Principles of Infrared - X-Ray Pump-Probe Spectroscopy

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Abstract

The present thesis concerns theoretical studies of molecular interactions investigated by infrared and X-ray spectroscopic techniques, with emphasis on using these two techniques combined in pump-probe experiments. Four main types of studies are addressed: the use of near-edge X-ray absorption fine structure spectra (NEXAFS) to manifest through-bond and through-space interactions; the role of hydrogen bonding in the formation of X-ray photoelectron spectra as evidenced by simulations of the water dimer; the development of theory, with sample applications, for infrared X-ray pump-probe spectroscopy; and molecular dynamics simulations of light-induced fragmentation of water clusters.

Ab initio calculations indicate that NEXAFS spectra give direct information about the through-bond and through-space interactions between vacant non-conjugated π* orbitals. It is found out that the X-ray photoelectron spectrum of the water dimer differs dramatically from the monomer spectrum in that two bands are observed, separated by the chemically shifted ionization potentials of the donor and the acceptor. The hydrogen bond is responsible for the anomalously strong broadening of these two bands. The studies show that X-ray core electron ionization of the water dimer driven by an infrared field is a proper technique to prove the proton transferred state contrary to conventional X-ray photoelectron spectroscopy.

The physical aspects of the proposed new X-ray spectroscopic method - phase sensitive Infrared - X-Ray Pump-Probe Spectroscopy - are examined in detail using the wave packet technique in three applications; the NO molecule and the dynamics of proton transfer in core ionized water dimer and glyoxalmonoxime. It is found out that the phase of the infrared pump field strongly influences the trajectory of the nuclear wave packet on the ground state potential, which results in a phase dependence of the X-ray pump-probe spectra. A proper choice of the delay time of the X-ray pulse allows the direct observation of the X-ray transition in the proton transferred well of the core excited potential. It is found out that the glyoxalmonoxime molecule possesses an important feature; proton transfer accompanied by core hole hopping. Special attention is paid to the quantum control of the populations of vibrational level which is of crucial importance to shape the wave packet of desirable size.

The wave packet technique becomes computationally very expensive when the number of nuclear degrees of freedom is large. Molecular dynamics is used instead in studies of light-induced nuclear kinetics in the water hexamer cluster. We predict a novel mechanism of the mechanical action of light on atoms and molecules. This mechanism is based on the rectification of the Lorentz force, which gives a unique opportunity of direct site selective mechanical action of light on atoms and molecules inside large systems like clusters or biomolecules.
Preface

The work in this thesis has been carried out at the Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Stockholm.

List of papers included in the thesis


**Paper VI**  V. C. Felicissimo, F. F. Guimarães, and F. Gel’mukhanov, *Coherent control of population of vibrational states by infrared pulses* (in manuscript).

List of papers not included in the thesis


Comments on my contributions in the papers included in the thesis

- I was responsible for theory, calculations, writing and editing of manuscript in Papers I, II, III, V and VI.
- I participated in discussions and theoretical work, and I was responsible for some calculations in Paper IV.
- I participated in discussions, analysis of the results of simulations, writing of the manuscript and I was responsible for few a calculations in Paper VII.
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Contents

1 Introduction .................................................. 1

2 NEXAFS and XPS studies of molecular interactions ............ 5
  2.1 Principle of NEXAFS ..................................... 5
  2.2 Principles of X-ray photoelectron spectroscopy (XPS) ......... 6
  2.3 Vibrational structure in X-ray spectra ........................ 8
  2.4 Study of through-bond and through-space interactions using NEXAFS .... 9
    2.4.1 Through-space interaction in ethylene dimer ............. 9
    2.4.2 Through-bond interaction in the p-benzoquinone molecule ...... 10
  2.5 XPS study of hydrogen bonding in the water dimer ............. 12

3 Infrared - X-ray pump-probe spectroscopy ..................... 17
  3.1 Principle of IR spectroscopy ................................ 18
  3.2 Theoretical background of IR -X-ray pump-probe spectroscopy .... 19
  3.3 Proton transfer in the core ionized states of water dimer .......... 21
  3.4 Intramolecular proton transfer mediated by vibronic coupling between the two O1s core ionized states of glyoxalmonoxime ............ 24
  3.5 Role of light coherence, duration and phase .................. 28
    3.5.1 X-ray spectrum in the field of incoherent pump radiation .... 29
    3.5.2 Role of duration of X-ray and IR pulses ..................... 29
    3.5.3 Phase memory versus shape of the IR pulse .................. 31
    3.5.4 Dephasing caused by z-dependence of the phase of the IR field .... 33
4 Coherent control of populations of excited vibrational levels 35

5 Dynamics of water clusters in strong IR fields 43
   5.1 IR induced dynamics in the ground state of the water dimer . . . . . . . . 45
   5.2 Dynamics of the water hexamer in strong IR fields . . . . . . . . . . . . . 47
      5.2.1 Light induced dynamics of the water cluster in a low frequency field.
           Breaking of the hydrogen bond . . . . . . . . . . . . . . . . . . . . . . . . 49
      5.2.2 Rectification of the Lorentz force. Break down of the OH bond caused
           by light-induced charge transfer . . . . . . . . . . . . . . . . . . . . . . . . 53
      5.2.3 Rectification of the Lorentz force. Break down of hydrogen bond . . 57

6 Summary of results 61
Chapter 1

Introduction

Molecular interactions are subject to great interest in chemistry, physics and biology because they hold the keys to an understanding of the properties and structure of matter. Every substance is made up of atoms, and all atoms are surrounded by electrons. Essential to understanding of all types of chemical bonding is the realization that bonds use electrons as the glue. By large, the difference between materials as diverse as diamond and graphite can be traced to how they are kept together by electrons forming chemical bonds.

The understanding and prediction of the properties of matter at the atomic level represents one of the great achievements of the twentieth-century science. The outstanding development of quantum mechanical ideas and computational facilities have widened old roads and drastically changed the understanding of molecular interactions. In the last decades, studies of molecular interactions have shown a fascinating progress. This is a result not only of the development of new theoretical methods and complex computations, but, of course, of many new experimental technologies that have become available for such studies. These advancements have made it possible to study molecular systems in gas phase, in liquids and in solids.

Spectroscopy serves as the main tool to probe molecular structure and intra/inter-molecular interactions. Perturbations resulting from molecular interactions affect spectra in various ways. Changes in the energy levels lead to shifts in absorption and emission peaks, appearance of new resonances, etc. Changes of the molecular wave functions result in a redistribution of intensities. The great challenge in any spectroscopic field is to find solutions of the inverse problem - to extract information about molecular interactions from spectral changes. The various spectroscopies permit in that context different aspects of the interactions to be
studied.

In this thesis two different types of molecular interactions are studied. One is the intramolecular interaction of orbitals localized on different functional groups or chromophores of organic compounds. The study of this orbital interaction is of great interest in chemistry as well as in biology because it is responsible, for example, for electron transfer. The concept of the building block is of general importance in the study of orbital interactions and spectroscopy. Indeed, one can often treat different functional groups as building blocks of a molecule. Such a concept is found to be extremely powerful in infrared (IR) spectroscopy as well as in X-ray spectroscopies which see clearly the fingerprints of different functional groups. The deviation of the molecular spectra from the spectra of individual functional groups gives information about the interaction between these groups. Localized orbitals can interact with each other directly through orbital overlap (through-space (TS) interaction) or indirectly, through other bonds in the molecule (through-bond (TB) interaction). The TB interaction may operate over long distances. The existence and distinction between through-bond and through-space interactions in non-conjugated unsaturated molecular systems were originally introduced by Hoffmann and co-workers in Refs.\textsuperscript{1,2} These milestone articles triggered detailed investigations of TS and TB interactions by different spectroscopic techniques and stimulated also our study in this field.

The second kind of molecular interaction which is studied in this thesis is represented by the hydrogen bond. Such bonds are formed by linking a hydrogen atom between two electronegative atoms. The hydrogen bond can occur as intramolecular as well as intermolecular bonds. The intermolecular hydrogen bonds that hold water molecules together have a strength in between the weak van der Waals and the strong covalent bond. The hydrogen bond which determines the properties of water and ice is also very important in proteins and nucleic acids and therefore in life processes. We study in this thesis the hydrogen bonding in the core electron ionized water dimer. Different experimental techniques are found to be useful in studies of these interactions: electron energy loss (EELS), electron transmission (ETS), ultraviolet (UV), electron moment (EMS), infrared (IR) and infrared pump-probe spectroscopies. In this thesis we investigate theoretically the manifestation of these interactions in three qualitatively different spectroscopies, namely, near edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS) and IR - X-ray pump-probe spectroscopy, the latter being the main theme of the thesis.

X-ray spectroscopies have experienced a great progress in recent years due to the impact provided by the new generation of synchrotron radiation sources. Synchrotrons produce very intense, tunable and polarized electromagnetic radiation covering a wide range of the electromagnetic spectrum: X-ray, UV, IR, and visible light to which the human eye is sensitive. Soon the X-ray free electron lasers will be in operation, something that will
drastically increase the brilliance of the produced light. The free electron laser will also provide the opportunity to study dynamical processes down to 100 fs of resolution. A way to study ultrafast processes on time scales down 0.1 fs is based on harmonic generation X-ray lasers.\(^3\) Other ways to obtain short X-ray pulses are based on slicing techniques\(^4-6\) (\(\sim 50\) fs) and on so-called wakefield-induced energy chirps\(^7\) (\(\sim 10\) fs). A main theme of the thesis is that these large achievements in creation of new sources for ultrashort X-ray pulses will, when synchronized with short IR pulses, make IR - X-ray pump-probe spectroscopy a most interesting technique for forthcoming experimental studies. The development of theory of IR - X-ray pump-probe spectroscopy and investigations of the physics of X-ray interaction with laser driven molecules yield the way to select more important applications of this new type of X-ray spectroscopy and to focus experimental research along promising directions. The development of an IR - X-ray pump-probe theory and an outline of its possible applications is precisely the main effort conducted in this thesis.

The wave packet technique is a central theoretical tool used in the presented papers. This technique allows to study the dynamical aspects of molecular interactions. Unfortunately, at the present time the wave packet method is applicable only to small system or to somewhat large molecules only by propagating the wave packet along certain reaction coordinates. The strict quantum mechanical techniques can not be applied directly to real systems due to the large degrees of freedom of polyatomic molecules, clusters and liquids. The realistic way to study the nuclear dynamics of polyatomic molecules is to use some approximations which reduce computational costs. It looks reasonable to assume that the classical approach can be appropriate to describe such highly excited systems. This is supported by the wave packet simulations of the nuclear dynamics which show strong resemblance with classical motion in the region of the strong field. This motivates us to study the light-induced kinetics of rather large water clusters using molecular dynamic simulations. It is found that the variable laser field induces a synchronous periodical charge transfer between different parts of the water hexamer cluster. This results in a rectification of the Lorentz force, which is a novel mechanism of the site selective mechanical action of the photons on molecules.

The thesis firstly presents a study of NEXAFS spectra of non-conjugated diene molecules possessing through-bond and/or through-space interactions. The effects caused by the hydrogen bonding in the formation of core-level XPS spectra of the water dimer is then analyzed. IR - X-ray pump-probe spectroscopy is employed to study the dynamics of proton transfer in the core ionized water dimer and the glyoxalmonoxime (GM) molecule. The different physical aspects of the proposed new type of X-ray spectroscopy - phase sensitive X-ray pump-probe spectroscopy - are studied in detail for the NO molecule using the wave packet technique. We applied the Born-Oppenheimer molecular dynamics method to study the laser-induced dynamics of the water hexamer cluster.
Chapter 2

NEXAFS and XPS studies of molecular interactions

X-ray spectroscopy can be subdivided in a few branches: X-ray absorption,8-10 X-ray emission,9 resonant X-ray Raman scattering,11-17 Auger,18 and X-ray photoelectron spectroscopies.9,19 Here we will focus our attention to X-ray absorption and core level XPS spectra.

