Theoretical Studies on Electronic and Vibrationally Resolved Multi-Photon Absorption and Dichroism

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Stockholm, Sweden 2009
To Zhitai and my parents
Abstract

This thesis presents time-dependent density functional theory studies on electronic and vibronically resolved linear and nonlinear optical absorption and dichroism spectra of organic molecules. Special attention has been paid to the influence of solvent environment and molecular vibrations on one-, two- and three-photon absorption and one- and two-photon circular dichroism.

It is found that dielectric medium as described by polarizable continuum model can enhance remarkably three-photon absorption cross section of a highly conjugated fluorene derivative, for which the simplified two-state model is shown to be largely inadequate. Origin-invariant density functional calculations on one- and two-photon circular dichroisms of a chiral molecule confirm that the recently developed CAMB3LYP functional performs better than the popular B3LYP functional for Rydberg-states. The first experimental measurement of TPCD spectra is performed on an axial chiral system in tetrahydrofunan, where the double L-scan technique is applied. Theoretical calculations well reproduce the experimental profiles when both the electron correlation and the solvent effect are taken into account. Vibronically resolved one- and two-photon absorption spectra of charge-transfer molecules have been obtained using a Linear Coupling model, where the ‘borrowing mechanism’ for the so-called Herzberg-Teller contribution is analyzed in detail. It is shown that Herzberg-Teller contribution can introduce a change of sign to the chiral responses of a molecule without the involvement of different electronic states, which has important consequences for the assignment of absolute configurations of chiral molecules. Adiabatic harmonic Franck-Condon model is also applied to simulate vibronically resolved one- and two-photon circular dichroism spectra of the same chiral system, where the sign-inversion and the interference between Franck-Condon and Herzberg-Teller contributions are also observed.
Preface

The work presented in this thesis was carried out at the Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden; and at the Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche (IPCF-CNR), Pisa, Italy.

List of papers included in the thesis


**Paper V. Na Lin**, Fabrizio Santoro, Antonio Rizzo, Xian Zhao, Seth R. Marder, Yi Luo, *Vibronically induced shift between one- and two-photon absorption spectra*, in
manuscript.


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**List of papers not included in the thesis**


**Paper II.** Na Lin, Xian Zhao, Antonio Rizzo, *Ab initio study of the circular intensity differences in electric-field-induced second harmonic generation on chiral natural amino acids*, in manuscript.

**Paper III.** Sonia Coriani, Roger E. Raab, Antonio Rizzo and Na Lin, *The quadrupole-quadrupole polarizability of non-magnetic molecules: an ab initio study*, in manuscript.
Comments on my contribution to the papers included

- I was responsible for most of calculations and the writing of the first draft of the papers where I am the first author, that is Papers I, IV, V, VI, VII, VIII.

- I was responsible for part of calculations and part of writing of Paper II.

- I was responsible for all the calculations and theoretical analysis of Paper III.

- I was participating in all the analysis and interpretation of the results of all the papers.
Acknowledgments

This thesis would never come into being without the assistance of many people whom I would like to thank.

First of all, I wish to express my great thanks to my supervisor Prof. Yi Luo, who is not only a fantastic supervisor but also a great friend, in both scientific and my personal lives. I cannot find a word to express all my gratitude to him. Thanks for giving me the opportunity to work under his instruction, for introducing me into the interesting field of nonlinear optics, for his enormous patience and fluent scientific ideas, for his support and help in my daily life. Many thanks also to Luo's enviable family: Considerate Dr. Kezhao Xing, Oscar and pretty Linda, for all the joyful memories we have shared together. Thank you very much.

I would like to express sincerely my deep gratitude to Prof. Antonio Rizzo, my supervisor in Pisa. Thanks for all the patient guidance and everlasting optimistic attitude to my scientific work and daily life. His way of doing science impressed me very much and what I learned from him will be a great treasure in my life. “Reading is more important than writing”, Antonio always kept repeating this to me. I know very well he is absolutely right, although sometimes I need to be reminded. Antonio is also a very great and kind friend, and I would very like to keep him as one of my best friends in the future. I hope he feels in the same way ☺

A good few of my projects concerning vibronically resolved spectroscopy were carried out with my third “young” supervisor Dr. Fabrizio Santoro. Thanks very much for the extremely fruitful guidance, for the always helpful and interesting discussions and for the constant readiness to answer my questions and invaluable advice in this work. Without his generous help, the thesis will never reach the present level. Thanks for trying to explain “physics” to me in a simple way and helping me to understand the world of vibronic coupling; thanks for always giving me continuous encouragement when I was depressed; thanks for always being there when I met problems. Grazie Mille!

Special thanks to my supervisor in China, Prof. Xian Zhao, who always tries his best to help me, both in scientific work and in my personal life. Thank you for giving me the opportunity to study abroad; thank you for the constant trust and support; thank you for your kindness to me all the time no matter how difficult the situation was. Great thanks to Zhao’s graceful wife, Ms. Xiufeng Cheng, and their lovely son, Bangbang. The days with you are always my precious memory.

I am deeply thankful to the head of the Department of Theoretical Chemistry, Prof. Hans Ågren, for his warmly welcome to accept me as a member of our wonderful department. Thank you for creating such a good atmosphere for doing scientific work. Happy 10th anniversary to our department!

Many thanks to Prof. Boris Minaev, Prof. Faris Gel'mukhanov, Dr. Fahmi Himo, Dr. Pawel Salek and Dr. Zilvinas Rinkevicius, Dr. Olav Vahtras, Dr. Yaoquan Tu for all
their good lectures and helpful discussions. Thanks to Lotta and Pia, for kindly help with so many administrative problems.

Great thanks reserved to Prof. Vincenzo Barone, for the wonderful collaborations and many generous help.

Many thanks to Prof. Vincenzo Carravetta for always being available to help me in many housing problems during my stay in Pisa.

The considerable technical assistance of Prof. Kenneth Ruud from University of Tromso, is very much appreciated. Thanks for providing me amazing computational resources, friendly help and many exciting collaborations. Thank Dr. Maxime Guillaume, Harald Solheim, and Dr. Lara Ferrighi from the same group for many helpful discussions.

Many thanks to Dr. Sonia Coriani from University of Trieste for very beautiful collaborations and beneficial discussions.

Thanks to the experimental collaborators, Prof. Bob Compton’s group and Prof. Florencio E. Hernández’s group. Thanks for the remarkably good results.

I am very thankful to all my present and past colleagues, for their friendship and the help they have offered me in many occasions, especially to Dr. Jun Jiang and Dr. Yanhua Wang for their help during my first days abroad. Thank Dr. Bin Gao for helping me to solve some technical problems. Thank Hao Ren for his hospitality and delicious meals.

Special thanks to Dr. Wenhua Zhang for always being like “twins” with me for the last three years, for the encouragement to each other. There are also some other good friends in our group deserved special mentions: Feng Zhang, Qiong Zhang (QQ), Keyan Lian, Yuejie Ai, Shilu Chen, Dr. Tian-Tian Han (TT), Kai Fu, Xiaofei Li, Rongzhen Liao, Qiang Fu, Ying Zhang, Fuming Ying, Guangde Tu, Kai Liu, Yong Zeng, Hui Cao, Guangjun Tian, Sai Duan, Xin Chen, Xiao Cheng, Ke Zhao, Jicai Liu, Yuping Sun, Weijie Hua, Andre, Cornel, Peter, Kathrin, Elias, and many other friends in our group, I really treasure all the happy time we shared together.

I wish to thank Dr. Weiliu Fan in Shandong University for many friendly help to deal with many fussy procedures during my stay abroad.

Great thanks to my parents, their endless love and support sustain me in every moment.

Last but not least, my infinite heartful gratitude goes to my husband Dr. Zhitai Jia, for encouraging me all the time, for being by my side every day, and for his sweetest love.

Thank you all very much!
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Physics would be dull and life most unfulfilling if all physical phenomena around us were linear. Fortunately, we are living in a nonlinear world.”

—Y. R. Shen

1. Introduction

The study of interaction between light and molecules has been and will continue to be of great importance for understanding the nature surrounding us. With the conventional light source, only linear optical processes can be observed. The invention of Laser in 1960 marked the birth of nonlinear optics which has made huge impact on the development of modern technology and to our daily life. In recent decades, the advances in theoretical understanding of light-matter interaction have extended the applications of nonlinear optics into many new fields, including information technology, biological imaging and medical photodynamic therapy. For the latter applications, organic molecules can be particularly useful. Organic molecules with outstanding luminescence have already been widely used as dye-molecules in biological imaging. It is worth to mention that the Nobel Prize of Chemistry in 2008 has been awarded to Shimomura, Chalfie, and Tsien for their discovery and development of the green fluorescent protein (GFP), which provides interesting spectral windows for bio-imaging, and might result in a technical resolution related to a miraculous property of the chromophore that is responsible for its fluorescence.

With the development of powerful laser sources, multi-photon spectroscopy has become an interesting field of research. The possibility of using multi-photon absorption property of organic molecules has significantly improved the quality of biological and medical applications. Multi-photon \((n\)-photon) absorption in general is characterized by several attractive features. From a spectroscopic point of view, it enables the exploration of states that are inaccessible for ordinary one-photon excitations due to parity rules.
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Since it is accomplished at a frequency of $1/n$ the actual energy gap, multi-photon process furthermore stretches the accessible range of conventional lasers. Basically, the technical applications are based on two key features of multi-photon absorption, namely the ability to create excited states with photons of $1/n$ the nominal excitation energy, which can provide improved penetration in absorbing or scattering media, and the $I^n$ dependence of the process, where $I$ is the intensity of the laser pulse, which allows a high degree of spatial selectivity in three dimensions for excitation of chromophores through the use of a tightly focused laser beam. Moreover, since longer wavelength is used for multi-photon excitation than that for one-photon excitation, the influence of scattering on beam intensity is greatly reduced. These are clear advantages for applications in imaging of absorbing or scattering media, like biological tissues. The use of multi-photon absorption processes for bio-imaging and photodynamic therapy has thus attracted great attention in recent years.\textsuperscript{1-3}

The design and the synthesis of organic molecules with promising multi-photon application potentials have contributed greatly to the development of the related fields.\textsuperscript{4-6} One way to achieve this goal is to establish the so-called structure-to-property relationship by exploring all possible chemical structures to get optimal optical responses. Theory and computation can be helpful in guiding experiments that are often time-consuming and expensive. It is well known that both one- and multi-photon absorption processes are heavily determined by the property of the charge-transfer (CT) excited states. CT states often possess huge transition probability and dominate the entire spectra from the electronic transition point of view. It should also be noted that many experiments are performed with ultra-fast laser sources, therefore, the dynamics of CT state becomes another important issue. A good understanding of vibrational structures of optical excitation provides the first clue to the dynamics of CT states. Computationally, one can nowadays routinely calculate electronic states and transitions between them. However, due to the large size of organic molecules employed in realistic applications, the inclusion of vibrational contributions has been a challenge for first principles theoretical simulations.

