from Paper VII.

The molecular orientation occurs during the lifetime of the core-ionized state. The time information in our experiment stems from the natural delay between the core-ionization and the ejection of the Auger electron. Because we are unable to change the lifetime of the core-ionized state, we visualize this dynamics via the asymmetry of the Auger profile which is controlled by changing the rotational speed using X-ray photons of different energies.
Chapter 7

Summary

This chapter collects a summary of the main results obtained in this thesis.

- We developed new theoretical methods to compute the vibrational RIXS and XAS spectra of multi-mode molecules, which we denote $mD+nD$ mixed representation, where the $m$ nuclear degrees of freedom are treated time-dependently while the remaining $n$ degrees of freedom are treated through the time-independent Franck-Condon amplitudes.

- We have described the vibrational RIXS spectra of $\text{H}_2\text{O}(g)$ through the $|O1s^{-1}4a_1^1\rangle$, $|O1s^{-1}2b_2^1\rangle$ and $|O1s^{-1}2b_1^1\rangle$ states, and demonstrated how these intermediate states act as “gates” to different ground state vibrational modes.

- We propose a novel technique for extraction of one-dimensional cuts through the PES of multi-mode systems using water as a showcase.

- We predict a strong polarization dependence of the vibrational progression in $\text{H}_2\text{O}(g)$ due to a break-down of the Franck-Condon approximation leading to scattering anisotropy of different vibrational levels in a single channel RIXS process.

- We developed a classical-quantum framework for accurate description of the vibrationally resolved RIXS spectrum of liquids. Our model makes use of $ab$ $initio$ MD combined with quantum wave packet dynamics. The proposed model is capable of accounting for the most relevant quantum nuclear dynamics effects seen in modern RIXS spectroscopy.

- We have computed the vibrationally resolved RIXS of liquid water at the pre-edge in very good agreement with experiment. We are able to explain the shortening of the
vibrational progression in comparison with the gas-phase spectrum, the formation of a quasi-continuum of vibrational levels. We provide a description of the core-excitation dynamics in the liquid and a detailed assignment of the spectrum in terms of the partial densities of vibrational states of the liquid.

- It was shown that both D_1 and D_2 classes of local structures are important to the formation of the RIXS spectrum of liquid water.

- It is explained the opposite shift of the maximum of IR absorption and the \( \nu_f = 1 \) peak in the RIXS spectrum due to opposite spectral dependence by the IR and RIXS transition dipole moments.

- We identify a strong analogy between the dynamics in methanol and water, both manifested as an ultra-fast dissociation of the OH bond upon excitation to the lowest core-excited state. This analogy is reflected in the vibrational RIXS spectrum as well as in the lowest inelastic band.

- We demonstrate that the splitting of the 2\( a'' \) peak in the RIXS of gas-phase methanol arises due to nuclear dynamics, thus hinting at the origin of this splitting in the liquid phase. We have good agreement with the experiment and accurately describe the isotopic substitution effect.

- It was developed a theory for a dynamical rotational Doppler effect which explains the asymmetry of the Auger spectrum of the CO molecule induced by hard X-rays.
Bibliography