2.1 Principle of NEXAFS

When X-rays path through a sample the intensity of the incident beam is reduced due to photoabsorption. The X-ray photons excite core electrons to an unoccupied molecular orbital when the photon energy is smaller than the core ionization potential (Fig.2.1). Near the photoionization threshold one can also observe weak transitions to so-called Rydberg levels. When the photon energy exceeds the ionization threshold, the core electron is excited to continuum states. These states differ qualitatively going from atoms to molecules. Due to the multiple scattering of the photoelectron on the surrounding atoms in a molecule, resonances then appear also in the continuum.20,21 Such resonances are known as shape resonances. The alternative interpretation of the shape resonances is related to the effective barrier22 which creates quasi-stationary states (see Fig.2.1), the barrier is shaped by the molecular potential. Quite often the X-ray absorption profile is disturbed by weak two-electron transitions. Both near edge (NEXAFS) and extended X-ray absorption fine structure (EXAFS) spectroscopies are widely used in material sciences to study structure of compounds. We will restrict our attention in this thesis to NEXAFS spectra as shown schematically in Fig.2.1. As NEXAFS spectra are formed by transitions of core electrons of specific atoms to vacant orbitals which are very sensitive to inter- and intra-molecular
interactions, NEXAFS has become one of the most powerful tools in studies of molecular interactions as well as molecular structure.

![Diagram](image)

Figure 2.1: Formation of X-ray absorption spectra in atoms (left) and molecules (right).

### 2.2 Principles of X-ray photoelectron spectroscopy (XPS)

When the energy \( \omega \) of the incident photon exceeds the ionization threshold, the molecule is ionized. The photoelectron spectrometer detects the emitted electron with certain energy and in a certain direction. The change of the angle between the polarization vector \( \mathbf{e} \) and the photoelectron momentum \( \mathbf{k} \) allows to study the anisotropy of photoionization. Photoelectron spectroscopy gives direct information about occupied molecular levels. If the incident photon has high energy (X-ray photons), photoelectron spectroscopy is designated as X-ray photoelectron spectroscopy (XPS) which maps both valence shells as well as core levels (Fig.2.2).

When the electron spectrometer detects photoelectrons with the binding energy

\[
BE = \omega - E
\]  

(2.1)

near the core ionization potential \( I_c \), one talks about core level XPS or ESCA (electron spectroscopy for chemical analysis). The XPS spectrum has resonances when

\[
BE = I_c.
\]  

(2.2)
2.2 Principles of X-ray photoelectron spectroscopy (XPS)

In molecules, the ionization potential of the core electron experiences chemical shifts which are different for different atoms or atoms of the same chemical element but which are nonequivalent chemically. This has made XPS a powerful technique to study the structure of molecules. This is illustrated in Fig. 2.3 where we see that the O1s spectrum of the water dimer has two resonances. The origin of such a splitting is the nonequivalence of the two oxygen atoms in each water molecule which constitute the dimer. Thus, one oxygen has the donor role (O_d) and the other oxygen is an acceptor (O_a).

![Diagram](image1)

**Figure 2.2:** Principle of XPS or ESCA spectroscopies.

![Diagram](image2)

**Figure 2.3:** X-ray photoelectron spectrum of the water dimer split due to different chemical shifts of donor and acceptor oxygens.
2.3 Vibrational structure in X-ray spectra

X-ray absorption as well as core ionization transitions in molecules also show fine structure caused by vibrations\(^8,^{19,23}\) (see Fig. 2.4). The origin of such vibrational structure is the change of the shape and position of the potential surface of the core excited state relative to the ground electronic state. Quite often the potential of the core excited state is dissociative. In this case the X-ray resonance experiences dissociative broadening. The shape of a vibrational profile is defined by the overlap between vibrational wave functions of initial and final states or Franck-Condon (FC) amplitudes. In the harmonic approximation this amplitude results in a Poisson distribution\(^{23,24}\)

\[
\prod_\alpha \langle 0_\alpha | \nu_\alpha \rangle, \quad \langle 0_\alpha | \nu_\alpha \rangle \approx \frac{S_{\alpha}^{\nu_{\alpha}/2}}{\nu_\alpha!} e^{-S_{\alpha}/2}, \quad S_{\alpha} = \frac{F_{\alpha}^2}{2\omega_{\alpha}^3}
\]  

(2.3)

where \(S_{\alpha}\) is the partial Huang-Rhys (HR) parameter of the \(\alpha\)th vibrational mode with the frequency \(\omega_{\alpha}\). \(F_{\alpha} = \partial E_c/\partial Q_{\alpha}\) is the gradient of the energy of the core excited state in the point of the vertical transition. The gradient, \(F_{\alpha}\), is the main parameter which defines the FC distributions for both bound-bound and bound-continuum transitions (see Fig. 2.4).

\[\text{Figure 2.4: Vibrational broadening of NEXAFS and XPS spectra. Left and right panels display schematically transitions to bound and dissociative core excited states, respectively.}\]
2.4 Study of through-bond and through-space interactions using NEXAFS

As was mentioned in the Introduction, two functional groups can interact through-space (TS) and/or through-bond (TB).\textsuperscript{1,2} We decided to study if and how NEXAFS spectroscopy can manifest such interactions of unoccupied orbitals. Below we highlight two illuminating results of these studies.

2.4.1 Through-space interaction in ethylene dimer

Let us start from the simplest case of NEXAFS spectra of the ethylene dimer (Fig.2.5).

![Diagram of ethylene dimer]

Figure 2.5: Illustration of the TS interaction in the ethylene dimer.

Two ethylenic groups do not interact when they are separated (R=\infty). In this case the C\textsubscript{2}H\textsubscript{4} \cdots C\textsubscript{2}H\textsubscript{4} system has two degenerate unoccupied orbitals, \pi\textsubscript{1} and \pi\textsubscript{2}, which means that the NEXAFS spectrum displays a single strong resonance (see Fig.2.6) caused by the transition

$$1s \rightarrow \pi_{1,2}$$

(2.4)

in isolated ethylene. The NEXAFS spectrum of the ethylene dimer at the distance R=5.3 Å does not show any difference from the spectrum corresponding to R=\infty because the interaction between the ethylene molecules is then still rather small. When the ethylenic groups approach each other they start to interact because of the increase of the overlap of the \pi\textsuperscript{*} orbitals (Fig.2.5). Such a TS interaction results in the splitting

$$\Delta\epsilon = \epsilon(\pi\textsuperscript{*}) - \epsilon(\pi\textsubscript{1}) \propto \langle \pi\textsubscript{1} | \pi\textsubscript{2} \rangle, \quad \pi\textsubscript{1,2} \rightarrow \pi\textsubscript{\perp} = \pi\textsubscript{1} \pm \pi\textsubscript{2}$$

(2.5)
which thus is absent for large intermolecular distances. When the distance is small (R=2.5 Å), the two groups interact and form the dimer. In this case the splitting is large and is clearly resolved in the NEXAFS spectrum (Fig.2.6). This splitting evidences directly the TS interaction in the ethylene dimer. According to eq.(2.5) one can expect to see two peaks (1s → π\textsuperscript{-} and 1s → π\textsuperscript{+}) with the same intensities in the NEXAFS spectrum. However, the simulations show that the first peak has larger intensity (see Fig.2.6). The reason for this is that eq.(2.5) ignores the interaction of the π\textsuperscript{±} electron with the core hole. As is well established this interaction quite often results in a strong enhancement of the first peak due to the so-called excitonic effect.\textsuperscript{25}

![Image of spectral data](image)

**Figure 2.6:** Theoretical C1s NEXAFS spectra of ethylene dimer at different R([C\textsubscript{2}H\textsubscript{4}⋯C\textsubscript{2}H\textsubscript{4}]) intermolecular distances (see Paper I).

### 2.4.2 Through-bond interaction in the p-benzoquinone molecule

Let us consider a qualitatively different mechanism of interaction between molecular orbitals localized on different functional groups. To be specific we consider the p-benzoquinone (pBQ) molecule. When two subsets (HC=CH)⋯(HC=CH) and O=C⋯C=O approach each other they interact and form the pBQ molecule. This interaction is depicted schematically in Fig.2.7. As it was shown in the previous subsection, the two ethylenic or carbonylic
2.4 Study of through-bond and through-space interactions using NEXAFS

Figure 2.7: Illustration of the TB interaction in the pBQ molecule.

Figure 2.8: C1s NEXAFS spectrum of p-benzoquinone (pBQ) calculated by the DFT method. The experimental spectrum, in broken lines, has been uniformly shifted so that the experimental and theoretical first $\pi^*$ peak energies coincide.
groups interact through the space. The rather weak TS interaction removes slightly the degeneracy of the \( \pi^+_{\pi}(C=O) \) and \( \pi^+_{\pi}(C=C) \) as well as of the \( \pi^+_{\pi}(C=O) \) and \( \pi^+_{\pi}(C=C) \) orbitals. A stronger interaction takes place between the effectively overlapping \( \pi^+_{\pi}(C=O) \) and \( \pi^+_{\pi}(C=C) \) orbitals which have appropriate symmetry to interact.\(^{27}\) These orbitals form two new \( \pi^* \) molecular orbitals, \( 1\pi^* \) and \( 4\pi^* \), delocalized on the ethylenic and carboxylic groups. As it is illustrated in Fig.2.7 the \( \pi^* \) orbitals of the ethylenic groups interact indirectly, namely, they influence each other through the \( \pi^* \) orbitals of the carboxylic groups. This through-bond interaction is very strong and leads to a large splitting between the \( 1\pi^* \) and \( 4\pi^* \) orbitals.

Our simulations (see Paper I) show that the interaction through-bond in pBQ is much stronger than through-space. The large TB splitting between the \( 1\pi^* \) and \( 4\pi^* \) orbitals is clearly seen in the partial Cls(C=C) NEXAFS spectrum, where the first and third peaks correspond to the transitions Cls(C=C) \( \rightarrow 1\pi^* \) and Cls(C=C) \( \rightarrow 4\pi^* \) (Fig.2.8). The A and D peaks in the total NEXAFS spectrum (Fig.2.8) correspond to transitions to the \( 1\pi^* \) and \( 4\pi^* \) orbitals, respectively. Thus these two peaks directly evidence the TB interaction in the pBQ molecule. The calculated spacing between the \( 1\pi^* \) and \( 4\pi^* \) transitions, 7.3 eV, is in good agreement with the experimental splitting\(^{26}\) of 6.96 eV (Fig.2.8).

### 2.5 XPS study of hydrogen bonding in the water dimer

We shall now discuss another type of molecular interaction, namely, the hydrogen bond and its role in formation of the XPS spectrum of the water dimer.

The two water molecules in the ground state of the water dimer are weakly bound by the hydrogen bond.\(^{28}\) The core ionization of the donor or acceptor oxygens of the water dimer results in a drastic change of the potential (see in Fig.2.9). The interaction between the two water molecules in the core-ionized state looks roughly like an ion-dipole interaction, which is much stronger than the dipole-dipole interaction between neutral polar molecules in the ground state. Contrary to the ground state, the global minimum is shifted to the proton transfer region when the core hole is created in the donor oxygen. In other words, the core ionization in the donor oxygen of the water dimer leads to a formation of a proton transferred state and consequently to a strengthening of the hydrogen bond.

One can expect that the asymmetry of the water dimer as well as change of the interaction between the monomers under core ionization strongly influence the XPS spectrum of the water dimer. Indeed, our simulations (Fig.2.3) show a qualitative distinction between XPS spectra of the dimer and the monomer\(^{29}\) (see Fig.2.3 and Paper II). The photoelectron spectrum of the water dimer shows two very broad bands separated by 1.29 eV. This energy corresponds to the difference between the donor and acceptor O1s ionization potentials
2.5 XPS study of hydrogen bonding in the water dimer

Figure 2.9: Potential surfaces of the ground state and core ionized states in donor and acceptor oxygens of the water dimer.