In the present thesis, the vibronic profiles are explored for many linear and nonlinear optical processes based on two foundation stones: the harmonic approximation and the adiabatic approximation. The harmonic approximation is a
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convenient and widely-used model to introduce the vibronic contribution to the optical spectra, where the atoms are treated as harmonic oscillators and bonds between them as weightless springs. The adiabatic approximation, which has been shown reliable when the excited states in concern are well-separated from each other, is another basic foundation of the present thesis. Two kinds of vibronic models have been applied: the adiabatic harmonic Franck-Condon (AFC) model, which requires information on both minimum geometries of the initial and final states, can provide accurate results and confident assignment of the vibrational peaks; the Linear coupling model (LCM), which is less accurate but also less computational intensive by avoiding the often cumbersome excited-state geometry optimization, is also applied to capture the major features of the vibronically resolved spectra.

Organic molecules are often applied in solutions. Theoretical calculations performed on an isolated molecule thus meet a difficulty in direct comparison with experimental measurements. Effect of solvent environment on linear and nonlinear optical properties of organic molecules is an important issue to be addressed. It is often the case that the presence of polar solvents can lead to a red-shift of CT states of organic molecules. Moreover, it can have strong influence on both the geometrical and optical responses of the solute molecule. In this thesis, the solvent effect on the molecular optical properties of interest is modeled by means of the so-called polarizable continuum model, which treats the solvent environment as a homogenous dielectric continuum medium characterized by its dielectric constant. In the presence of an external electromagnetic field, the field induced by the solvent molecules can in turn screen the effects of the external field, which can be described by the so-called local field factor.

In this thesis, special attentions have been paid to one-, two- and three-photon absorption properties of charge-transfer organic molecules. Circular dichroism, which can be regarded as a special kind of absorption spectroscopy, is strongly associated with chirality of molecules. It is based on the different absorption abilities between left and right circularly polarized lights. Here we focus on one- and two-photon circular dichroism spectra of chiral molecules, for which the state-of-the-art response theory is applied.

The basic quantum mechanical theory related to the studies presented in this thesis
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is outlined in Chapter 2. In the following two chapters, relevant theories and computational methods for linear and nonlinear molecular optical absorption and circular dichroism, are discussed. A summary of my own publications included in this thesis is given in Chapter 5.
2. Basic quantum chemical methods

This chapter introduces basic methods of quantum mechanics, which are classified into two categories, the one based on the representation of the wavefunction and the other one on density, respectively. Wavefunction based methods are introduced in Sec. 2.1 and Density Functional Theory (DFT) in Sec. 2.2.

2.1 Wavefunction based methods

We can get all the information of a given system through the wavefunction, and the current section collects the basic ideas of quantum chemical methods based on wavefunctions. The starting point for a nonrelativistic quantum mechanical description of stationary states in an N-particle system is the time-independent Schrödinger equation

\[
\hat{H}\Psi(r_1, r_2, \ldots, r_N) = E\Psi(r_1, r_2, \ldots, r_N)
\]

The total wavefunction is very complicated since it depends on the coordinates of both electrons and nuclei. Due to the considerable difference in mass between the nuclei and the electrons which leads to a remarkable difference in velocity, electronic motion normally is separated from the much slower nuclear motion, in the so-called Born-Oppenheimer (BO) approximation. Although the problem is reduced to the determination of the electronic wavefunction at fixed nuclear positions, further approximations are still needed in order to obtain a solution to Eq. (2.1).

Since electrons are fermions, the electronic wavefunction has to be anti-symmetric with respect to interchange of any two electrons (Pauli exclusion principle). A wavefunction written in the form of a single Slater determinant composed by
2 Basic quantum chemical methods

one-electron functions (molecular orbitals), which automatically takes the Pauli exclusion principle into account, is the basis of Hartree-Fock (HF) approximation. For an $n$-electron system, the HF wavefunction can be written as

$$
\psi(1, 2, \ldots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix}
\phi_1(1) & \phi_1(2) & \cdots & \phi_1(n) \\
\phi_2(1) & \phi_2(2) & \cdots & \phi_2(n) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_n(1) & \phi_n(2) & \cdots & \phi_n(n)
\end{vmatrix}
$$

(2.2)

With the variational principle, under the constraint of orthonormality, the orbitals can be optimized till the entire system reaches its energy minimum. In this way, we can derive a set of $n$ coupled equations, known as HF equations, which can be solved by using the self-consistent field (SCF) method.

HF method provides a cheap and relatively simple \textit{ab initio} approach for the calculation of electronic structures, turning the many-electron problem into a set of one-electron equations by applying the so-called mean field approximation, in which the actual electron-electron interaction is replaced with an averaged effective potential generated by the other $n-1$ electrons of the system. However, the effects of electron correlation, being defined as the difference between the exact energy and the HF energy, are neglected in HF approach. Many so-called post-HF approaches have been developed to deal with the electron correlation problem, such as Configuration Interaction (CI), multiconfiguration SCF (MCSCF), Coupled Cluster (CC), and Møller-Plesset perturbation theory (MP2, MP3, MP4, etc) methods. All the improved approaches mentioned here are possibly very accurate, though with the price of higher computational cost, to various degrees forbidding the treatment of large molecules.

2.2 Density functional theory

2.2.1 Ground-state density functional theory

HF and the post-HF methods are based on the complicated many-electron wavefunction, which depends on three spatial variables for each of the $n$ electrons, i.e. $3n$ variables in total (neglecting spin here). For large systems these methods will encounter a huge computational problem. Instead, the ground-state electron density,
2.2 Density functional theory

which only depends on three spatial coordinates, was proven to be sufficient to get all the information of the system, by Hohenberg and Kohn. In 1964, they gave the proofs of two important theorems:

**Theorem I:** For any system of electrons, the external potential $V_{ext}(r)$ is determined uniquely, except for a constant, by the ground state density $\rho_0(r)$.

In other words, once the electron density is known, the external potential, and consequently the Hamiltonian of the system are in principle uniquely determined. The knowledge of the Hamiltonian in turn determines the total electronic wavefunction. Every quantum mechanical observable is a functional of the ground-state density.

**Theorem II:** There exists a universal functional for the energy $E[\rho]$ of the density $\rho(r)$. For a given $V_{ext}(r)$, the global minimum of $E[\rho]$ is the exact ground state energy which occurs for the exact ground state density $\rho_0(r)$.

This is to say that the exact ground state density, which can be obtained from a variational principle method, is the density that minimizes the energy as a functional of the density.

In Hohenberg-Kohn (HK) theory, the Hamiltonian of a many-particle system in the external potential of $V_{ext}(r)$ can be written as

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$  \hspace{1cm} (2.3)

And the corresponding energy functional is

$$E_{HK}[\rho] = T[\rho] + U[\rho] + \int d^3r V_{ext}(r) \rho(r)$$  \hspace{1cm} (2.4)

where $T[\rho]$ is the kinetic energy of the system, $U[\rho]$ is the potential energy of the interaction of the system, and $V_{ext}(r)$ contains the external potential including that due to the nuclei.

In the above equation, the explicit expressions of $T[\rho]$ and $U[\rho]$ are unknown. In 1965, Kohn and Sham\textsuperscript{8} considered a system of non-interacting particles, moving in an effective local potential, of which the density would be identical to the associated interacting particle system. No proof is available that such an effective potential should exist. If it exists, however, it is unique. For this fictitious system, the electronic density is defined as
2 Basic quantum chemical methods

\[ \rho(r) = \sum_{i} |\phi_i(r)|^2 \]  \hspace{1cm} (2.5)

where \( \phi_i(r) \) is the one-electron orbitals (Kohn-Sham orbitals).

The expectation value of the total kinetic energy can be written as the sum of the kinetic energies of all electrons

\[ T_s[\rho] = -\frac{1}{2} \sum_i \int d^3 r \rho_i(r) \nabla^2 \phi_i(r) \]  \hspace{1cm} (2.6)

The main part of \( U[\rho] \), the Hartree potential from the Coulomb interaction with the electron cloud, can be written as

\[ U_H[\rho] = \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho(r)\rho(r')}{|r-r'|} \]  \hspace{1cm} (2.7)

The unknown part is defined as the exchange-correlation energy

\[ E_{xc} = E_{tot} - T_s - U_H - V = (T - T_s) + (U - U_H) \]  \hspace{1cm} (2.8)

Applying the variational theorem we can derive the well-known Kohn-Sham (KS) equations

\[ (-\frac{1}{2} \nabla^2 + v_{ext}(r) + v_H(r) + v_{xc}(r))\phi_i = \varepsilon_i \phi_i \]  \hspace{1cm} (2.9)

where \( v_{ext}(r) \), \( v_H(r) \), and \( v_{xc}(r) \) are respectively the external, the Hartree, and the exchange-correlation (xc) potentials. The xc potential is an unknown functional of the density. It contains all the many-body exchange and correlation effects. Several xc functionals will be discussed in section 2.2.3. Similar to HF orbitals, the KS orbitals are obtained by using an SCF procedure.

2.2.2 Time-dependent Kohn-Sham equations

While we have briefly introduced the DFT for ground-state properties, extension is still needed to solve time-dependent problems. We start with Runge-Gross theorem for time-dependent density functional theory (TDDFT): the densities \( \rho(r,t) \) and \( \rho'(r,t) \) of two systems evolving from the same initial state \( \psi(t_0) \) under the influence of, respectively, the potentials \( V_{ext}(r,t) \) and \( V'_{ext}(r,t) \), both Taylor expandable about \( t_0 \) and differing by more than a purely time-dependent function \( c(t) \), will always differ.
This is the time-dependent analogue of HK theorem I. The time-dependent KS equation can be written as

\[
\frac{\partial \phi_j(r,t)}{\partial t} = (-\frac{1}{2} \nabla^2 + v_{\text{ext}}(r,t) + v_{\text{H}}(r,t) + v_{\text{xc}}(r,t)) \phi_j(r,t)
\]  

where \( v_{\text{ext}}(r,t) \), \( v_{\text{H}}(r,t) \), and \( v_{\text{xc}}(r,t) \) are respectively the time-dependent external, the Hartree, and the exchange-correlation potentials. In the ground-state DFT, one applies the variation minimum principle for the total energy. In TDDFT, instead we need to find the stationary point of the action integral \( A \)

\[
A = \int_0^t dt \langle \psi(t) \mid \frac{i}{\partial t} H(t) \mid \psi(t) \rangle
\]

### 2.2.3 Functionals

Since the exact functional for the exchange and correlation part is not known except for the free electron gas, approximations must be introduced. The first approximation for the xc potential was the local density approximation (LDA), based upon the theory of the homogeneous electron gas. The idea of LDA is that a system can locally be described as an electron gas with a density equal to the local density of the system. This assumption seems reliable in systems with slowly varying densities (like metals), but not in molecules, where the density changes rapidly. In that case LDA can be drastically improved by using generalized gradient approximations (GGA), which also take the gradient of the density into account, in addition to the density itself. In the 1990s, Becke suggested to bring the HF exchange into the xc functional, and constructed a series of hybrid functionals. A rapidly growing list of hybrid functionals has been developed for different needs. Here we just mention two of them which we applied in this thesis. One is the popular Becke’s three-parameter gradient-correlated exchange functional with the Lee-Yang-Parr gradient-correlated correlation (B3LYP)\(^{10-12}\), which has the form of

\[
E_{\text{xc}}^{\text{B3LYP}} = aE_s^{\text{HF}} + (1-a)E_s^{\text{LSDA}} + bE_s^{\text{B88}} + cE_s^{\text{LYP}} + (1-c)E_s^{\text{LSDA}}
\]

where \( a = 0.2 \), \( b = 0.72 \), \( c = 0.81 \), obtained by fitting to experimental data. However, B3LYP is not sufficient in some cases due to the lack of the description of long-range exchange, as for example for the description of Rydberg or charge-transfer states in
which the electron travels far away from the nucleus. The CAMB3LYP\textsuperscript{13,14} functional by Yanai, Tew and Handy, was developed to adjust the long- and short-range exchange potentials through three parameters $\alpha$, $\beta$, $\mu$, with the form of

$$
\frac{1}{r_{12}} = \frac{1}{r_{12}} - \left[ \alpha + \beta \cdot \text{erf}(\mu r_{12}) \right] + \frac{\alpha + \beta \cdot \text{erf}(\mu r_{12})}{r_{12}}
$$

(2.13)

The standard parametrization ($\alpha = 0.19$, $\beta = 0.46$, $\mu = 0.33$) of CAMB3LYP in Dalton2.0\textsuperscript{15} is applied in the present work.
3. Molecular optical properties

The papers included in this thesis focus on the study of the interaction of light with molecules. In section 3.1 we give a brief introduction and the basic formulism for the calculation of molecular linear and nonlinear absorption processes, with special attention to one-, two-, and three-photon absorption. In section 3.2, we turn the attention to the linear and nonlinear circular dichroism properties of chiral molecules, mainly on one-, and two-photon circular dichroism spectra. In section 3.3 we give a brief description on response theory which has been applied throughout the thesis. The effects of solvent environment will be discussed briefly in section 3.4.

3.1 Linear and nonlinear absorption

3.1.1 Introduction

One-photon absorption (OPA), as schematically shown in Fig. 3.1 (a), is a process where a molecule in an initial state absorbs one photon and is excited to a final state. If simultaneously more than one photon is absorbed, the process is called multi-photon absorption (MPA). With a conventional light source, only OPA can be detected. Although OPA has been tremendously successful in gaining a microscopic understanding of molecules, its limitations are equally obvious. Only a small fraction of the possible eigenstates of molecules can be explored due to the strict dipole selection rule.

The possibility of simultaneously absorbing two photons (TPA, as shown in Fig. 3.1 (b)), which is the lowest order multi-photon absorption (MPA) process, was
3 Molecular optical properties

predicted in 1931 by Göppert—Mayer. It took a period of 30 years to make the first experimental observation possible, after lasers were developed as intense incident light sources. Since the mid-1990s, TPA has gained considerable attention both in experimental and theoretical studies due to its various promising practical applications, including three-dimensional optical storage, fluorescence excitation microscopy, optical power limiting, up-converted lasing and photodynamic therapy.

Three-photon absorption (3PA, shown in Fig. 3.1 (c)) gains more and more attention due to the fact that for many applications it is even better suited than TPA, such as optical limiting, fluorescence imaging, and stimulated emission. Higher-order processes, are far less popular, due to the much more demanding experimental realizations.

![Graphical representation of (a) one-photon absorption, (b) two-photon absorption, and (c) three-photon absorption.](image)

3.1.2 Theoretical description

Theoretical design and characterization of non-linear chromophores should in principle allow accurate prediction of the structures of stable molecules and their non-linear optical responses, in particular, with wavefunction based highly correlated *ab initio* methods. However, these computational techniques are in most cases computationally intractable for molecules of practical interest. Semi-empirical methods are numerically feasible, but can only provide qualitative insight into the nature of the physical phenomena involved, with very limited quantitative information. TDDFT, which can give reliable predictions with moderate computational cost, is instead currently the choice for the calculations of large molecular systems. The overall performance of TDDFT methods is found to be good when combined with appropriate
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functionals and basis sets. The results are expected to improve with development of more accurate new density functionals. However, TDDFT with common-used xc functionals can yield substantial errors for charge-transfer (CT) states. The excitation energies of such states are usually drastically underestimated, and the potential energy curves of CT states do not exhibit the correct 1/R dependence along a charge-separation coordinate R. New functionals are developing to cover this failure, with CAMB3LYP being one of them. We applied TDDFT throughout the excited-state calculations in the present thesis, and the performance of two different functionals B3LYP and CAMB3LYP has been well examined.

In the following we give the brief formulism for the calculation of one-, two- and three-photon absorption. In accordance with the theory given in Chapter 4, where the vibronically resolved spectra are discussed, we give formulae fully taking both the electronic and vibrational states into account.

**One-photon absorption:**

For OPA, when both electronic and vibrational states are taken into account, the extinction coefficient can be written as

\[
\varepsilon_{\text{OPA}}(\omega) = \frac{(2\pi)^2 \times \omega \times N_A}{3 \times 1000 \times \ln(10) \times \hbar c_0 \times (4\pi\varepsilon_0)} \times \sum_{g, f} \sum_{v_g, v_f} p_{v_g} \epsilon(g, \omega_g, v_g) \sum_{a=x,y,z} \left| \mu_{g, v_g}^{a} \right|^2 \times (3.1) 
\]

where \(N_A\) is Avogadro’s number, \(c_0\) the speed of light in vacuo and \(\varepsilon_0\) the vacuum permittivity. \(\omega\) is the circular frequency of the laser, \(\omega_g, \omega_f\) the transition energy from the initial state \(|g_{v_g}\rangle\) to the final state \(|f_{v_f}\rangle\). Here \(|g\rangle\) and \(|f\rangle\) label the vibrational states of the electronic states \(g\) and \(f\), respectively. \(p_{v_g}\) is the Boltzmann thermal population of the initial vibrational state \(|v_g\rangle\). The transition electric dipole moment is evaluated explicitly as
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\[ \mu_{\alpha}^{g'v'f_f} = \langle g'v_f | \mu_{\alpha} | f_f \rangle \]  \hspace{1cm} (3.2)

with \( \mu_{\alpha} \) denoting the Cartesian (\( \alpha = x, y, z \)) component of the electric transition dipole operator. \( g(\omega, \omega_{g'v'f_f}) \) is the line broadening function. For a general \( n \)-photon absorption process it is usually described by a Lorentzian function

\[ L(n\omega, \omega_{g'v'f_f}) = \frac{1}{\pi} \frac{\Gamma_{f_f}}{(\omega_{g'v'f_f} - n\omega)^2 + \Gamma_{f_f}^2} \]  \hspace{1cm} (3.3)

or by a Gaussian function

\[ G(n\omega, \omega_{g'v'f_f}) = \frac{1}{\sqrt{2\pi}\Gamma_{f_f}} e^{-\left((\omega_{g'v'f_f} - n\omega)^2 / 2\Gamma_{f_f}^2\right)} \]  \hspace{1cm} (3.4)

The last row of Eq. (3.1) yields the OPA observable in units of dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) starting from circular frequencies and transition dipole moments given in atomic units.

The oscillator strength, defined as

\[ \delta_{OPA} = \frac{2\omega_{g'v'f_f}}{3} \sum_{\alpha} |\mu_{\alpha}^{g'v'f_f}|^2 \]  \hspace{1cm} (3.5)

is often used.