Figure 2.10: Potential energy curves of the ground state and core ionized states in donor and acceptor oxygens of the water dimer.
which have a characteristic shift to lower and higher energy, respectively. The vibrational fine structure observed in the monomer spectrum\textsuperscript{29} is not resolved in the XPS spectrum of the water dimer due to the extra broadening caused by the drastic change of the core ionized potential in the region near the vertical transition along the low frequency intermolecular vibrational motions related mainly to the hydrogen bond. The origin of such a broadening is clearly seen from the right panel of Fig.2.10. This anomalous broadening is different for the donor (\(\approx 0.6\) eV) and acceptor (\(\approx 0.4\) eV) peaks. It is important to note that these different vibrational broadenings are due to weak hydrogen bonding which changes differently under core ionization of the donor and acceptor oxygens (see right panel in Fig.2.10).

One can conclude that the broadenings and splitting in the two vibrationally unresolved bands in the XPS spectrum of the water dimer serve as the fingerprints of the hydrogen bonding in the dimer. Unfortunately, the conventional XPS spectrum of the water dimer (Fig.2.3) does not reveal anything about the dynamics of proton transfer in the donor core ionized state. The reason for this is twofold; firstly, the proton transfer region is shifted too far away from the point of the vertical transition; secondly, the dynamics of the nuclear wave packet in the core-ionized state is rather slow compared with the lifetime of the core-ionized state (\(\approx 8\) fs), see Fig.2.11.

Figure 2.11: Propagation of the wave packet in the donor core ionized potential surfaces. The continuous arrow shows over-barrier or tunneling path. The classical pathway is shown by the dashed arrow.
2.5 XPS study of hydrogen bonding in the water dimer

The wave packet can reach the proton transfer region in the donor core ionized potential by two pathways: tunneling (or over-barrier) propagation and along the classical trajectory. The classical pathway starts from a slow approach of the heavy monomers followed by a quick transfer of the light proton along the r(O-H) coordinate. Our simulations show that the propagation of the wave packet along the classical pathway is indeed very slow. The bottleneck here is the slow motion along O-O which takes $\approx 28-34$ fs (Fig.2.11). However, the dynamics of proton transfer by the way of tunneling or over-barrier motion takes smaller time, $\approx 8 - 16$ fs, which actually is comparable with the lifetime of the core ionized state. As one can see from Fig.2.11, a part of the wave packet has time to approach the proton transfer region during 8 fs. The appearance of the wave packet in the proton transfer region can be detected making use of Auger or X-ray emission spectroscopies.
Chapter 3

Infrared - X-ray pump-probe spectroscopy

We have shown in the previous section that conventional XPS spectroscopy is not able to register the spectral transitions to the proton transfer region. However, it is possible to accomplish this by exciting the OH stretching mode using an IR pulse and measuring the XPS spectrum of such a vibrationally excited molecule (see Fig.3.1). Let us first describe the principle of IR - X-ray pump-probe spectroscopy. Some applications of this technique are presented in sections 3.3 and 3.4 for the study of proton transfer in the core ionized water dimer and glyoxalmonoxime, respectively. In section 3.5 the benefits of X-ray pump-probe spectroscopy are explored for the NO molecule.

It is worthwhile to note that the time independent and time resolved pump-probe schemes have served as revolutionary tools in the microwave, IR and optical regions.\textsuperscript{30,31} One of the major successes of femtosecond pump-probe spectroscopy is the establishment of the field of femtochemistry which addresses the fundamental time scale at which molecular motion occurs.\textsuperscript{31} Extensions of the pump-probe scheme into the X-ray region is at the cutting edge of current X-ray science.

The IR - X-ray pump-probe technique is composed by two steps as illustrated in Fig.3.1. In the first step a strong IR field excites the molecular system vibrationally and the wave packet propagation is initiated in the ground state potential. After that, at a certain delay time, a short X-ray pulse promotes the wave packet to a certain point of the core excited/ionized potential. As one can see from Fig.3.1 the change of the delay time allows to map approximately the shape of the potential of the core excited/ionized state. This gives a unique opportunity to directly detect the spectral transitions in the proton transfer state which form a lower energy band (see band PT in Fig.3.1). Such a detection of the proton transfer
state is almost impossible using other nowadays available X-ray spectroscopies due to the extremely short lifetime of the core ionized state. The ultra fast X-ray snapshots of the nuclear wave packet in the ground state potential make the X-ray pump-probe spectra very sensitive to the phase of the IR pulse, and to the duration and delay time of the X-ray pulse. The coherent excitation of vibrational levels by a strong IR field is a key feature of IR - X-ray pump-probe spectroscopy. This motivates us to recall the principles of IR spectroscopy.

![Diagram](image)

Figure 3.1: Formation of the O1s X-ray absorption spectrum of the water dimer in a strong IR field.

### 3.1 Principle of IR spectroscopy

The frequencies of molecular vibrations span the IR region. Different functional groups of the molecule have specific vibrational frequencies which makes IR spectroscopy a powerful tool in studies of the molecular structure and molecular interaction. To illustrate the principle of IR spectroscopy we consider a diatomic molecule with zero electronic momentum. When the IR field with the frequency $\omega_L$ exposes the molecule it excites the vibrational levels $\nu$ and rotational states $|JM\rangle$ with the probability

$$\rho_J \propto \sum_{J,M} \frac{|\langle J'M'|e_L \cdot d_{\nu 0}|JM\rangle|^2}{(\omega_L - \omega_{\nu J',0J})^2 + \gamma^2} \rho_J, \quad d_{\nu 0} = \langle \nu |d|0\rangle. \quad (3.1)$$

Here $\omega_{\nu J',0J}$ is the resonant frequency of the rotational-vibrational transition, $\gamma$ is the width of the IR transition. The IR spectrum strongly depends on the temperature through the Boltzmann distribution of rotational levels, $\rho_J$. It is to note that the vibrational spectrum
3.2 Theoretical background of IR -X-ray pump-probe spectroscopy

has fine structure caused by rotational transitions. We see from eq.(3.1) that vibrational transitions are allowed only when the gradient of the molecular dipole moment, \( d'(r_0) = \frac{\partial d(r)}{\partial r}|_{r=r_0} \) is different from zero

\[
\langle 0|d(r)|\nu \rangle = d' \langle 0|x|\nu \rangle \propto \delta_{\nu,1}.
\]  

(3.2)

Here \( x = r - r_0 \) and \( r_0 \) is the equilibrium internuclear distance. The \( r \)-dependence of the molecular dipole moment is illustrated in Fig.3.2 for the water dimer. The excitation of rotational levels origins from the angular dependence of the scalar product of \( \mathbf{d}_{\nu,0} \) and polarization vector of the IR photon, \( \mathbf{e}_L; \mathbf{e}_L \cdot \mathbf{d}_{\nu,0} \propto \cos \theta \).

In the current thesis the rotational degrees of freedom are treated classically, which is a reasonable approximation because the rotational structure is not resolved in X-ray spectra due to the large lifetime broadening. We will also ignore the weak temperature population of the vibrational levels.

![Figure 3.2: Dependence of the dipole permanent dipole moment of the water dimer on r(O-H) bond length (see Paper III).](image)

3.2 Theoretical background of IR -X-ray pump-probe spectroscopy

We consider molecules that interact with IR pump field (L) and weak X-ray radiation (X) (see Fig. 3.1)

\[
\mathbf{E}_n(t) = \mathbf{E}_n(t) \cos(\omega_n t + \varphi_n), \quad n = L, X.
\]  

(3.3)
Atomic units are used everywhere unless otherwise stated. The amplitude of the electric field is expressed through the envelope of the pulse intensity

\[ E_n(t) = e_n \sqrt{\frac{2I(t)}{c \varepsilon_0}}, \quad I(t) = I_0 \exp \left[ - \left( \frac{t - t_0}{\tau} \right)^{2k} \ln 2 \right], \quad (3.4) \]

where \( \tau \) is the half width at half maximum (HWHM), \( e_n, \varphi_n, t_0, I_0 \) are the polarization, the phase, peak position and peak intensity of the pulse, respectively, and \( k = 1, 2, 3, \ldots \). Expression (5.3) is convenient because it describes a smooth transition from a Gaussian \((k = 1)\) to a rectangular function \((k = \infty)\).

The duration of standard X-ray measurements is longer than the pulse duration. This motivates us to use the integral (over time) probability which gives the spectrum of the probe signal

\[ P(\Omega) = \langle \phi_c(\Omega) | \phi_c(\Omega) \rangle, \quad |\phi_c(\Omega)\rangle = \int_{-\infty}^{\infty} dt \ e^{-\omega t} \ EX(t) \ |\phi_c(t)\rangle. \quad (3.5) \]

\( P(\Omega) \) is simply the norm of WP in the frequency domain, \( |\phi_c(\Omega)\rangle \). Here \( |\phi_c(t)\rangle \) is the nuclear wave packet that evolves in core-excited potential energy surface,

\[ |\phi_c(t)\rangle = e^{ihc t} \zeta \psi(t), \quad \zeta = \frac{1}{2} (d \cdot \psi X), \quad (3.6) \]

and, \( \psi X \) is the polarization vector of the X-ray photon.

It is worth to mention that the wave packet \( \phi_c(t) \) (3.6) does not depend on the photon frequency \( \omega_X \). The calculation of \( \phi_c(t) \) is performed along the contour (Fig. 3.3) where the ground state wave packet \( \phi(t) \) evolves from the moment 0 up to \( t \)

\[ i \frac{\partial}{\partial t} \phi(t) = [h_0 - (d \cdot E L(t))] \cos(\omega_L t + \varphi_L)] \psi \quad (3.7) \]

The X-ray field promotes \( \phi(t) \) at the instant \( t \) to the excited states where the newly formed wave packet \( \phi_c(t) \) evolves in the inverse direction from moment \( t \) up to 0. The dynamics in the inverse direction is seen from the fact that the wave packet \( \phi_c(t) \equiv \phi_c(0, t) \) is the solution of the Schrödinger equation

\[ i \frac{\partial}{\partial \tau} \phi_c(\tau, t) = H_c \psi_c(\tau, t) \quad (3.8) \]

from \( \tau = t \) till 0 with the initial condition \( \phi_c(t, t) = \zeta \psi(t) \).
3.3 Proton transfer in the core ionized states of water dimer

Let us explore the IR - X-ray pump-probe spectroscopy in more detail for the water dimer as this technique gives a unique opportunity to investigate the dynamics of proton transfer in core ionized states. As was mentioned already the main advantage of such a technique is that a strong IR field at the certain instant can localize the nuclear wave packet directly in the proton transfer region (see Fig.3.1).

When the IR field is incoherent the only role of the IR field is to change the populations of the vibrational levels, $\rho_\nu$. In this case the probability of core excitation is to produce an incoherent sum of the partial probabilities, $P^{(\nu)}(\omega_X)$, of core ionization from certain vibrational levels, $|\nu\rangle$

$$P(\omega_X) = \sum_\nu \rho_\nu P^{(\nu)}(\omega_X). \quad (3.9)$$

This probability does not depend on the phase of the IR field (see Sec.3.5.1). This scenario changes qualitatively if the IR field is coherent having a constant phase, $\varphi_L$. The coherence of the light is transferred to the molecule. Indeed the coherent IR light creates a coherent superposition of vibrational states or wave packet

$$\phi(t) \propto |0\rangle + a(t)|1\rangle e^{-i(\omega_1 t + \varphi_L)} + \ldots \quad (3.10)$$

$$\propto \left[ 1 + a(t) \sqrt{2} (r - r_e)/a_0 e^{-i(\omega_1 t + \varphi_L)} + \ldots \right] \exp \left( -\frac{(r - r_e)^2}{2a_0^2} \right)$$

where $r$ and $r_e$ denote the internuclear distance and equilibrium distance, respectively. $a_0$ is the amplitude of vibrations and the coefficient $a(t)$ is proportional to the strength of
the electromagnetic interaction. One finds that the characteristic time of the wave packet propagation is given by the period of vibrations $2\pi/\omega_0$. Eq. (3.10) explains the physical ground of the wave packet propagation in the potential well. This dynamics is quenched when the phase randomly fluctuates (incoherent light). Thus the coherence of the IR field is the key element of the here discussed X-ray pump-probe spectroscopy and it makes the X-ray ionization/absorption profile sensitive to the phase $\varphi_L$.