Two-photon absorption:

The TPA cross section \( \sigma_{TPA} \), for two photons of equal frequency \( \omega_1 = \omega_2 = \omega \), is given in a form directly comparable to experiment by the expression

\[ \sigma_{TPA} = \frac{4\pi^3 a_0^5 \alpha}{15c_0} \omega^2 \sum_{f_f} \sum_{v_x, v_y} p_{v_x} g(2\omega, \omega_{g'v'f_f}) \times \delta_{TPA}^{g'v'f_f} (\omega) \]  \hspace{1cm} (3.6)

Here \( \alpha \) is the fine structure constant, \( a_0 \) is Bohr radius, and the orientationally averaged two-photon probability \( \delta_{TPA}^{g'v'f_f} (\omega) \) is given by

\[ \delta_{TPA}^{g'v'f_f} (\omega) = \sum_{a\beta} (F \times S_{a\alpha}^{g'v'f_f} S_{\beta\beta}^{g'v'f_f} + G \times S_{a\beta}^{g'v'f_f} S_{\beta\alpha}^{g'v'f_f} + H \times S_{a\beta}^{g'v'f_f} S_{\beta\alpha}^{g'v'f_f}) \]  \hspace{1cm} (3.7)

where \( S_{a\beta}^{g'v'f_f} \) is the two-photon transition matrix element, which is defined by the Sum-Over-State (SOS) expression as
### 3.1 Linear and nonlinear absorption

\[
S_{a_{ij}b_{ij}}^{g_{ij}f_{ij}}(\omega) = \sum_{k_{ij}} \left[ \frac{\langle g_{ij}v_{k} | \mu_{a} | k_{ij} \rangle \langle k_{ij} | \mu_{b} | f_{ij} \rangle}{\omega_{k_{ij}} - \omega} + \frac{\langle g_{ij}v_{k} | \mu_{b} | k_{ij} \rangle \langle k_{ij} | \mu_{a} | f_{ij} \rangle}{\omega_{k_{ij}} - \omega} \right] \quad (3.8)
\]

\( F \), \( G \) and \( H \) assume values of 2, 2, 2 for linearly and -2, 3, 3 for circularly polarized beams, respectively.

The resulting unit of \( \sigma_{TPA} \) is \( \text{cm}^4 \text{s photon}^{-1} \text{molecule}^{-1} \) (\( 10^{-50} \text{ cm}^4 \text{s photon}^{-1} \text{molecule}^{-1} = 1 \text{ Göppert-Mayer, 1 GM} \) starting from \( a_{0} \) and \( c_{0} \) given in CGS units, and circular frequencies and two-photon transition probabilities given in atomic units.

**Three-photon absorption:**

Though being a fifth-order property, the 3PA cross section can be obtained from the third-order transition matrix elements (here given for three photons of identical circular frequency \( \omega_1 = \omega_2 = \omega_3 = \omega \))

\[
T_{abc}^{g_{ij}f_{ij}} = \sum_{m_{ij},m_{ij}} \sum_{\rho_{a,b,c}} \langle g_{ij}v_{m} | \mu_{a} | m_{ij}v_{m} \rangle \langle m_{ij}v_{m} | \mu_{b} | m_{ij}v_{m} \rangle \langle m_{ij}v_{m} | \mu_{c} | f_{ij} \rangle \quad (3.9)
\]

where \( \sum_{\rho_{a,b,c}} \) denotes the intrinsic permutation operator with respect to the Cartesian indices \( a, b, \) and \( c \). The 3PA cross section, \( \sigma_{TPA} \), relates to the three-photon transition probability, \( \delta_{TPA}^{g_{ij}f_{ij}}(\omega) \), by

\[
\sigma_{TPA} = \frac{4\pi^4\alpha_{a_{0}}^8\omega^3}{3c_{a_{0}}^2} \sum_{g_{ij}f_{ij}} p_{ij} g(3\omega, \omega_{g_{ij},f_{ij}}) \times \delta_{TPA}^{g_{ij}f_{ij}}(\omega) \quad (3.10)
\]

The resulting SI unit for the cross section is \( \text{cm}^6 \text{s}^2 \text{ photon}^{-2} \text{ molecule}^{-1} \).

The orientationally averaged values for the 3PA probability \( \delta_{TPA}^{g_{ij}f_{ij}} \) for linearly (\( L \)) and circularly polarized light (\( C \)) can be written as\(^{29}\)

\[
\delta_{LP}^{g_{ij}f_{ij}} = \frac{1}{35} (2\delta_{a} + 3\delta_{f}) \quad (3.11)
\]

\[
\delta_{CP}^{g_{ij}f_{ij}} = \frac{1}{35} (5\delta_{a} - 3\delta_{f}) \quad (3.12)
\]

where

\[
\delta_{f} = \sum_{i,j,k} T_{ij}^{g_{ij}f_{ij}} T_{kij}^{g_{ij}f_{ij}} \quad (3.13)
\]
3 Molecular optical properties

\[ \delta_G = \sum_{i,j,k} T_{ij}^{\mu_1 \nu_1} T_{jk}^{\mu_2 \nu_2} \]  

(3.14)

For some special molecular systems, such as one dimensional \( \pi \) conjugated charge-transfer (CT) molecules, the nonlinear optical properties mainly depend on a few charge transfer states. An approximation to only include the influence of the most important CT states starting from the SOS expression is known as the so-called few-state models. Presently, the most often used one is the two-state (TS) model. In paper I we examined the two-state model to calculate the 3PA cross section. If only the contributions from two states are taken into account, the dominant component of the third-order transition moment \( T_{zzz}^{TS} \) along the molecular \( z \) axis, can be written as

\[ T_{zzz}^{TS} = 27 \left[ \frac{2 \mu_0^{gf} (\mu_0^{gg} - \mu_0^{ff})^2}{2\omega_j^2} \right] \]

\[ = 27 \left[ \mu_0^{gf} \frac{2(\Delta \mu_j)^2 - (\mu_0^{gf})^2}{2\omega_j^2} \right] \]  

(3.15)

Under these assumptions, the total three-photon absorption probability \( \delta_{SPA}^{TS} \) for linearly polarized light becomes

\[ \delta_{SPA}^{TS} = \frac{(T_{zzz}^{TS})^2}{7} \]  

(3.16)

3.2 Linear and nonlinear circular dichroism

3.2.1 Introduction

![Graphical representation of (a) one-photon circular dichroism, (b) one of possible transition schemes for two-photon circular dichroism.](image)

*Fig. 3.2 Graphical representation of (a) one-photon circular dichroism, (b) one of possible transition schemes for two-photon circular dichroism.*
3.2 Linear and nonlinear circular dichroism

One-photon circular dichroism, also known as electronic circular dichroism (ECD)\textsuperscript{30,31}, is the difference between the one-photon absorption of left and right circularly polarized lights. It is strictly allied to chirality, and is widely used to assign molecular absolute configurations due to the fact that enantiomers of a chiral molecule yield mirror-imaged (hence opposite sign at each frequency) ECD spectra. ECD may be regarded as one of the most powerful techniques for stereochemical analysis: it is sensitive to the absolute configuration as well as to conformational features, which are often completely obscured in the ordinary absorption spectrum.

Two-photon circular dichroism (TPCD)\textsuperscript{27} arises from the difference in two-photon absorption of left and right circularly polarized lights. It combines the advantages of TPA, i.e. 3D confocality, reduced frequency, enhanced penetration power \textit{etc.},\textsuperscript{32} with the fingerprinting capabilities of ECD. Studies on ECD have been available both in theory and experiment for many years. Great interest on TPCD has just recently been revived thanks to the development of new theoretical approaches.\textsuperscript{33-36} Experimental verification has proven to be rather challenging. Very recently, Hernández and coworkers made a remarkable progress in the experimental measurement of TPCD by developing a double L-scan technique,\textsuperscript{37} which can yield well resolved TPCD and two-photon linear-circular dichroism (TPLCD, defined essentially as the difference between circularly and linearly polarized TPA) spectra for chiral samples in solution. Progresses in both theoretical modeling and experiment could therefore make of TPCD a promising tool for various applications in biology, pharmaceutical, medical and nanoscience.

3.2.2 Theoretical description

In the following we briefly give the formulae for the calculation of both one- and two-photon circular dichroism, fully taking into account both electronic and vibrational contributions.

\textbf{One-photon circular dichroism:}
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The anisotropy of the molar absorptivity \( \varepsilon (\omega) \), defined as the difference between the absorptivity for left (L) and right (R) circularly polarized lights, \( \Delta \varepsilon_{\text{ECD}}(\omega) = \varepsilon_L(\omega) - \varepsilon_R(\omega) \), can be written as

\[
\Delta \varepsilon_{\text{ECD}}(\omega) = \frac{16 \times (2\pi)^2 \times \omega \times \hbar}{9 \times 1000 \times \ln(10) \times (4\pi\varepsilon_0) \times h c} \sum_{\nu_g,\nu_f} \sum_{f} p_{\nu_g} g(\omega, \omega_{\nu_g,\nu_f}) \times R_{\text{ECD}}^{\nu_g,\nu_f}
\]

\[
\approx 2.73719 \times 10^{-2} \times \omega \times \sum_{\nu_g,\nu_f} p_{\nu_g} g(\omega, \omega_{\nu_g,\nu_f}) \times R_{\text{ECD}}^{\nu_g,\nu_f}
\]

(3.17)

The ECD rotatory strength, \( R_{\text{ECD}}^{\nu_g,\nu_f} \), is proportional to the imaginary part of the scalar product of the electric dipole (\( \hat{\mu} \)) and magnetic dipole (\( \hat{m} \)) transition moments,

\[
R_{\text{ECD}}^{\nu_g,\nu_f} = \frac{3}{4} \sum_{a=x,y,z} \text{Im} \left[ \mu_a^{\nu_g,\nu_f} m_a^{\nu_g,\nu_f,*} \right]
\]

(3.18)

The last row of Eq. (3.17) yields the ECD observable in unit of \( \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \) starting from circular frequencies and transition dipole moments given in atomic units.

Two-photon circular dichroism:

TPCD was theoretically described by Tinoco Jr. in the 1970s,27 see also Power,39-41 and Andrews.42 In Ref. 33 definitions were given and a computational approach to the ab initio determination of TPCD spectra was discussed. In Ref. 34 a selection of origin invariant approaches was presented. The one based on Tinoco’s original formulation, labeled as the “TI” approach, is employed throughout the present thesis. For two photons of equal frequency \( \omega \), starting from the expressions given in Refs. 27 and 34, the TPCD, \( \Delta \delta_{\text{TPCD}}(\omega) = \delta_L(\omega) - \delta_R(\omega) \), can be written as

\[
\Delta \delta_{\text{TPCD}}(\omega) = \frac{4 (2\pi)^2 \times \omega^5 \times \hbar}{15 c \times (4\pi\varepsilon_0)^2} \sum_{\nu_g,\nu_f} \sum_{f} p_{\nu_g} g(2\omega, \omega_{\nu_g,\nu_f}) \times R_{\text{TPCD}}^{\nu_g,\nu_f}
\]

\[
\approx 4.67299 \times 10^{-32} \times \omega^2 \times \sum_{\nu_g,\nu_f} p_{\nu_g} g(2\omega, \omega_{\nu_g,\nu_f}) \times R_{\text{TPCD}}^{\nu_g,\nu_f}
\]

(3.19)

The circular frequency is assumed throughout to be the same for the two absorbed photons. \( R_{\text{TPCD}}^{\nu_g,\nu_f} \) is the TPCD rotatory strength, and it can be obtained in an origin invariant form, independent of the completeness of the one-electron basis set employed in the calculation, as34
3.2 Linear and nonlinear circular dichroism

\[ R_{\text{TPCD}}^{(\nu_f \nu_i)} = -b_1 B_1^{\text{TI}}(\omega) - b_2 B_2^{\text{TI}}(\omega) - b_3 B_3^{\text{TI}}(\omega) \]  \hspace{1cm} (3.20)

The results presented in this work correspond to an experimental setup with two left circularly polarized beams propagating parallel to each other. For this arrangement, \( b_1 = 6, \) and \( b_2 = b_3 = 2.7 \)

\[ B_1^{\text{TI}}(\omega) = \frac{1}{\omega^3} \sum_{\rho \sigma} M_{\rho \sigma}^{(\nu_f \nu_i)}(\omega) P_{\rho \sigma}^{(\nu_f \nu_i)}(\omega) \]  \hspace{1cm} (3.21)

\[ B_2^{\text{TI}}(\omega) = \frac{1}{2\omega^3} \sum_{\rho \sigma} T^{(\nu_f \nu_i)}_{\rho \sigma}(\omega) P_{\rho \sigma}^{(\nu_f \nu_i)}(\omega) \]  \hspace{1cm} (3.22)

\[ B_3^{\text{TI}}(\omega) = \frac{1}{\omega^3} \sum_{\rho \sigma} M_{\rho \sigma}^{(\nu_f \nu_i)}(\omega) P_{\rho \sigma}^{(\nu_f \nu_i)}(\omega) \]  \hspace{1cm} (3.23)

Summations in above equations run over Cartesian (\( x, y, z \)) components. The tensors \( P_{\alpha \beta}^{(\nu_f \nu_i)}(\omega), \) \( M_{\alpha \beta}^{(\nu_f \nu_i)}(\omega) \) and \( T_{\alpha \beta}^{(\nu_f \nu_i)}(\omega) \) are defined by the SOS expressions:

\[ P_{\alpha \beta}^{(\nu_f \nu_i)}(\omega) = \sum_{k \nu} \left[ \langle g_{\nu i}, \mu_{\alpha}^{\nu} | k \nu \rangle \langle k \nu, \mu_{\beta}^{\nu} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} + \left[ \langle g_{\nu i}, \mu_{\beta}^{\nu} | k \nu \rangle \langle k \nu, \mu_{\alpha}^{\nu} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} \]  \hspace{1cm} (3.24)

\[ M_{\alpha \beta}^{(\nu_f \nu_i)}(\omega) = \sum_{k \nu} \left[ \langle g_{\nu i}, \mu_{\alpha}^{\nu} | k \nu \rangle \langle k \nu, m_{\beta} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} + \left[ \langle g_{\nu i}, m_{\beta} | k \nu \rangle \langle k \nu, \mu_{\alpha}^{\nu} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} \]  \hspace{1cm} (3.25)

\[ T_{\alpha \beta}^{(\nu_f \nu_i)}(\omega) = \varepsilon_{\rho \sigma} \sum_{k \nu} \left[ \langle g_{\nu i}, \mu_{\alpha}^{\nu} | k \nu \rangle \langle k \nu, \mu_{\beta}^{\nu} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} + \left[ \langle g_{\nu i}, \mu_{\beta}^{\nu} | k \nu \rangle \langle k \nu, \mu_{\alpha}^{\nu} | f \nu \rangle \right] \frac{1}{\omega_{k \nu} - \omega} \]  \hspace{1cm} (3.26)

Here the summations run over all the intermediate electronic (\( |k\rangle \)) and vibrational (\( |\nu_k\rangle \)) states. \( \varepsilon_{\alpha \beta \gamma \delta} \) is the Levi Civita alternating tensor, \( \mu_{\alpha}^{\nu} \) is the \( \alpha \) component of the dipole velocity operator, defined as

\[ \mu_{\alpha}^{\nu} = \sum_{i} \frac{q_i}{m_i} p_{\alpha i} \]  \hspace{1cm} (3.27)

and \( T_{\alpha \beta}^{+} \) is the \( \alpha \beta \) component of the mixed length-velocity form of the quadrupole operator

\[ T_{\alpha \beta}^{+} = \sum_{i} \frac{q_i}{m_i} (p_{\alpha i} r_{\beta i} + r_{\alpha i} p_{\beta i}) \]  \hspace{1cm} (3.28)

The last row of (3.19) yields the TPCD in unit of cm\(^4\) sec mol\(^{-1}\) starting from circular frequencies and two-photon rotatory strengths given in atomic units. Divided by
Avogadro’s number and multiplied by $10^{50}$ the observables can be obtained in often used unit of GM (Göppert-Mayer).

The application of the SOS method to calculate the tensors in the TPA and TPCD expressions is limited due to its requirement of the knowledge of all excited states, which makes the *ab initio* calculations very expensive. In practice, the SOS expression is truncated to include only the dominating states and the convergence rates with respect to the inclusion of states in summation are known to be slow. Nowadays modern response theory has become the most accurate and rigorous method, and it is used throughout the whole thesis. In section 3.3 we give a brief introduction of response theory.

### 3.3 Response Theory

Modern response theory\(^43\) is a way of formulating time-dependent perturbation theory. As the name implies, response functions describe how a system responds to an external perturbation. The main advantage is that the explicit summation over excited states is substituted by the solution of a set of coupled response equations. The properties studied in the present thesis can be identified from appropriate response functions or their residues.

#### 3.3.1 Response functions

The Hamiltonian operator of a molecular system which experiences an external field can be expressed as

$$H = H_0 + V(t) \quad \text{(3.29)}$$

where $H_0$ is the time-independent Hamiltonian of the unperturbed system, and $V(t)$ is the time-dependent perturbation.

In the frequency domain, the perturbation operator can be written as

$$V(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega t} d\omega \quad \text{(3.30)}$$

where $\epsilon$ is a small positive infinitesimal that ensures the field vanishes at $t = -\infty$. 

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3.3 Response Theory

The average value of time-dependent operator $A$ can be expanded in the series

$$
\langle A(t) \rangle = \langle A \rangle_0 + \int_{-\infty}^{\infty} \int_{0}^{1} \left( \langle A; V^{\omega} \rangle \right) e^{-i(a_0 + \omega \epsilon)} \, d\omega_1
$$

$$
+ \frac{1}{2!} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \langle A; V^{\omega_1}, V^{\omega_2} \rangle \right) e^{-i(a_0 + \omega_1 + \omega_2)} \, d\omega_1 d\omega_2
$$

$$
+ \frac{1}{3!} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle \right) e^{-i(a_0 + \omega_1 + \omega_2 + \omega_3)} \, d\omega_1 d\omega_2 d\omega_3 + \cdots
$$

(3.31)

where $\langle A; V^{\omega} \rangle$, $\langle A; V^{\omega_1}, V^{\omega_2} \rangle$, and $\langle A; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \rangle$ denote the linear, quadratic, and cubic response functions, respectively. From these response functions, all time-dependent properties of the molecule can be determined. For example, when $A$ denotes the electric dipole operator, the total dipole moment induced by the external field may be expressed by response functions which correspond to, for instance, the polarizability and hyperpolarizabilities of the molecule.

$$
\alpha_{ij}(\omega_1; \omega_2) = -\left\langle \mu_j, \mu_i \right\rangle_{\omega_1}
$$

$$
\beta_{ijkl}(\omega_1, \omega_2; \omega_1, \omega_2) = -\left\langle \mu_j, \mu_i, \mu_k \right\rangle_{\omega_1, \omega_2}
$$

$$
\gamma_{ijkl}(\omega_1 - \omega_2, \omega_3; \omega_1, \omega_2, \omega_3) = -\left\langle \mu_j, \mu_i, \mu_k, \mu_l \right\rangle_{\omega_1, \omega_2, \omega_3}
$$

(3.32)

For exact states these response functions can be given as

$$
\left\langle \left( V^{\omega_1}; V^{\omega_2} \right) \right\rangle_{\omega_1} = -\text{P}(0,1) \sum_n \frac{\langle 0 | V^{\omega_1} | n \rangle \langle n | V^{\omega_2} | 0 \rangle}{\omega_n - \omega_1}
$$

(3.33)

for the linear response function, and

$$
\left\langle \left( V^{\omega_1}; V^{\omega_2} \right) \right\rangle_{\omega_1, \omega_2} = -\text{P}(0,1,2) \sum_{nm} \frac{\langle 0 | V^{\omega_1} | n \rangle \langle n | (V^{\omega_2} - \langle 0 | V^{\omega_2} | 0 \rangle) | m \rangle \langle m | V^{\omega_2} | 0 \rangle}{(\omega_n + \omega_m)(\omega_2 - \omega_m)}
$$

(3.34)

for the quadratic response function, and

$$
\left\langle \left( V^{\omega_1}, V^{\omega_2}, V^{\omega_3} ; V^{\omega_1}, V^{\omega_2}, V^{\omega_3} \right) \right\rangle_{\omega_1, \omega_2, \omega_3} = -\text{P}(0,1,2,3)
$$

$$
\times \sum_{klm} \frac{\langle 0 | V^{\omega_1} | k \rangle \langle k | (V^{\omega_2} - \langle 0 | V^{\omega_2} | 0 \rangle) | l \rangle \langle l | (V^{\omega_3} - \langle 0 | V^{\omega_3} | 0 \rangle) | m \rangle \langle m | V^{\omega_3} | 0 \rangle}{(\omega_k + \omega_l)(\omega_2 + \omega_3 - \omega_l)(\omega_3 - \omega_m)}
$$

$$
+ \sum_k \frac{\langle 0 | V^{\omega_1} | k \rangle \langle k | V^{\omega_2} | 1 \rangle \langle 1 | V^{\omega_3} | 0 \rangle}{\omega_1 - \omega_k} \sum_{ij} \frac{\langle 0 | V^{\omega_1} | i \rangle \langle i | V^{\omega_2} | 0 \rangle}{\omega_j - \omega_i}
$$

(3.35)
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for the cubic response function. \( \omega_b = - (\omega_1 + \omega_2 + \cdots) \), and \( P \) is the intrinsic permutation operator.