To observe the proton transfer state in the X-ray photoionization spectrum we have rather to populate the high vibrational levels, $\nu \gtrsim 9$ (see Fig.2.10). However, due to the strong anharmonicity of the ground state potential, the resonant condition breaks down and the efficiency to populate high vibrational levels by the continuum wave IR laser is strongly suppressed if the X-ray pulse is long. This difficulty is overcome for short IR pulses with rather large spectral widths, $1/\tau_L$. Our simulations (see Paper III) show that the short IR pulse with the duration $\tau_L = 7.9$ fs is able to populate vibrational states up to $\nu = 10$ for a reasonable intensity, $I_L = 5.4 \times 10^{14}$ W/cm². This coherent IR pulse creates a nuclear wave packet (3.10) which moves in the ground state potential well along the trajectory

$$\bar{r}(t) = \langle \phi(t) | r | \phi(t) \rangle.$$  \hspace{1cm} (3.11)

Here $\bar{r}(t)$ is the center of gravity of the wave packet. This trajectory depends strongly on the phase of the IR pulse, $\varphi_L$ (Fig.3.4). This explains the strong phase sensitivity of the XPS spectrum (Fig.3.5).

Figure 3.4: The phase dependence of the trajectory of the wave packet in the ground state potential created by a strong IR field.
3.3 Proton transfer in the core ionized states of water dimer

Figure 3.5: IR - XR pump-probe spectrum of the water dimer versus time delay ($\Delta t$) and different phases [(a) $\varphi_L=3.8$ rad and (b) $\varphi_L=(3.8-\pi)/2$ rad] for different orientations ($\varphi$) of the dimer relative to the IR polarization vector. $\tau_L=7.9$ fs, $I_L=5.4 \times 10^{14}$ W/cm² and $\omega_L = \omega_{01}=0.45$ eV. The duration of the X-ray pulse is $\tau_X = 2.2$ fs.

The first and the second terms at the right hand-side of eq.(3.10) give an alternative and useful interpretation of the phase effect. The phase dependence arises from the interference of one- and two-photon core ionization channels: direct absorption of an X-ray photon from the lowest vibrational state $\nu = 0$ and absorption of an X-ray photon from the next vibrational level $\nu = 1$ which is populated by one IR photon (see Fig.3.6). At the instant when the wave packet arrives at the proton transfer region the short X-ray pulse excites the molecular system in the proton transfer site (see Fig.3.1). The XPS band related to this transition has lower energy (see Fig.2.10) and due to this circumstance the proton transfer (PT) band is nicely distinguished in the XPS spectrum at low energy, see Fig. 3.5.

The profile of the X-ray pump-probe spectrum turns out to be very sensitive in several respects; it is sensitive to the phase of the IR field, to the orientation of the molecular system relative to the IR polarization vector, as well as to the delay time ($\Delta t$) and the duration time ($\tau_X$) of the X-ray pulse. The molecules are usually randomly oriented which means that the XPS spectra (Fig.3.5) have to be averaged over molecular orientations. The X-ray pump-probe spectra of randomly oriented molecules differ considerably from spectra of fixed-in-space molecules (see Paper III). It is necessary to note that powerful techniques exist in X-ray spectroscopy which allows to obtain spectra of fixed-in-space molecules even
for randomly oriented samples.\textsuperscript{10,35,36} This follows from the fact that the core excited state experiences Auger decay to a multitude of final states most of which are dissociative. The detection of the ionic fragment of dissociation thus selects a certain orientation of the molecule. The measurement of X-ray absorption in the ion yield mode or detection of photoelectrons in coincidence with the ions are widely used in studies of X-ray spectra of fixed-in-space molecules.\textsuperscript{10,35,36} These methods are thus nicely adapted for the observation of the discussed phase effect.

3.4 Intramolecular proton transfer mediated by vibronic coupling between the two O1s core ionized states of glyoxalmonoxime

Let us apply the IR - X-ray pump-probe spectroscopy for a hand-picked molecular system, the glyoxalmonoxime molecule (GM) shown in Fig.3.7 (see Paper V). In the GM molecule, contrary to the water dimer, the hydrogen bond is intramolecular. With this feature it is expected that the O$_1$O$_2$ distance will be rather constant during the interaction with the IR
3.4 Intramolecular proton transfer mediated by vibronic coupling between the two O1s core ionized states of glyoxalmonoxime

field and the nuclear dynamics during the proton transfer will be quite localized on the O1H stretching vibrational mode. This phenomenon is not observed for the water dimer. The molecular dynamics simulations performed for the water dimer (Sec. 5.1) show that during the interaction with the IR light not only the O3H bond is excited but also the low frequency intermolecular vibrational modes. This results in a breakdown of the hydrogen bond. Due to this, the dynamics of proton transfer in the water dimer is not described properly along the one dimensional O3H stretching as it was shown in previous section. Due to the huge computational cost which is necessary to perform wave packet simulations, we are restricted to use only few dimensions to describe our problem. In this case, the GM molecule proves to be an appropriate molecular system for studies of the intramolecular proton transfer dynamics by quantum mechanics simulations.

\[
\begin{align*}
\text{GM} & \quad \text{NE} \\
\end{align*}
\]

Figure 3.7: Glyoxalmonoxime (GM) and 2-nitrosoethanol (NE).

Another interest in this molecule arises from the principle that it contains two distinct organic functions: aldehyde (−CHO) and oxime (HO–N=C<). Due to this, two different electronic states are possibly created when one electron is ionized from the O1(1s) or O2(1s) core orbitals (see Fig. 3.8). The difference between the vertical ionization potentials of these two core ionized states is approximately 1 eV. Due to this, the O1(1s\textsuperscript{-1}) and O2(1s\textsuperscript{-1}) ionization bands in the X-ray spectrum of GM can be easily distinguished. The O1(1s\textsuperscript{-1}) and O2(1s\textsuperscript{-1}) core ionized states with the same symmetry (\textsuperscript{2}A') show a crossing of their potential energy curves (see Fig. 3.8) along the coordinate q related to the proton transfer channel, which leads to the formation of the tautomer 2-nitrosoethanol (NE). These are the diabatic potential curves which describe the two electronic states not interacting between themselves. In this case the O1s core hole is localized in one or the other oxygen atom. On the other hand, the existence of a coupling between these two electronic states which promotes the O1s core hole delocalization leads to adiabatic potential curves where the crossing is avoided, see Fig.3.8. The stronger the coupling between the two core ionized states, the larger will be the energy difference between the adiabatic curves at the surroundings of the crossing.
Figure 3.8: Potential energy curves of ground and core ionized states along the cartesian coordinate $q$ related to the proton transfer channel. Dashed lines mark the adiabatic potentials $E_{\pm}(q)$. Minimum of $E_{0}(q)$ is situated at $q_0=1.74$ a.u. The diabatic potentials (solid lines) cross each other in the point $q_c=2.18$ a.u. The initial gaussian wave packet excited in the higher energy region performs back and forth motions from GM to NE wells.

point. At the crossing point the radial coupling is maximum. The vibronic coupling (VC)

$$H_{12} = H_{21} = \lambda q$$

(3.12)

between the $O_1(1s^{-1})$ and $O_2(1s^{-1})$ core ionized states in GM occurs via the O-H stretching mode $q$ associated to the intramolecular proton transfer channel. The dynamics of the nuclear wave packet accompanied by the vibronic coupling is described similar to eq.(3.6)

$$\phi_c(t) = \begin{pmatrix} \phi_1(t) \\ \phi_2(t) \end{pmatrix} = e^{iHt} \zeta \phi(t), \quad \zeta = \begin{pmatrix} \zeta_1 \\ \zeta_2 \end{pmatrix}, \quad \zeta_n = \frac{1}{2}(D_{n0}\cdot e_X).$$

(3.13)
3.4 Intramolecular proton transfer mediated by vibronic coupling between the two O1s core ionized states of glyoxalmonoxime

with the Hamiltonian

$$\mathcal{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix},$$  \hspace{1cm} (3.14)

where $H_{11}$ and $H_{22}$ are the nuclear Hamiltonians associated with the potentials $E_{O_1(1s^{-1})}(q)$ and $E_{O_2(1s^{-1})}(q)$, respectively. Contrary to eq. (3.5) the photionization probability is the sum of two contributions related to core holes in different oxygenes

$$P(\Omega) = \langle \varphi_1(\Omega) | \varphi_1(\Omega) \rangle + \langle \varphi_2(\Omega) | \varphi_2(\Omega) \rangle, \quad |\varphi_n(\Omega)\rangle = \int_{-\infty}^{\infty} dt \ e^{-i\Omega t} \ E_X(t) \ |\varphi_n(t)\rangle. \quad (3.15)$$

The IR - X-ray pump-probe spectra of GM are presented in Fig. 3.9 for different values of the vibronic coupling constant $\lambda$ and different delay times $\Delta t = t_X - t_L$ between the X-ray and IR pulses. The spectra for $I_L = 0$ are presented in the sequence of panels in the first row of Fig. 3.9 while lower panels show the spectra for $I_L \neq 0$. Fig. 3.9 presents each partial contribution $P_1(\Omega)$ (dotted line) and $P_2(\Omega)$ (dashed line) to the total photionization probability $P(\Omega)$ (continuum line).

The conventional X-ray photoelectron spectrum of GM for $\lambda = 0$ shows two absorption bands, $GM_1$ and $GM_2$, which are attributed, respectively, to the vertical transitions from the bottom of the ground state potential ($q_0 = 1.74 \text{ a.u.}$) to the O$_1(1s^{-1})$ and O$_2(1s^{-1})$ core ionized states. When GM is previously shined by an IR field, a coherent wave packet is created which has enough energy to reach the proton transfer region where the tautomer NE is formed. Due to this, two new bands, NE$_1$ and NE$_2$, are observed in the IR - X-ray pump-probe spectrum. The intensities of these two new bands depend on the delay time between the IR and X-ray pulses.

Simulations in Fig. 3.9 show that the X-ray photoelectron spectra of GM are influenced by the vibronic coupling (eq. 3.12) in both cases, with or without the previous interaction with the IR field. What occurs is a partial delocalization of the core holes due to the constructive and destructive interference of the localized (adiabatic) core hole states ($\phi_1$ and $\phi_2$) which create two new delocalized (adiabatic) states

$$\phi_+ = \phi_1 \sin \beta + \phi_2 \cos \beta, \quad \phi_- = \phi_1 \cos \beta - \phi_2 \sin \beta, \quad (3.16)$$

respectively. The XPS intensities of these new states are given by squared transition dipole moments $d_{\pm} = \langle \psi_\pm | d | \psi_n \rangle$. The upper panels of Fig. 3.9 show for a large value of the VC constant $\lambda$ the suppression of the "dark" $\phi_-$ state ($GM_2$ band) and enhancement of the "bright" $\phi_+$ state ($GM_1$ band) when $\lambda > 0$. The "bright" and "dark" states are interchanged
when the sign of VC is inverted, \( \lambda < 0 \) (Fig. 3.10). The formation of the delocalized state \( \phi_- \), for \( \lambda > 0 \), evidences the competition between the processes of intramolecular proton transfer and core hole transfer during the reaction of \( \text{GM}[O_1(1s^{-1})] \rightarrow \text{NE}[O_2(1s^{-1})] \) interconversion.

### 3.5 Role of light coherence, duration and phase

We outlined the principles of IR - X-ray pump-probe spectroscopy in the previous chapter. Now we would like to highlight some important features of this spectroscopy making use of a simple system the; NO molecule.

![Figure 3.9](image)

**Figure 3.9:** IR - X-ray pump-probe spectra of the oriented GM molecule (\( \vec{\delta}_L \parallel \vec{x} \)) for different values of the vibronic coupling constant \( \lambda \) and different delay times \( \Delta t = t_X - t_L \) between the X-ray and IR pulses. The crossing point of the diabatic \( O_1(1s^{-1}) \) and \( O_2(1s^{-1}) \) potentials is \( q_c = 2.18 \) a.u.. Upper panels show XPS profiles for \( I_L = 0 \), while the lower panels show the spectra of molecules driven by the IR field. The parameters of the IR pulse are \( I_L = 2.3 \times 10^{14} \) W/cm\(^2\), \( t_L = 200 \) fs, \( \tau_L = 10 \) fs, \( \varphi_L = 0.53 \) rad and \( \omega_L = \omega_{10} = 0.33 \) eV. The duration of the X-ray pulse is \( \tau_X = 4 \) fs. The full lines show the total photoionization probabilities. The dotted and dashed curves are the partial photoionization probabilities \( P_1(\Omega) \) and \( P_2(\Omega) \), respectively. The vibrationally resolved XPS profile depicted in the left upper panel was calculated for a longer X-ray pulse, \( \tau_X = 15 \) fs.
3.5 Role of light coherence, duration and phase

3.5.1 X-ray spectrum in the field of incoherent pump radiation

As was mentioned above even incoherent pump radiation influences the probe X-ray spectra, see eq.(3.9).