### 3.3.2 Residues of response functions

In the present section, we will show that the linear and nonlinear absorption and circular dichroism properties can be evaluated from the residues of response functions.

The linear response function has poles at frequencies equal to plus or minus the excitation energies of the unperturbed system. When \( V^{eb} \) refers to the electric dipole moment in Eq. (3.33), the corresponding residues

\[
\lim_{\omega_i \to \omega_f} (\omega_i - \omega_f) \langle \mu_i; \mu_j \rangle = - \langle 0 \mid \mu_i \mid f \rangle \langle f \mid \mu_j \mid 0 \rangle
\]

(3.36)

\[
\lim_{\omega_i \to -\omega_f} (\omega_i + \omega_f) \langle \mu_i; \mu_j \rangle = \langle 0 \mid \mu_i \mid f \rangle \langle f \mid \mu_j \mid 0 \rangle
\]

(3.37)

thus provide information about the excitation energies from the initial state \( |0\rangle \) to the final state \( |f\rangle \) and the corresponding transition dipole moments. It can be used to describe the OPA process.

If we replace \( \mu_i \) with \( m_i \), the corresponding residues of the linear response function are proportional to the rotational strength of the ECD process.

When \( V^{eb} \) refers to the electric dipole moment in Eq. (3.34), the single residue of the quadratic response function gives the information on the TPA transition matrix elements

\[
\lim_{\omega_i \to \omega_f} (\omega_i - \omega_f) \langle \mu_i; \mu_j, \mu_k \rangle = - \sum_n \frac{\langle 0 \mid \mu_i \mid n \rangle \langle n \mid (\mu_j - \langle 0 \mid \mu_j \mid 0 \rangle \mid f \rangle}{\omega_n - \omega_i}
\]

(3.38)

\[
+ \frac{\langle 0 \mid \mu_j \mid n \rangle \langle n \mid (\mu_i - \langle 0 \mid \mu_i \mid 0 \rangle \mid f \rangle}{\omega_n - \omega_i} \langle f \mid \mu_k \mid 0 \rangle
\]

where \( \omega_i + \omega_2 = \omega_f \). It is noted that the two-photon absorption cross section is an observable which is described by the cubic response function. The quadratic response function may only be used to identify the formal expression for the TPA matrix element. However, this turns out to be important since it makes calculations much easier.
3.3 Response Theory

If we replace \((\mu_i, \mu_j)\) respectively with \((\mu_i^p, m_j)\), \((\mu_i^p, \mu_j^p)\), and \((T_i^+, \mu_j^p)\), the single residues of the appropriate quadratic response functions give the tensors \(M^p, P^p, T^+\) entering the expression of the rotatory strength of TPCD.

From the double residue of the quadratic response function, one can deduce the transition dipole moments between excited states. The transition matrix element between state \(|i\rangle\) and state \(|f\rangle\) can be evaluated at both the poles \(\omega_2 = \omega_{ij}\) and \(\omega_1 = -\omega_f\):

\[
\lim_{\omega_1 \to -\omega_f} (\omega_1 + \omega_f) \left( \lim_{\omega_2 \to \omega_{ij}} (\omega_2 - \omega_{ij}) \langle \mu_i; \mu_j, \mu_k \rangle \right)_{\omega_1, \omega_2}
\]

\[
= -\langle 0 | \mu_i | f \rangle \langle f | (\mu_j - \langle 0 | \mu_j | 0 \rangle) | i \rangle \langle i | \mu_k | 0 \rangle
\]

When \(V^{\text{rb}}\) refers to the electric dipole moment in Eq. (3.35), from the single residue of the cubic response function

\[
\lim_{\omega_1 \to -\omega_f} (\omega_1 + \omega_f) \langle \mu_i; \mu_j, \mu_k, \mu_l \rangle_{\omega_1, \omega_2, \omega_3}
\]

\[
= \sum_{\mu, n, m > 0} \frac{\langle 0 | \mu_i | m \rangle \langle \mu_k - \langle 0 | \mu_k | 0 \rangle | n \rangle \langle \mu_j - \langle 0 | \mu_j | 0 \rangle | f \rangle}{(\omega_0 + \omega_m)(\omega_2 + \omega_k - \omega_m)} \]

\[
+ \frac{\langle 0 | \mu_i | f \rangle \langle f | \mu_j | 0 \rangle}{(\omega_h + \omega_f)} \sum_{\mu, n > 0} \frac{\langle 0 | \mu_i | n \rangle \langle n | \mu_j | 0 \rangle}{(\omega_j - \omega_n)}
\]

\[
+ \sum_m \frac{\langle 0 | \mu_i | m \rangle \langle m | \mu_j | 0 \rangle}{(\omega_h + \omega_m)(\omega_j - \omega_m)} \langle 0 | \mu_i | f \rangle \langle f | \mu_j | 0 \rangle
\]

one can identify the 3PA transition matrix elements in the same way the TPA matrix elements were determined from the quadratic response function. It is worth to note that the 3PA cross section is an observable determined by the fifth hyperpolarizability.

3.4 Solvent effects

Most current calculations of molecular optical properties only consider single isolated molecules, in most cases not directly related with the experiments carried out mostly in solution. A solvent environment can modify both the geometrical and the electronic structures of solvated molecules and it may have significant influence on optical properties. Therefore, it is highly relevant to apply theoretical methods that can effectively describe the effects of the solvents.
3 Molecular optical properties

3.4.1 Polarizable continuum model

Over the years, different models have been developed to fulfill different needs. Basically there are two fundamentally different ways to account for the solvent effects\textsuperscript{44}: the discrete and the continuum approaches.

Many discrete models have wide applications in practice, like Supermolecular approach, Molecular Mechanics, Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM), Molecular Dynamics (MD), just name a few of them. The Supermolecular model, describes the solute molecule and some of its neighboring solvent molecules together and all in a quantum mechanical manner, by which the specific short-range intermolecular interaction can be explicitly treated; In the Molecular Mechanics approach, the classical electrostatic interactions of an ensemble of molecules are evaluated between the charge distributions of the molecules (point charges, dipoles, etc); In QM/MM, one or a few molecules are treated quantum mechanically, while the surrounding molecules are described in the classical molecular mechanical way. Molecular dynamics (MD) treats a large part of the molecule motions by Newton’s classical equations. The theoretically or empirically fitted intermolecular potentials are used to model the trajectories of the molecules. A statistical averaging of the property over generated configurations is used.

Continuum models view the solvent environment as a homogenous dielectric continuum medium characterized by its dielectric constant \(\varepsilon\), while the solute molecule inside a cavity embedded in the continuum medium is described by quantum mechanics. The Onsager reaction field model, which is one of the earliest continuum models, simulates the molecule in solution as a classical point polarizable dipole in a spherical or a more generally ellipsoidal cavity surrounded by a dielectric continuum. The charge distribution of the solute polarizes the dielectric continuum, which in turn polarizes the solute charge distribution and at the end a stabilization is reached through an iterative procedure. Polarizable Continuum Model (PCM)\textsuperscript{45,46} is a commonly used model which applies such a self-consistent procedure. It is worth to note that the short-range interactions such as hydrogen bonding are not well described in continuum models, and the so-called semi-continuum model which combines the supermolecular model and PCM can be used to cover this problem.
3.4 Solvent effects

PCM has been applied in the present thesis to take into the effect of the solvent surroundings. PCM is based on a molecular-shaped cavity, whose size is defined through interlocking spheres centered on the solute atoms with appropriate radii. In this way, the cavity models the solute in a more realistic way than a single spherical cavity was used. A schematic representation of a cavity is given in Fig. 3.3.

![Fig. 3.3 Graphical representation of the PCM cavity (From Ref. 46)](image)

The cavity surface, which is also called Solvent Excluded Surface (SES), defined by the van der Waals-spheres centered at atomic positions, represents the nearest distance the solvent molecules can get close to the solute. It is used for the calculation of the electrostatic contribution to the free energy. The Solvent Accessible Surface (SAS), which is formed on basis of SES but with additional consideration of the solvent radius, is used to calculate the dispersion-repulsion contribution to the solution free energy. Localization and calculation of the surface charges is obtained through a systematic division of the spherical surface in small regions (tesserae) of known area and the calculation of one point charge per surface element.

To model electron transitions in the PCM formulism, the non-equilibrium formulism was used in order to take into account the fact that the reaction of the solvent to a fast change of the solute charge distribution is not instantaneous. In a fast process, the time required for a change in the solute charge distribution is much smaller than the time needed by the solvent to relax towards a new equilibrium state. A scheme of a non-equilibrium process is shown in Fig. 3.4, where one-photon absorption (left red line) and emission (right blue line) are taken as examples.
3 Molecular optical properties

The apparent surface charge can be partitioned into two components: a dynamic \((q^d)\) one, which can be calculated by making use of the optical dielectric constant \(\varepsilon_{\text{opt}}\), is connected to the polarization of the electronic clouds and considered to be instantaneously equilibrated with the new density; an inertial part \((q^i)\), which can be calculated from the static dielectric constant \(\varepsilon_{\text{sta}}\), is connected with the solvent molecular motions and considered to be kept frozen to the corresponding density of the initial reference state and needs a longer time to come to equilibrium.

3.4.2 Local field corrections

The solvent models mentioned above describe the interaction between the solute and the solvents, without considering the effect from the external field. In that case, an induced field can be produced by the solvent molecules. This in turn screens the effects of the external field, results in the so-called local field effect. The system under investigation can be assumed to consist of polarizable entities, and when an external field is applied to the system, each entity induces a field. The field felt by one entity is termed as the local field (the combination of the external field and the sum of the induced fields from the other entities), and can be represented by a local field factor. However, the explicit expression for the local field factors depends on structural details of solvent and solute molecules and is very difficult to obtain. When employing a
spherical cavity, the local field factor $L$ can be expressed as a function of the optical dielectric constant $\varepsilon_{opt}$:\textsuperscript{47}

$$L = \frac{3n^2}{2n^2 + 1} = \frac{3\varepsilon_{opt}}{2\varepsilon_{opt} + 1}$$

(3.41)
3 Molecular optical properties
4. Vibronically resolved spectra

Theoretical studies on electronic spectra that rest on the approximation of vertical excitations can only give a rough estimate for the band maximum of a transition and miss all the vibrational fine structures in a spectrum. This limitation prompts us to calculate vibronically resolved spectra, which is one of the most important subjects of the present thesis.

We first give the basic theoretical background, with introductions mainly focused on two approximations applied in the present thesis: Adiabatic and harmonic approximations. Afterward, we describe the basic computational approach for computing various vibronically resolved spectra with two different vibronic models.

4.1 Adiabatic approximation

The molecular stationary states can be found from the time-independent Schrödinger equation

\[ H(q,Q)\Psi(q,Q) = \varepsilon \Psi(q,Q) \]  

(4.1)

where the vibronic wavefunctions are represented by \( \Psi(q,Q) \), and the eigen-energies by \( \varepsilon \). The molecular Hamiltonian \( H(q,Q) \) is given by

\[ H(q,Q) = T(q) + T(Q) + U(q,Q) + V(Q) \]  

(4.2)

The set \( \{q_i\} \) and \( \{Q_j\} \) are respectively the electronic and nuclear coordinates, and \( T(q) \) and \( T(Q) \) are respectively the corresponding kinetic energies. \( U(q,Q) \) includes the potential energy of interactions between the electrons and between the electron and the nuclei, and \( V(Q) \) gives the potential energy of interaction between the nuclei. The exact solutions for Schrödinger equation cannot be obtained in practice when the Hamiltonian does not allow a separation of the variables \( q \) and \( Q \). Thus,
approximations have to be introduced to overcome this problem.

The electronic Hamiltonian can be obtained by setting the nuclear kinetic energy to be zero: $T(Q) = 0$,

$$H_e(q, Q) = T(q) + U(q, Q) \tag{4.3}$$

$H_e$ obviously depends on the nuclear coordinates $Q$ parametrically, from which we obtain the electronic Schrödinger equation

$$H_e(q, Q)\Phi_n(q, Q) = E_n(Q)\Phi_n(q, Q) \tag{4.4}$$

The electronic wavefunctions $\{\Phi_n(q, Q)\}$ form a complete basis in the electronic space for every nuclear configuration specified by $Q$. Therefore, the eigenfunctions of the total molecular Hamiltonian may be expanded in terms of these electronic wavefunctions

$$\Psi(q, Q) = \sum_n \Phi_n(q, Q)\chi_n(Q) \tag{4.5}$$

where $\chi_n(Q)$ is the corresponding nuclear wavefunction.

Inserting Eqs. (4.2), (4.3), (4.4), and (4.5) into Eq. (4.1), multiplying on the left by $\Phi'_m(q, Q)$ and integrating over the electronic coordinates, we can get

$$[T(Q) + V(Q) + E_n(Q)]\chi_n(Q) + \sum_m \Lambda_{mn}\chi_m(Q) = \epsilon_n\chi_n(Q) \tag{4.6}$$

where $\Lambda_{mn}$ represent the nonadiabatic couplings describing the dynamical interaction between the electronic and nuclear motion.

$$\Lambda_{mn} = \langle \Phi_n | T(Q) | \Phi_m \rangle + \sum_{m,n} \langle \Phi_n | T_n | \Phi_m \rangle - \sum_k \langle \Phi_n | \frac{\partial}{\partial Q_k} | \Phi_m \rangle \frac{\partial}{\partial Q_k} \tag{4.7}$$

Neglecting $\Lambda_{mn}$ is commonly called the *Born-Oppenheimer adiabatic* (BOA) approximation or briefly the *adiabatic approximation*. The above discussion also implies that as long as $\Lambda_{mn}$ is small, descriptions within the BOA approximation will be reliable. However, once $\Lambda_{mn}$ is sizeable, the adiabatic ansatz itself will become doubtful and an electronic multistate description may be needed. This is usually the case when $\Phi_n(q, Q)$ and $\Phi_n(q, Q)$ energies are close to degeneracy. Specifically, in the presence of conical intersections of the potential surfaces, the nonadiabatic couplings diverge and the adiabatic approximation becomes meaningless. From the above we may
4.1 Adiabatic approximation

expect that the adiabatic approximation is appropriate for an electronic state well separated energetically from all other electronic states. In the present thesis we assume that the nonadiabatic couplings can be neglected and the adiabatic approximation has been used throughout.

The adiabatic approximation assumes that the molecular Hamiltonian can be truly separable in the degrees of freedom defined by \( q \) and \( Q \). The total molecular wavefunction thus read as the product of the electronic and nuclear wavefunctions

\[
\Psi_n^{BOA}(q,Q) = \Phi_n(q,Q)\chi_n^{BOA}(Q). \tag{4.8}
\]

The electrons and the nuclei satisfy respectively their corresponding Schrödinger equations

\[
[T(q)+U(q,Q)]\Phi_n(q,Q) = E_n(Q)\Phi_n(q,Q) \tag{4.9}
\]

\[
[T(Q)+V(Q)+E_n(Q)]\chi_n^{BOA}(R) = \varepsilon_n^{BOA}\chi_n^{BOA}(Q). \tag{4.10}
\]

4.2 Harmonic approximation

4.2.1 Harmonic model

A simple ‘ball-and-spring’ model can be built for a molecule by replacing the binding electrons with elastic springs which hold the nuclei at approximately fixed distances and with approximately fixed valence angles. However, even the ‘ball-and-spring’ model is still too complicated to begin with and some other simplifications have to be introduced. It is convenient to assume that the atoms are point masses and that the springs holding them together are weightless and obey Hooke’s Law. This is the famous harmonic approximation which is also applied in the present work. In the harmonic approximation, the nuclear wavefunction can be written as the product of wavefunctions of all harmonic vibrational normal modes

\[
|\chi_n\rangle = \prod_a |n_a\rangle \tag{4.11}
\]

where \( |n_a\rangle \) represents the vibrational wavefunction of normal mode \( a \), while \( n_a \) denotes the quantum number of mode \( a \).
4 Vibronically resolved spectra

4.2.2 Normal coordinates and normal modes

The movements of the nuclei are described by the nuclear Schrödinger equation, and the expressions of the kinetic energy $T$ and the potential energy $V$ are needed. The kinetic energy will take a simple form by making use of a set of mass-weighted Cartesian coordinates $q_i = \sqrt{m_i} x_i$

$$T = \frac{1}{2} \sum_{i=1}^{3N} q_i^2$$  \hspace{1cm} (4.12)

The analytical form of the potential energy of the system is unfortunately not known. Nonetheless, for small displacements, the best we can do is to expand the potential energy in a power series of the displacement coordinates at the vicinity of the molecule equilibrium position where the first derivative is zero. We keep the terms up to the second derivative and get

$$V = V_0 + \frac{1}{2} \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{0} q_i q_j$$  \hspace{1cm} (4.13)

The expression above is complicated since it contains all possible cross-product terms, which prevent the vibrational problem from being separated into $3N$ problems. It is possible to introduce a new coordinate system in which both the potential and the kinetic energy term are diagonal. These new coordinates, known as ‘normal coordinates’, can be obtained by a linear transformation of mass-weighted Cartesian coordinates. This means that each normal coordinate is a linear combination of the $3N$ Cartesian coordinates

$$Q_k = \sum_{i=1}^{3N} l'_{ki} q_i$$  \hspace{1cm} (4.14)

For each normal coordinate, the molecule undergoes a simple motion in which all the nuclei move in phase with the same frequency but with different amplitudes. In other words, all the nuclei will pass through the equilibrium positions at the same time, reach their maximum displacement in a given direction, pass again through the equilibrium positions, reach their maximum displacement in the opposite direction and so forth. A mode of motion of this kind is called a ‘normal mode’ of vibration, and the frequency associated with it is called a “normal or fundamental frequency” of vibration.
4.2 Harmonic approximation

Diagonalization of the potential matrix yield 6 (or 5 for linear molecules) modes with zero frequency corresponding to the translations and rotations of the molecule.

In the normal coordinate system, the potential energy surface and the kinetic energy term of a molecular system can be respectively written as

\[ V = V_0 + \frac{1}{2} \sum_a \omega_a^2 Q_a^2, \quad T = \frac{1}{2} \sum_a \dot{Q}_a^2 \]  

(4.15)

4.3 Theory for vibronically resolved spectra

4.3.1 General formulism

As discussed in Chapter 3, OPA is related with the electric transition dipole moment, \( \mu_{\alpha}^{gf} \); ECD with \( \mu_{\alpha}^{gf} \) and also magnetic transition dipole moment \( m_{\alpha}^{gf} \); TPA with the two-photon transition matrix element \( S_{\alpha\beta}^{gf} \); TPCD with the two-photon transition tensors \( M_{\alpha\beta}^{gf}, P_{\alpha\beta}^{gf}, T_{\alpha\beta}^{gf} \). In the following we give the basic formulism to introduce the contributions from the vibrational states into the tensors mentioned above.