The main distinction of X-ray spectra of molecules driven by incoherent pump radiation is that such a pump field lacks a certain weak-defined phase and can therefore not create a coherent nuclear wave packet. In this case the X-ray spectrum becomes a sum of partial spectra corresponding to different vibrational levels of the ground state. The partial OK X-ray absorption spectra of the NO molecule differ strongly from each other (Fig.3.11), which can be referred to the different Franck-Condon distributions for different initial vibrational states $\nu$ (see Paper IV).

3.5.2 Role of duration of X-ray and IR pulses

Let us now explore the X-ray spectra of molecules in strong fields of coherent IR radiation. To be specific only the lowest OK X-ray $^2\Pi - ^2 \Sigma^-$ absorption band of NO will be considered.

The duration ($\tau_X$) of the X-ray pulse ($E_X(t) = E_X^0 \exp[-(t - t_X)/\tau_X^2 \ln 2/2]$) influences strongly the phase effect (Fig.3.12). The role of the duration of the X-ray pulse is seen from

![Figure 3.10](image)

Figure 3.10: A) XPS intensities $(d_+/d)^2$ versus the coupling strength, $\zeta/2 = \lambda q/\Delta(q)$. $\Delta(q_0) = 1.02$ eV. B) XPS spectra for positive and negative VC strengths (no IR field). Other parameters are the same as in Fig. 3.9.
Figure 3.11: Partial OK X-ray absorption spectra of NO excited incoherently in the ground state vibrational levels $\nu = 0, 1, 2$ for different core excited electronic states: $^2\Sigma^-, ^2\Delta$ and $^2\Sigma^+$. The total spectral profiles are shown by the thin continuum lines.

eq(3.10). This equation indicates that the interference contribution in the X-ray excitation

Figure 3.12: Difference between probabilities of X-ray absorption ($O1s \rightarrow 2\pi$) of NO, $\Delta P = P(\varphi_L = 0) - P(\varphi_L = \pi/2)$ versus duration of the X-ray pulse, $\tau_X$. $\Delta t=610$ fs.
probability experiences oscillations with the vibrational frequency
\[
P_{\text{int}}(t) \propto \Re \ e^{i\omega(t)+\varphi_L}.
\] (3.17)

When the pulse is long: \(\tau_X \gg 2\pi/\omega_{10}\), the integration of \(P_{\text{int}}(t)\) over the time of measurement quenches the interference term. So the phase sensitivity of the X-ray spectrum is suppressed for long X-ray pulses. The phase effect takes maximum value when \(\tau_X\) is one fourth of the period of vibrations, \(\pi/2\omega_{10}\) (see Fig.3.12). In the opposite limiting case, \(\tau_X \ll 2\pi/\omega_{10}\), the interference and, hence, the phase effect is also suppressed. The reason for this is that short X-ray pulses have broad spectra. The convolution of the X-ray spectra depicted in Fig.3.5 with such a broad spectrum strongly diminishes the phase sensitivity of the X-ray profile.

The duration of the IR pulse affects the X-ray profile in another way. As it was mentioned above the shortening of the IR pulse can be useful to overcome the anharmonicity which prevents the excitation of high vibrational levels. The temporal shape of the IR pulse influences strongly the memory effect as discussed in the next section.

### 3.5.3 Phase memory versus shape of the IR pulse

The vibrational levels of the ground electronic state of a gas phase molecule have rather long lifetimes; \(\lesssim 1\) ms for diatomic molecules. This means that the coherence created by the IR pulse lives a long time after that the IR pulse left the system. This also means that the X-ray spectra continue to be sensitive to the phase during a long time. Such a memory effect depends strongly on the frequency and shape of the IR pulse (see Papers IV and VI and Sec. 4). The memory effect is destroyed if the IR pulse is switched off adiabatically and off-resonant transitions are important. This physical picture of the memory effect is illustrated in Fig.3.13. We see that the population of the first vibrational state follows very approximately the Rabi solution 37

\[
\rho_1(t) \equiv |\langle \phi(t)|1 \rangle|^2 \sim \sin^2 \frac{G_R t}{2}, \quad G_R = E_L \cdot d_{10}.
\] (3.18)

Fig.3.13A shows the case of fast off-switching of the IR field with detuning \(\Omega = \omega - \omega_{10} = 3.4\) meV: The duration of the IR pulse \(\tau = 100\) fs is then shorter than the inverse detuning \(1/|\Omega| \approx 200\) fs and the interaction with the light ceases to be adiabatic (see Sec. 4). In this case the molecule remains in the coherent superposition of vibrational states and the X-ray spectrum keeps the phase memory after that the IR pulse left the system. (We here would like to pay attention to the misprint in figure caption of Fig. 7 in Paper IV: \(\omega_L = \omega_{10} = 0.241\) eV must be replaced by \(\Omega_L = \omega_L - \omega_{10} = 3.4\) meV.)

The intermediate case between fast and adiabatic shut down of the IR radiation (\(\Delta T \sim 400\) fs \(\lesssim 1/|\Omega| \approx 200\) fs) is shown in Fig.3.13B. The first impression is that the molecule
Figure 3.13: Populations ($\rho_v$) of the vibrational levels of the ground state versus time for different durations of switching off of the pump field, which is $\tau_L = 100$ fs $< T_R$ for short pulse (A), and $\Delta T \sim 400$ fs $\gtrsim 1/|\Omega|$ for long pulse (B). $\zeta_L(t)$ is the shape of the envelope of the IR field. $\Omega = 3.4$ meV and $I_L = 2.3 \times 10^{12}$ W/cm$^2$. The details of calculations are described in Paper IV.
3.5 Role of light coherence, duration and phase

adiabatically follows the slow decrease of the IR intensity because the molecule evolves to the lowest vibrational state. In this case the molecule loses the memory about the phase and the X-ray spectrum ceases to depend on the phase after that the IR pulse left the system (see Paper IV). However, the slight change of the pulse duration changes drastically the dynamics of the populations and hence the memory effect (see Fig. 4.2, k=3).

3.5.4 Dephasing caused by z-dependence of the phase of the IR field

Until now we assumed that the phase of the IR field is constant. This is not true in general due to the extra phase, $k_L z$, which describes the propagation of the IR field, $E_L(t) \cos(\omega_L t - k_L z + \varphi_L)$. To take this extra phase into account we have to use a z-dependent phase $\varphi_L(z)$:

$$\varphi_L(z) = \varphi_L - k_L z, \quad k_L = \frac{2\pi}{\lambda_L} \quad (3.19)$$

where $\varphi_L = \text{const.}$ If the size of the irradiated region is larger than the wave length of the IR field, $\lambda_L$, the z-dependence of the phase (3.19) can quench the phase effect because the X-ray spectrometer collects signals from molecules localized in different points, $z$. To avoid this difficulty one can use the orthogonal intersection of the X-ray and IR beams (Fig.3.14) with the size of X-ray beam

$$a \ll \lambda_L \sim 10^{-3} \text{ cm.} \quad (3.20)$$

The focusing of the X-ray beam in such a spot is possible in current experiments.\(^{38}\)

![Figure 3.14: Orthogonal orientation of X-ray and IR beams which allows to reduce the dephasing caused by the phase factor, $k_L z$.](image-url)
Chapter 4

Coherent control of populations of excited vibrational levels

Different applications\textsuperscript{31,39} need the selective population of the certain vibrational levels in many level systems using light pulses. For example, as it was already discussed in Sec. 3.3 and Sec. 3.4, such a selectivity is important for the formation of the nuclear wave packet of desirable shape and length. Such a quantum control of the population is not an easy task.\textsuperscript{40} We outline here some ideas and give few examples (see Figs. 4.1, 4.3, 4.5) which demonstrate how the population of the excited state can be controlled varying the duration, shape and peak intensity of the pulse as it is outlined in detail in Paper VI.

An important starting point is the dynamics of a two-level system (0, 1) in the rotating wave approximation (RWA)\textsuperscript{41}

\begin{align}
\dot{a}_0(t) &= -\frac{G(t)}{2} e^{-\Omega t} a_0(t), \\
\dot{a}_1(t) &= -\frac{G(t)}{2} e^{\Omega t} a_1(t),
\end{align}

(4.1)

where $\Omega = \omega - \omega_{10}$ is the detuning from the resonance, $G(t) = E(t)d_{10}$ is the Rabi frequency, $a_0(t)$ and $a_1(t)$ are amplitudes of the ground and excited states, respectively.

When the detuning is equal to zero ($\Omega = 0$), the dynamics of the two-level system follows the so-called area theorem\textsuperscript{40,41}

\begin{align}
\rho_0(t) &= \cos^2 \theta(t), \\
\rho_1(t) &= \sin^2 \theta(t), \\
\theta(t) &= \frac{1}{2} \int_{-\infty}^{t} G_{10}(t_1) dt_1.
\end{align}

(4.2)

This equation says that the population depends on the intensity, duration and shape of the
pulse only through the parameter, namely, through its area \( \theta(\infty) \). This area reads

\[
\theta(\infty) = E_0 d_{01} \times 20.6774 \times \frac{\tau}{k} \left( \frac{2}{\ln 2} \right)^{\frac{1}{2}} \Gamma \left( \frac{1}{2k} \right)
\]  

(4.3)

for a pulse defined by eq. (5.3). Here \( \Gamma(x) \) is the Gamma function, the pulse duration \( \tau \) is given in fs and \( E_0 d_{01} \) in fs\(^{-1}\). The total area defines the populations of the molecule when the pulse leaves the system. The equation (4.3) is useful, since it allows to predict the populations immediately using a simple relation. This equation is valid until the two-level approximation is working well. We will see below that in some cases the two-level approximation (4.3) gives rather good agreement with strict simulations even for many-level systems. This happens under condition of strict resonance and when the light intensity is not high enough to excite more than one state.

The evolution of the two-level system changes drastically when the photon frequency is tuned from the resonance. Indeed, when the detuning is rather high

\[
|\Omega| \Delta T \gg 1
\]  

(4.4)

---

Figure 4.1: Population of vibrational level \( \nu' = 1 \) of NO molecule after the IR field has left the system \((t = \infty)\) versus the duration of the IR pulse. \( I = 2.3 \times 10^{10} \text{ W/cm}^2 \), \( \omega = \omega_{10} \) and \( k=1 \). The area theorem (4.2), (4.3) (solid line) is in nice agreement with the wave packet simulations (filled circles).
eq. (4.1) has the following solution

\[ a_0(t) = \frac{(1 + \kappa(t)) e^{-i \chi(t)}}{\sqrt{G^2(t)/\Omega^2 + (1 + \kappa(t))^2}} , \quad a_1(t) = \frac{(G(t)/\Omega) e^{-(\Omega t + i \chi(t))}}{\sqrt{G^2(t)/\Omega^2 + (1 + \kappa(t))^2}} \]  

(4.5)

with \( \kappa(t) = \sqrt{1 + G^2(t)/\Omega^2} \), and \( \chi(t) = \int_{-\infty}^{t} (\kappa(t) - 1) dt \). Here we introduced the characteristic time \( \Delta T \) of the change of the pulse. Contrary to the strict resonance (4.2) this solution displays a non-oscillatory evolution of the populations \( \rho_0(t) = |a_0(t)|^2 \) and \( \rho_1(t) = |a_1(t)|^2 \). Now the system adiabatically follows the pulse in the sense that the molecule returns to the ground state when the pulse is over. Another important distinction is that the light does not create inversion of the populations in the adiabatic limit (4.4). The largest effect by the

![Figure 4.2: Dynamics of the populations of the levels \( \nu = 0 \) (solid), \( \nu = 1 \) (dotted) and \( \nu = 2 \) (grey) of the NO molecule for different durations \( \tau \) and shapes of the pulse: \( k = 1, 2, 3 \) (see eq. (3.4)). \( I = 2.3 \times 10^{12} \text{ W/cm}^2 \). \( \omega_{10} = 0.2376 \text{ eV} \). \( \Omega = 3.4 \text{ meV} \). The adiabatic parameter (4.4) \( \Omega \Delta T \approx 5.2, 3.4 \) and 2 for \( k = 1, 2, \) and 3, respectively.](image)
pulse is to excite 50% of the molecules when $G(t)/|\Omega| \gg 1$. This resembles the dynamics of the two-level system with a finite decay rate of the excited state.\textsuperscript{41} Probably the detuning somehow results in decoherence or dephasing.

First we show an example when the area theorem (4.2) is working well (Fig. 4.1). This is the interaction of the NO molecule with the IR field tuned in strict resonance with the first vibrational transition $0 - 1$. The moderate intensity prevents excitation of higher vibrational levels. Due to this one can create a desirable population of the first excited state by a proper choice of the area of the pulse. The situation changes drastically when the frequency is tuned from resonance, $\Omega = \omega - \omega_{10} \neq 0$, and the area theorem ceases to be valid. The simulation shown in Fig. 4.2 for a gaussian pulse ($k = 1$) displays a complete depopulation of the excited state in agreement with the adiabatic solution (4.5), because in this case the adiabatic parameter $|\Omega|\Delta T \approx 5.2$ is large. Fig. 4.2 shows the dynamics of populations going from a smooth gaussian ($k = 1$) to a sharp "rectangular" ($k = 3$) pulse. Now we see a breakdown of the adiabatic solution because the adiabatic parameter approaches one: $|\Omega|\Delta T \approx 3.4$ for $k = 2$ and $|\Omega|\Delta T \approx 2$ for $k = 3$. The complete depopulation of the excited state in the adiabatic limit (4.4) is seen clearly in Fig. 4.3 which

![Figure 4.3: Population of the excited vibrational level ($\nu = 1$) at the time when the IR field has left the NO molecule ($t \to \infty$) versus the duration (HWHM) of the pulse. $I = 2.3 \times 10^{12}$ W/cm$^2$, $k = 3$, $\Omega = \omega - \omega_{10} = 3.4$ meV, $\omega_{10} = 0.2376$ eV.](image-url)
Figure 4.4: Populations by the IR pulse of the vibrational levels of spatially oriented glyoxalmonoxime (ε || x) in its ground electronic state versus time. $I=2.3 \times 10^{14}$ W/cm$^2$, $\omega = \omega_0=0.88$ eV, and $t_0=8000$ fs. $k=1$. The population of the vibrational levels $\nu = 0$ and $\nu' = 4$ are explicitly shown in this figure. The remaining population (grey) are mainly in the vibrational levels $\nu' = 3$ and $\nu' = 5$. 
Chapter 4  Coherent control of populations of excited vibrational levels

displays results of simulations for nonzero detuning $\Omega = 3.4 \text{ meV}$ and different durations of the pulse. One can see that the population of the excited state $\rho_1(\infty)$ tends to zero when the duration decreases and the adiabatic parameter $|\Omega|\Delta\tau$ becomes large.

Another example of the breaking of the area theorem is shown in Fig. 4.5. This is the case of the GM molecule (see Sec. 3.4) with $I_0 = 2.3 \times 10^{14} \text{ W/cm}^2$ and the frequency tuned in strict resonance with the $0 \rightarrow 4$ vibrational transition ($\Omega = 0$). It is worth to note that the 4th vibrational level is lying in the region of strong anharmonicity (see Fig. 3.8) where one can expect strong coupling with other vibrational modes and therefore a violation of the used one mode approximation. We use here high intensity because the dipole moment of the $0 \rightarrow 4$ transition is rather small. The matrix elements of the permanent dipole moment collected in Table I in Paper VI show that the resonant $0 \rightarrow 4$ transition is accompanied by off-resonant transitions, like $0 \rightarrow 3, 0 \rightarrow 5$ which are important as one can see from Fig. 4.4. This figure says that the area theorem is not valid here because the off-resonant population of other vibrational levels is rather high (about 25%) and due to this fact the studied system is not a two-level one. We would like to pay attention to the complete quenching of the

![Image](image-url)

Figure 4.5: Population by the IR pulse of the vibrational level $\nu' = 4$ of spatially oriented glyoxalmonoxide ($\vec{e} \parallel x$) in its ground electronic state versus the duration of the pulse. $I=2.3 \times 10^{14} \text{ W/cm}^2$ and $\omega = \omega_0=0.88 \text{ eV}$. $k = 1$. Continuum and dashed lines show wave packet simulations for the many level GM molecule and the Rabi solution for the two level system (4.2), respectively.
populations of off-resonant levels when the pulse leaves the system (see grey area in Fig. 4.4). The reason for this is that the remaining levels follow the adiabatic solution (4.5) at the end of the pulse because $\Omega \neq 0$ for these levels. The populations of nonresonant levels display Rabi oscillations in the time domain of the pulse where their dynamics is affected by the dynamics of the resonant levels 1 and 4.
Chapter 4  Coherent control of populations of excited vibrational levels
Chapter 5

Dynamics of water clusters in strong IR fields

In the 80-th a lot of experimental and theoretical efforts\textsuperscript{42} were devoted to studies of the selective breaking of chemical bonds in simple molecules. One of the main applications of such studies was isotopic separation. Another important application was related to the control of the rate of chemical reactions by selective excitation of vibrational levels of certain vibrational modes.\textsuperscript{43-45} Nowadays, it is of interest to study light-induced dynamics of large molecules like DNA or proteins for different applications in chemistry and biotechnology.

The understanding of the photo-induced dynamics of polyatomic molecules is a great experimental and theoretical challenge. Quantitative modeling of the photo-induced dynamics of a system involves two key steps: the construction of accurate multidimensional potential energy surfaces and the quantum dynamics simulations on these surfaces. Such calculations are very demanding on computer resources. As a result, experimental and theoretical studies have so far mainly been limited to small systems. Unfortunately, conventional quantum mechanical techniques can not be applied for large systems. The realistic way to study the nuclear dynamics of polyatomic molecules is to use some approximations which reduce computational costs. Apparently we then sacrifice the accuracy of the simulations. However, we have to find a compromise between accuracy and size of the system. One promising treatment of multidimensional quantum dynamics is based on the large amplitude motion of the wave packet along a one-dimensional reaction coordinate coupled to orthogonal harmonic motions of the remaining nuclear degrees of freedom.\textsuperscript{46} However, when the intensity of the light is high the amplitude of the motion becomes large along all degrees of freedom. In this case we are forced to simplify the theoretical model. Nowadays we evidence the efficiency of classical approaches in different branches of physics and chemistry, e.g. structure studies
of solids and biomolecules. Recently the ultrafast migration of hydrogen atoms in the core-ionized water dimer,\textsuperscript{47,48} and ice and liquid water\textsuperscript{49} was evidenced using the wave packet technique and ab initio molecular dynamic simulations, respectively.

In the present thesis we apply for the first time the Born-Oppenheimer (BO) molecular dynamics (MD) method for a detailed study of the dynamics of water clusters in the field of strong and short IR pulses. One important effect which is ignored by the MD method is tunneling. However, we study the nuclear dynamics using rather high intensities of the light. In this case one can expect that the over barrier propagation of the atoms dominates and therefore that the classical approach gives reasonable accuracy.

The nuclear dynamics is described by the classical mechanics based on the forces derived from density functional theory (DFT) calculations (see articles\textsuperscript{50,51} and references therein)

\[ m_I \dot{\mathbf{R}}_I = \mathbf{F}_I, \quad \mathbf{F}_I = -\nabla_I \langle \Psi | H | \Psi \rangle \]  

(5.1)

with the hamiltonian being equal to the sum of the electronic hamiltonian of the molecule \( H_0 \) and the interaction \( V(t) \) of the laser field

\[ H = H_0 + V(t), \quad V(t) = -\mathbf{E}(t) \cdot \left[ \sum_I Z_I \mathbf{R}_I - \sum_i \mathbf{r}_i \right] \]  

(5.2)

with nuclei (of charges \( Z_I \)) and electrons having the coordinates \( \mathbf{R}_I \) and \( \mathbf{r}_i \), respectively. At each time step, the IR field \textsuperscript{(5.3)}, \( \mathbf{E}(t) = \mathbf{E}_0(t) \cos(\omega t + \varphi) \), is treated in the DFT simulations as a static field and the interaction of the field with the molecular system is accounted for incorporating the field into the Hamiltonian of the system \textsuperscript{(5.2)}. We use the same shape of the envelope \( I(t) \) as in previous sections (see eq.\textsuperscript{(3.4)}) except for the expression for the electric field

\[ \mathbf{E}(t) = e \sqrt{ \frac{2I(t)}{c \varepsilon_0} } \cos(\omega (t - t_0) + \varphi). \]  

(5.3)

Contrary to eq.\textsuperscript{(3.4)}, now the peak positions of the envelope \( I(t) \) and of the field comb coincide with each other when \( \varphi = 0 \). (We omit for brevity in this section the index of the IR field, \( \nu \).)

It is worthwhile to note that we use both restricted (RB3LYP) and unrestricted (UB3LYP) DFT methods with two different basissets 6-31G(d,p) and 6-31G+(d,p).\textsuperscript{52} The DFT method and basissets are indicated in the figure captions. The time step used in the MD simulations is 0.2 fs.
5.1 IR induced dynamics in the ground state of the water dimer

Our wave packet simulations of the water dimer in Sec. 3.3 are performed using 1D-approximations. To understand the limitations of this model we perform also MD calculations of this smallest water cluster. While the main advantage of MD calculations is that this method takes into account all nuclear degrees of freedom, it ignores the quantum effects in the nuclear

![Diagram](image)

Figure 5.1: Decomposition of the water dimer in the field of a strong IR pulse. The parameters of the IR pulse are: \( \tau = 8 \) fs, \( \omega = \omega_{\text{OH}} = 0.46 \) eV, \( I_0 = 5.4 \times 10^{14} \) W/cm\(^2\), \( t_0 = 36 \) fs, \( \varphi = 0 \). The level of the DFT simulations is UB3LYP/6-31+G(d,p).

![Graph](image)

Figure 5.2: The evolution of the total energy of the water dimer under interaction with an IR pulse. The input parameters are the same as in Fig. 5.1 except the intensities which are shown in the figure.
dynamics. Fig. 5.1 shows the classical dynamics of the water dimer in the IR field with the same intensity of the IR field which was used in the quantum simulations, $I_0 = 5.4 \times 10^{14}$ W/cm$^2$. One can see clearly that such an intensity results in the decomposition of the dimer in two water molecules. The reason of this effect one can be traced in Fig. 5.2 which indicates that the water dimer acquires $\approx 5$ eV from the IR pulse. This energy is shared between the vibrational excitations of the covalent OH and hydrogen (OO) bonds. Unfortunately, we cannot say which part of this energy is transferred to the OO bond. We see

Figure 5.3: Interatomic distances in the water dimer and electric field versus time. The duration and frequency of the IR pulse are $\tau = 8$ fs and $\omega = \omega_{OH} = 0.46$ eV. $t_0 = 36$ fs and $\varphi = 0$. UB3LYP/6-31+G(d,p). The O$_2$H distance is marked by $\times$, HO$_a$ and OO distances are shown by dashed dotted lines, respectively; the continuum line indicates the electric field. The inserts show the comparison the evolution of interatomic distances with and without (dashed-dotted line) IR field.
that the transferred energy is sufficient to break the OO bond with the energy of dissociation about \( \approx 0.13 \text{ eV} \) (see Fig. 2.10). The lower panel in Fig. 5.3 shows that the lower intensity \( I_0 = 5.4 \times 10^{13} \text{W/cm}^2 \) is not sufficient to decompose the water dimer which in this case acquires about 2 eV (Fig. 5.2). This means that the quantum simulations are valid only below the dissociation threshold, \( \lesssim 5.4 \times 10^{13} \text{ W/cm}^2 \).

Fig. 5.3 shows the time dependence of the R(O\(_a\)H), R(O\(_a\)H) and R(OO) distances for IR pulses with the intensities below and above the dissociation threshold. In both cases we observe a strong enlargement of the amplitude of the OH oscillations comparing with the amplitude of oscillations without a field. One can see that the proton approaches the proton transfer region for \( I_0 = 5.4 \times 10^{14} \text{ W/cm}^2 \) in agreement with the quantum calculations (Fig.3.4).

5.2 Dynamics of the water hexamer in strong IR fields

Let us study now the light induced dynamics of a larger water cluster, the hexamer, which consists of 6 water molecules (H\(_2\)O)\(_6\). As well known this cluster has many isomers.\(^{53,54}\) The 5 isomers with lowest energies\(^{55}\) are shown in Fig. 5.4. The global minimum corresponds to the prism structure. Simulations were earlier performed by Guimarães et al\(^{54,55}\) using an empirical ST2 potential.\(^{56}\) The order of the energies are in agreement with ab initio calculations.\(^{57}\) All of these structures occur at room temperature because of the small energy difference between different structures (\( \lesssim 2 \text{ kcal/mol} \approx 0.083 \text{ eV} \)). We have chosen the ring structure for our MD simulations. In the simulations we oriented the polarization vector \( \mathbf{e} \) of the IR field along the O(1)–O(7) bond (x-axis) as it is shown in Fig. 5.5.

In our calculations we use short (8 and 30 fs) and strong (\( \sim 10^{13} – 10^{14} \text{W/cm}^2 \)) laser pulses of the IR radiation, which generates strong variable electric fields. It is worthwhile to note that such a huge strength of the electric field is accessible only using lasers or in the vicinity of nuclei, but not using conventional sources of static electric fields, like capacitors.

The water cluster has two qualitatively and quantitatively different bonds, the hydrogen and the covalent OH bond. Let us estimate the intensities \( (I_{\text{HB}}, I_{\text{OH}}) \) of the IR pulse which are sufficient to break the hydrogen bond or the covalent OH bond

\[ Ed \sim W. \quad (5.4) \]

The energy of the hydrogen bond is about \( W \sim 5 \text{ kcal/mol} \approx 0.2 \text{ eV} \) and the energy of dissociation of the OH bond in the water molecule is \( W \approx 4.96 \text{ eV} \).\(^{58}\) For the dipole moment of the water molecule, \( d \approx 2.6 \text{ Debye} \), we get the following estimates of the threshold
Figure 5.4: Structures of $(\text{H}_2\text{O})_6$ computed using empirical ST2 potential.\textsuperscript{55}

Figure 5.5: Initial ring structure of the water hexamer cluster.
5.2 Dynamics of the water hexamer in strong IR fields

Intensities

\[ I_{\text{HB}} \sim 10^{12} \frac{\text{W}}{\text{cm}^2}, \quad I_{\text{OH}} \sim 10^{15} \frac{\text{W}}{\text{cm}^2} \]  \hspace{1cm} (5.5)

The IR pulse can influence the nuclear dynamics of the cluster by direct excitation of the hydrogen bond or the covalent OH bond, characterized by the vibrational frequency \( \omega_{\text{OO}} \approx 0.024 \text{ eV} \) and \( \omega_{\text{OH}} \approx 0.46 \text{ eV} \), respectively.

5.2.1 Light induced dynamics of the water cluster in a low frequency field. Breaking of the hydrogen bond

Let us first analyze the dynamics for the low frequency field \( \omega = \omega_{\text{OO}} = 0.024 \text{ eV} \) (we have defined this frequency directly from the oscillations of the OO bond using the MD simulations). This is the intermolecular stretching mode between two water molecules bound due to the hydrogen bond which is weaker than the covalent OH bond. We use half- and one-cycle pulses (5.3) of three different shapes varying the peak position \( t_0 \) relative to the field comb and the phase of the field \( \varphi \) (see Fig. 5.6). Fig. 5.6 shows that the pulses have the same maxima of electric field \( E_0 \), while different peak intensities. This is because the peak position of the envelope \( I(t) \) (3.4) coincides with the maximum of the comb when \( \varphi = 0 \) and with zero of the comb when \( \varphi = \pm \pi / 2 \). The IR field increases the amplitude of vibrations and rotates the water molecule, which results in a heating of the cluster. One can see (Fig. 5.7) a decomposition of the water hexamer when the intensity of the pulse exceeds the threshold of the hydrogen bond breaking \( I(t) > I_{\text{HB}} \) (5.5). Both Fig. 5.6 and Fig. 5.7 show the asymmetry of the decomposition: One can see that the water cluster is decomposed starting either from the left or the right "dimers", something that depends on the initial orientation of the electric field (defined by the phase). The physical origin for this asymmetry is the opposite polarizations of the electron subsystems of the "left" and "right" water dimers by the electromagnetic field due to the opposite orientations of these dimers. Only at the ab initio MD level we are able to treat precisely the rearrangement of the electron cloud caused both by the laser field and by the change of the cluster geometry. The different charge distributions result in distinct light induced forces between water molecules in these dimers. Simulations show that the light induced forces by the half-cycle pulse (Fig. 5.6 A, D) compresses and stretches the water molecules in the "left" and "right" dimers, respectively. Moreover, the left dimer gets more energy during the compression than the right dimer during stretching. Due to this circumstance the field breaks the hydrogen bond only in the left dimer (see Fig. 5.7 A and B). The picture is opposite for the inverted pulse (Fig. 5.7 C).

The nuclear dynamics, for example the fragmentation, is strongly affected by the heating of the cluster by the laser field. The quantitative characteristic of the heating is the absorbed
energy $E_{\text{abs}}$ which is the difference between the total energies of the cluster before and after the laser pulse:

$$E_{\text{abs}} = E_{\text{tot}}(\infty) - E_{\text{tot}}(0), \quad E_{\text{tot}}(t) = T(t) + U(t) - U(0), \quad U(t) = \langle \Psi | H | \Psi \rangle.$$  \hspace{1cm} (5.6)

We define the total energy of the cluster $E_{\text{tot}}(t)$ relative to its initial potential energy $U(0)$ at the instant $t = 0$ when the field was absent. The deviation of the relative total energy (Fig. 5.8) from zero for a zero electric field $E = 0$ derives from the kinetic energy $T(0) = (3N - 3)k_B T/2$. Fig. 5.8 (see also Fig. 5.15) shows the sign changing behavior of $E_{\text{tot}}(t)$ in the transient region. This is due to oscillations of the interaction between the molecule and the field $V(t)$ (see eqs. (5.2) and (5.3)). One can see clearly (Fig. 5.8) that the absorbed

Figure 5.6: Interatomic distances and electric field versus time. The left and right panels show the dynamics of internuclear distances of the left and right "dimers" (Fig. 5.5). The duration and frequency of the IR pulse are $\tau = 30$ fs and $\omega = \omega_{\text{IR}} = 0.024$ eV. a) and d) $I_0 = 1.30 \times 10^{13}$ W/cm$^2$, $t_0 = 200$ fs and $\varphi = 0$, b) and e) $I_0 = 3.26 \times 10^{13}$ W/cm$^2$, $t_0 = 150$ fs and $\varphi = \pi/2$, c) and f) $I_0 = 3.26 \times 10^{13}$ W/cm$^2$, $t_0 = 150$ fs and $\varphi = -\pi/2$. The level of the DFT simulations is RB3LYP/6-31G(d,p).
5.2 Dynamics of the water hexamer in strong IR fields

Figure 5.7: Nuclear dynamics of the water hexamer for different shapes of the IR field. The dashed ellipses mark stable fragments of dissociation. The duration and frequency of the IR pulse are, respectively, $\tau=30$ fs and $\omega = \omega_{\text{IR}}=0.024$ eV. A) $I_0=1.30 \times 10^{13}$ W/cm$^2$, $t_0=200$ fs and $\varphi = 0$, B) $I_0=3.26 \times 10^{13}$ W/cm$^2$, $t_0=150$ fs and $\varphi = \pi/2$, C) $I_0=3.26 \times 10^{13}$ W/cm$^2$, $t_0=150$ fs and $\varphi = -\pi/2$. The level of the DFT simulations is RB3LYP/6-31G(d,p).
energy $E_{\text{abs}}$ and, hence, the heating of the cluster grows when the laser intensity increases.

![Graph showing total energy over time for different settings.]

Figure 5.8: Total energy of the water hexamer under interaction with the same IR pulses as in Fig. 5.6. The duration and frequency of the IR pulse are, respectively, $\tau=30$ fs and $\omega = \omega_{\text{O}O}=0.024$ eV. The level of the DFT simulations is RB3LYP/6-31G(d,p).

**Formation of smaller clusters during fragmentation of the water hexamer cluster**

The simulations show clearly that the water hexamer cluster is decomposed not only into free water molecules. One can see clearly the formation of the water dimer and trimer (Fig. 5.7A), dimer (Fig. 5.7B) and tetramer (Fig. 5.7C). The movie of the decomposition shows that these fragments rotate and are excited in high vibrational states. The water molecules move relative to each other and continuously change the shape of the cluster. However, the size of the clusters is approximately the same. For example, the formation of the tetramer starts from a snake like shape (Fig. 5.7C) at $t \approx 1$ ps with the size about 8.8 Å. Then from $t \approx 2$ ps to $t = 3$ ps the size of the tetramer does not exceed 6.9 Å. The size of the trimer cluster (Fig. 5.7 A) is 4.9 Å at $t = 1$ ps and oscillates between 4.1 – 5.0 Å during $1.5 \geq t \leq 3$ ps. The OO distance of the water dimer in Fig. 5.7A oscillates between 2.9 Å and 3.2 Å, while this interval is 2.1 – 3.4 Å in Fig. 5.7B, in the time lapse 1 – 3 ps. Evidently, these results should be qualified by the fact that tunneling effects are ignored in the classical dynamics treatment.
5.2 Dynamics of the water hexamer in strong IR fields

5.2.2 Rectification of the Lorentz force. Break down of the OH bond caused by light-induced charge transfer

Let us discuss now the results of the MD simulations for a higher frequency of the IR light $\omega = \omega_{\text{OH}}=0.46$ eV, which heat the cluster through resonant excitation of the the covalent OH bond. We defined this resonant frequency directly from the MD simulations analyzing the dynamics of the OH bond. Contrary to the previous case the IR field is now a many cycle pulse because of the shorter period of field oscillations (compare Fig. 5.6 and Fig. 5.10).

![Diagram of water hexamer](image)

**Figure 5.9:** Light-induced nuclear dynamics of the water hexamer. The parameters of the IR pulse are: $\tau=8$ fs, $\omega = \omega_{\text{OH}}=0.46$ eV, $I_0=5.4 \times 10^{14}$ W/cm$^2$, $t_0=36$ fs and $\varphi = 0$. The level of the DFT simulations is UB3LYP/6-31+G(d,p).

Fig. 5.9 shows the interesting effect that the bond lengths $R(O(16)H(17))$ and $R(O(13)H(14))$ start to grow monotonously without oscillations when the IR intensity exceeds the threshold level (see Fig. 5.10). One can see that the threshold level of the breaking of the OH bond is different for the $R(O(16)H(17))$ and $R(O(13)H(14))$ bonds. Unfortunately our calculations based on the unrestricted DFT method were performed only until $t = 47.6$ fs. Due to the rather large $R(O(16)H(17))$ and $R(O(13)H(14))$ distances the used UB3LYP/6-31+G(d,p) method did not converge for larger times. However, the simulations for lower intensities show that the cluster is decomposed for larger times (see below). Let us explain the origin of the elongation of the $R(O(16)H(17))$ and $R(O(13)H(14))$ bonds using a simplified picture.

The electromagnetic field (5.2) mixes the ground state many-electron wave function with excited states. Thus the IR field changes the occupied MOs $\psi_i^{(0)}$ by inducing an admixture of unoccupied MOs $\psi_u^{(0)}$. Let us construct $\psi_i(n)$ at the instant $t_n$ through the occupied $\psi_i(n-1)$ and unoccupied $\psi_u(n - 1)$ wave functions at the previous instant $t_{n-1}$ using perturbation
theory
\[ \psi_i(n) \approx \psi_i(n-1) + \sum_{u} \frac{U_{ui}}{\epsilon_i(n-1) - \epsilon_u(n-1)} \psi_u(n-1). \] (5.7)

Here \( U \) is the perturbation caused by the interaction with the field and by the change of the cluster geometry from \( t_{n-1} \) to \( t_n \). In the studied cluster we have many delocalized occupied and unoccupied MOs. It is not hard to see that our system is rather symmetric. This allows us to divide very approximately the molecular orbitals into delocalized gerade and ungerade MOs. We analyze the charge transfer induced by the external electric field, which is nothing else than the localization of the electron on the top (14) or bottom (17) hydrogen atoms (see Fig. 5.9). Apparently, to get such a localization we need to mix occupied and unoccupied MOs of opposite parities
\[ \psi_i^{(0)} \approx \varphi(H(17)) \pm \varphi(H(14)) + \cdots, \quad \psi_u^{(0)} \approx \varphi(H(17)) \mp \varphi(H(14)) + \cdots. \] (5.8)

This expression shows immediately that the electromagnetic field mixing of these wave functions results in a partial localization of the electron density on the H(17) or H(14) atoms. The "direction of localization" depends on the sign of the electric field according to eq.(5.2). The electric field results in a charge transfer from the bottom to the top hydrogens and vise versa depending on the sign of \( E(t) \). Unfortunately, the dynamics of the electrons is not considered in MD simulations based on the BO approximation.

However, it reasonable to assume that the charge transfer is rather fast \(< 1 \text{ fs}\). In such a case the electron transfer follows instantaneously to the change of the electric field: The corresponding net charge of the hydrogen atom follows the change of the electric field, \( q(t) = q_0 \cos(\omega t + \varphi) \). This means that the discussed hydrogen atoms experience a force which has the same sign. We call this an effect of rectification of the Lorentz force
\[ \mathbf{E}(t)q(t) = E_0 q_0 \cos^2(\omega(t - t_0) + \varphi). \] (5.9)

Fig. 5.10 confirms nicely that starting from some threshold strength of the electric field, the Lorentz forces experienced by the H(17) or H(14) hydrogens cease to change the sign contrary to the electric field. To conclude, the hydrogen atoms move like in a permanent electric field because the light-induced charge follows adiabatically the oscillations of the electromagnetic field. The rectified Lorentz force (5.9) leads to a fast dissociation of the top and bottom hydrogen atoms. One can see also the rectification of the Lorentz force acting on the top and bottom whole water molecules. This means that the corresponding OH fragments also can leave the cluster. However, this happens later because the OH fragment is much heavier than the hydrogen atom.

The physical reason for the threshold of the rectification of the force (see the mid panels in Fig. 5.10) is that light-induced charge transfer is very sensitive to the strength of the
5.2 Dynamics of the water hexamer in strong IR fields

electromagnetic field. Indeed, the electric field changes the charge distribution in the cluster through the mixing of occupied and unoccupied wave functions. As one can see from eq. (5.7) that the charge transfer is stronger when the gap between LUMO and HOMO is small

\[ \Delta(t) = \epsilon_{\text{LUMO}}(t) - \epsilon_{\text{HOMO}}(t). \]  

(5.10)

This qualitative picture is nicely confirmed by comparison of Fig. 5.10 and Fig. 5.11. One can see clearly that the extrema of the electric field result in a small gap \( \Delta(t) \) and, hence, in a large light-induced charge on the hydrogen atom.

To see directly the light-induced charge transfer we have to analyze the dynamics of the charge distribution of the occupied MOs which have large contributions from the atomic

Figure 5.10: Rectification of the Lorentz forces \( F_L = Eq \) acting on the hydrogen atoms (H(14), H(17)) results in a fast elongation of the bond distances \( R(\text{O}(13)\text{H}(14)) \) and \( R(\text{O}(16)\text{H}(17)) \). Net charges (Mulliken) \( q(t) \) and Lorentz forces \( E(t)q(t) \) of the top and bottom hydrogen atoms and water molecules. The parameters of the IR pulse are: \( \tau=8 \) fs, \( \omega = \omega_{\text{OH}}=0.46 \) eV, \( I_0=5.4\times10^{14} \) W/cm², \( t_0=36 \) fs and \( \varphi = 0 \). The level of the DFT simulations is UB3LYP/6-31+G(d,p).
Figure 5.11: The field induced evolution of the orbital energies and HOMO-LUMO gap of the water hexamer cluster. The input parameters are the same as in Fig. 5.10.

<table>
<thead>
<tr>
<th>$t$/fs</th>
<th>0</th>
<th>36.0</th>
<th>38.2</th>
<th>40.4</th>
<th>42.8</th>
<th>44.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>HOMO</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 5.12: The IR-induced dynamics of HOMO and LUMO orbitals of the water hexamer cluster during the interaction with the electric field. The input parameters are the same as in Fig. 5.10.
5.2 Dynamics of the water hexamer in strong IR fields

orbitals of the top and bottom hydrogen atoms. An analysis of data indicates about 5 such occupied MOs. We show here only one of such orbital, namely the HOMO orbital (Fig. 5.12). One can see clearly that positive \((t = 36 \text{ fs})\) and negative \((t = 40.4 \text{ fs})\) electric fields (Fig. 5.10) induce charge on the atoms H(14) and H(17), respectively (Fig. 5.12). This is in agreement with Fig. 5.10. The analysis shows that the charge transfer is defined by both the strength of the electric field and the field-induced change of the geometry of the cluster.

5.2.3 Rectification of the Lorentz force. Break down of hydrogen bond

When the intensity is decreased, \(I = 4.0 \times 10^{14} \text{ W/cm}^2\), \(3.0 \times 10^{14} \text{ W/cm}^2\) we get a qualitatively different result: Dissociation of the top and bottom water molecules (Fig. 5.13), instead of dissociation of the top H(14) and bottom H(17) hydrogens which we got for higher intensity (Fig. 5.9).

The simulations indicate that the slightly lower intensity \(I = 1.0 \times 10^{14} \text{ W/cm}^2\) is not sufficient to decompose the cluster. It is important to note that the hydrogen bond is broken for the lower intensity if the laser field is tuned in resonance with the OO bond (see Fig. 5.6).

Let us discuss in some detail the dynamics of the decomposition of the water hexamer for \(I = 3.0 \times 10^{14} \text{ W/cm}^2\). This intensity is not sufficient to break the covalent OH bond (5.5), but enough to break the weak hydrogen bond (5.5). What strikes the eye is that now we have dissociation of the top and bottom water molecules. The physics behind the dissociation of the water molecule is rather similar to the dissociation of the hydrogen atoms H(14) and H(17) discussed above. Calculations show that we now have periodical charge transfer in the top and bottom water molecules (Fig. 5.14). Due to this charge transfer we have again a rectification of the force. The rectification of the forces shown in Fig. 5.14 starts immediately with the appearance of the pulse. Fig. 5.13 shows that the decomposition of the cluster starts from the dissociation of the top and bottom molecules and the "formation" of the tetramer cluster. However, the tetramer is also heated by the light and, due to this, it is decomposed later on.

What is surprising is that now the top and bottom water molecules leave the cluster intact, contrary to Figs. 5.9 and 5.10 which indicate that this molecules fragment. The reason for this is that the lower intensity is not enough to overcome the molecular field and, hence, to rectify the forces acting on the hydrogen atoms (see Fig. 5.14), except a very small rectification on the top hydrogen. Because we now are free from the numerical problem
Figure 5.13: IR-induced dynamics of the water hexamer cluster. The input parameters are the same as in Fig. 5.10 except $I_0 = 3.0 \times 10^{14}$ W/cm$^2$.

Figure 5.14: The rectification of the Lorentz forces acting on the top and bottom water molecules (see Fig. 5.13) results in a fast elongation of the separation between these molecules $R(O(13)O(16))$. Net charges (Mulliken) $q(t)$ and Lorentz forces $E(t)q(t)$ of the top and bottom hydrogen atoms and water molecules. The input parameters are the same as in Fig. 5.13.
with large OH separations we succeeded to perform the MD simulations for large times in comparison with the simulations in Fig. 5.11.

Let us now to demonstrate how to preserve the destruction of the tetramer cluster which is seen in Fig. 5.13. As it was mentioned above the reason of this decomposition is the excessive heating caused by the the rather large absorbed energy. One can decrease the absorbed energy by tuning the light frequency off resonance with the OH bond or by replacing the hydrogen atoms by deuterium atoms in the hexamer except for the top and bottom water molecules, \((\text{H}_2\text{O})_6 \rightarrow (\text{H}_2\text{O})_2(\text{D}_2\text{O})_4\). The isotope substituted tetramer cluster \((\text{D}_2\text{O})_4\) is not in resonance with the light frequency, \(\omega = \omega_{\text{OH}} \neq \omega_{\text{OD}}\). Fig. 5.15 confirms nicely the decrease of the absorbed energy of the isotope substituted hexamer cluster comparing with the normal cluster. Numerical simulations of the light-induced dynamics of \((\text{H}_2\text{O})_2(\text{D}_2\text{O})_4\) show the formation of the stable tetramer

\[
(\text{H}_2\text{O})_2(\text{D}_2\text{O})_4 \xrightarrow{\omega} \text{H}_2\text{O} + \text{H}_2\text{O} + (\text{D}_2\text{O})_4
\]  

(5.11)

contrary to Fig. 5.13.

![Figure 5.15: Time evolution of the total energies of \((\text{H}_2\text{O})_6\) and isotope substituted \((\text{H}_2\text{O})_2(\text{D}_2\text{O})_4\) clusters shows that the isotope substitution decreases the heating of the hexamer by 1.5 times and preserves it against the destruction. The input parameters are the same as in Fig. 5.14.](image)
Chapter 6

Summary of results

- It is shown that NEXAFS spectroscopy can evidence through-space and through-bond interactions of unoccupied orbitals.
- Core ionization of the donor oxygen of the water dimer results in a drastic change of the potential, exhibiting the global minimum in the proton transfer region.
- The O1s photoelectron spectrum of the water dimer shows a significant qualitative difference from the monomer spectrum. The weak hydrogen bonding and the big change of the water dimer potential under core ionization are responsible for the anomalously strong vibrational broadening: 0.4 eV for the acceptor band and 0.6 eV for the donor band.
- It is shown that contrary to conventional XPS spectroscopy, X-ray pump-probe spectroscopy is a proper tool to explore the proton transfer in the water dimer under core ionization.
- It is shown that the trajectory of the nuclear wave packet changes drastically under change of the phase of the driving IR field.
- A new type of spectroscopy is proposed - phase sensitive IR - X-ray pump-probe spectroscopy.
- A dynamical theory of phase sensitive IR - X-ray pump-probe spectroscopy is developed.
- Variations of the duration, intensity and shape of the pump pulse allows a quantum control of the nuclear wave packet, which implies a selective population of certain group of vibrational levels and a preparation of the wave packet of desirable shape.
- The phase sensitivity of X-ray spectra of molecules driven by a strong IR field depends strongly on the duration of the X-ray pulse, the delay time, the shape of the IR pulse and on the orientational ordering of the sample.
• Vibronic coupling between $O_1(1s^{-1})$ and $O_2(1s^{-1})$ core-ionized states in glyoxalmonoxime results in a partial delocalization of the core holes. The vibronic coupling entangles core holes and results in “bright” and “dark” spectral bands.

• The dynamics of the dimer and hexamer water clusters in the field of a strong IR laser is studied using molecular dynamics simulations.

• The effect of the rectification of the Lorentz force is predicted.

• The IR pulse leads to the decomposition of the hexamer cluster into smaller vibrationally-rotationally excited clusters.

• The IR-induced fragmentation is very sensitive to the frequency, intensity and the phase of the IR pulse.

• The frequency detuning as well as the isotope substitution allow a site selective control of the radiative heating which is important for protection of the products of the photodissociation against radiative damage.
Bibliography