**One-photon processes:**

We have

\[ \mu_{\alpha}^{gf} = \langle g | \mu_{\alpha} | f \rangle \]  

(4.16)

corresponding to a transition between the initial state \( | g \rangle \) and a final state \( | f \rangle \), where \( | g \rangle \) and \( | f \rangle \) label the vibrational states of respectively the electronic states \( | g \rangle \) and \( | f \rangle \). In the frame of harmonic approximation, the vibrational states are direct products of 1D state for each mode, \( | v_{\nu} \rangle = | v_{1,\nu} \rangle \otimes | v_{2,\nu} \rangle \cdots \otimes | v_{N,\nu} \rangle \), where \( v_{\alpha,\nu} \) is the quantum number of \( | v_{\alpha,\nu} \rangle \) and the vector \( v_{\nu} \) is written as \( v_{\nu} = (v_{1,\nu}, v_{2,\nu}, \cdots, v_{N,\nu}) \).

Applying the BOA approximation in Eq. (4.16), we can obtain
4 Vibronically resolved spectra

\[ \mu_{\alpha}^{V,f,v_f} = \langle v_f | \mu_{\alpha}(Q) | v_f \rangle \]  

(4.17)

where \( Q \) is the set of normal coordinates and \( \mu_{\alpha}(Q) \) is the so-called electronic transition dipole moment. The latter can be expanded in a Taylor series with respect to the normal coordinates of the ground electronic state \( ^gQ \) around the equilibrium geometry \( ^gQ_0 \):

\[ \mu_{\alpha}^e(Q) = \mu_{\alpha}^e(^gQ_0) + \sum_a \frac{\partial \mu_{\alpha}^e(\omega, ^gQ)}{\partial ^gQ_a} ^gQ_a + \ldots \]  

(4.18)

Inserting this expansion to Eq. (4.17), limited to the first two terms, it yields

\[ \mu_{\alpha}^{V,f,v_f} = \mu_{\alpha}^e(^gQ_0) \langle v_g | v_f \rangle + \sum_a \frac{\partial \mu_{\alpha}^e(\omega, ^gQ)}{\partial ^gQ_a} \langle v_g | ^gQ_a | v_f \rangle \]  

(4.19)

Similarly we can also obtain an expression for the magnetic dipole operator

\[ m_{\alpha}^{V,f,v_f} = m_{\alpha}^e(^gQ_0) \langle v_g | v_f \rangle + \sum_a \frac{\partial m_{\alpha}^e(\omega, ^gQ)}{\partial ^gQ_a} \langle v_g | ^gQ_a | v_f \rangle \]  

(4.20)

The first quantity on the right side is the electronic transition moment of the initial state at the equilibrium position of the ground electronic state, multiplied by the Franck-Condon (FC) overlap. The second term arises from the vibronic coupling between different electronic states and it yields the so-called Herzberg-Teller (HT) contribution. Here we briefly recall the “borrowing mechanism” of the HT term, which could play important role for the forbidden transitions. The derivative of the electronic transition dipole moment can be written as

\[ \left( \frac{\partial \mu_{\alpha}^e}{\partial ^gQ_a} \right)^e_{\Phi \Phi} = \left( \langle \Phi_g | \mu_{\alpha} | \Phi_f \rangle \right)^e_{\Phi \Phi} \]

\[ = \left( \langle \Phi_g | \frac{\partial \Phi_f}{\partial ^gQ_a} | \Phi_f \rangle \right)^e_{\Phi \Phi} + \left( \langle \Phi_g | \mu_{\alpha} | \Phi_f \rangle \right)^e_{\Phi \Phi} \]  

(4.21)

since \( \langle \Phi_g | \frac{\partial \mu_{\alpha}}{\partial ^gQ_a} | \Phi_f \rangle \)^e_{\Phi \Phi} = 0 \) for electronic transitions. The derivatives of the electronic wavefunctions can be expanded as
4.3 Theory for vibronically resolved spectra

\[
\left( \frac{\partial \Phi_n}{\partial \xi Q_a} \right)_{\xi Q_a} = - \sum_{i \neq n} \left( \frac{\langle \Phi_i | \partial H_M / \partial \xi Q_a | \Phi_n \rangle}{E_i - E_n} \right)_{\xi Q_a} \Phi_i \tag{4.22}
\]

where \( H_M \) is the electronic Hamiltonian, \( E_i \) and \( E_n \) are the electronic eigenvalues evaluated at \( \xi Q_a \).

As we can see from Eq. (4.22), when the energy separation between the interacting states is large (i.e. \( E_i - E_n \) is large), the HT contribution will be very small since large energy separations hamper the coupling between the states. Therefore, the general behavior of the HT term can be rationalized by inspecting the layout of the excited state manifold. The presence of other states close by in energy with large intensities is the necessary pre-condition for a strong HT contribution of a given excited state.

**Two-photon processes:**

The two-photon transition matrix element is defined by the sum-over-state expression, \(^{44}\)

\[
S_{\alpha\beta}^{e, f_{ij}}(\omega) = \sum_{k \nu} \left[ \left\langle g_{\nu} | \mu_{\alpha} | k \nu \rangle \left\langle k \nu | \mu_{\beta} | f_{ij} \right\rangle + \left\langle g_{\nu} | \mu_{\beta} | k \nu \rangle \left\langle k \nu | \mu_{\alpha} | f_{ij} \right\rangle \right] \right] \tag{4.23}
\]

Here the summations run over all the intermediate electronic (\( |k \rangle \)) and vibrational (\( |\nu \rangle \)) states. Since the optical photon frequency \( \omega \) is far larger than any of the excitation energies of the vibrational states contributing significantly to the summation, we can assume \( \omega_{\nu} \approx \omega_k \). Therefore, using the closure relationship \( \sum |\nu \rangle \langle \nu \rangle \equiv 1 \), we have

\[
S_{\alpha\beta}^{e, f_{ij}}(\omega) = \left\langle v_{\beta} \left| S_{\alpha\beta}^{e}(\omega, Q) \right| v_{\alpha} \right\rangle \tag{4.24}
\]

where \( S_{\alpha\beta}^{e}(\omega, Q) \) is the electronic (vertical-transition) tensor, and

\[
S_{\alpha\beta}^{e}(\omega, Q) = \sum_k \left[ \left\langle g | \mu_{\alpha} | k \right\rangle \left\langle k | \mu_{\beta} | f \right\rangle + \left\langle g | \mu_{\beta} | k \right\rangle \left\langle k | \mu_{\alpha} | f \right\rangle \right] \tag{4.25}
\]

the summation includes the ground state \( |g \rangle \). The explicit dependence of \( S_{\alpha\beta}^{e}(\omega, Q) \) on the photon frequency introduces a severe complication with respect to the case of one-photon absorption. A very useful approximation is to compute \( S_{\alpha\beta}^{e}(\omega, Q) \) at the
4 Vibronically resolved spectra

fixed photon frequency $\omega_0$, corresponding to the two-photon vertical excitation (which roughly coincides with the maximum of the intensity). In this approach the dependence of the spectrum on the frequency is introduced by the line shape $g(2\omega, \omega_{g\nu_{e,f\nu'}})$ and by the $\omega^2$ prefactor (see Eq. (3.6)). Such an approximation may fail when resonances (or nearby resonances) exist with specific intermediate vibronic levels.

Expanding $S_{\alpha\beta}(\omega_0, \mathbf{Q})$ in a Taylor series with respect to the normal coordinates of the ground electronic state $^g\mathbf{Q}$ around the equilibrium geometry $^g\mathbf{Q}_0$, we have

$$S_{\alpha\beta}(\omega_0, \mathbf{Q}) = S_{\alpha\beta}(\omega_0, \mathbf{Q}_0) + \sum_a \frac{\partial S_{\alpha\beta}^e}{\partial \mathbf{Q}_a} (\omega_0, \mathbf{Q}_0) \mathbf{Q}_a + \ldots$$ (4.26)

and therefore in the limit of first order expansion we have

$$S_{\alpha\beta}^{e,f_{\nu'\nu}}(\omega_0) = S_{\alpha\beta}^e(\omega_0, \mathbf{Q}_0) \langle \nu'_g | \nu_f \rangle + \sum_a \frac{\partial S_{\alpha\beta}^e(\omega_0, \mathbf{Q})}{\partial \mathbf{Q}_a}(\nu'_g | \mathbf{Q}_a | \nu_f)$$ (4.27)

The tensors entering the TPCD expression are defined by the sum-over-state as

$$P_{\alpha\beta}^{e,f_{\nu'\nu}}(\omega_0) = P_{\alpha\beta}^e(\omega_0, \mathbf{Q}_0) \langle \nu'_g | \nu_f \rangle + \sum_a \frac{\partial P_{\alpha\beta}^e(\omega_0, \mathbf{Q})}{\partial \mathbf{Q}_a}(\nu'_g | \mathbf{Q}_a | \nu_f)$$ (4.28)

$$M_{\alpha\beta}^{e,f_{\nu'\nu}}(\omega_0) = M_{\alpha\beta}^e(\omega_0, \mathbf{Q}_0) \langle \nu'_g | \nu_f \rangle + \sum_a \frac{\partial M_{\alpha\beta}^e(\omega_0, \mathbf{Q})}{\partial \mathbf{Q}_a}(\nu'_g | \mathbf{Q}_a | \nu_f)$$ (4.29)

$$T_{\alpha\beta}^{e,f_{\nu'\nu}}(\omega_0) = T_{\alpha\beta}^e(\omega_0, \mathbf{Q}_0) \langle \nu'_g | \nu_f \rangle + \sum_a \frac{\partial T_{\alpha\beta}^e(\omega_0, \mathbf{Q})}{\partial \mathbf{Q}_a}(\nu'_g | \mathbf{Q}_a | \nu_f)$$ (4.30)

4.3.2 Analytical sum rules for total intensity

By summing over all final vibrational states, we can obtain the analytical total intensities for different processes, from which the convergences of the spectra calculations for each final state can be easily derived, defined as the ratio between the sum of state-to-state intensities explicitly considered in the computation of the spectrum and the total analytical intensities.

**One-photon absorption:**

The expression for the analytical total intensity for OPA reads as
4.3 Theory for vibronically resolved spectra

\[
\sum_{\nu_{g},\nu_{f}} \delta_{\text{OPA}}(\omega) = \frac{2}{3} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \langle v_{g} | \mu^{e}(\epsilon) \mathbf{Q} | v_{f} \rangle \langle v_{f} | \mu^{e}(\epsilon) \mathbf{Q} | v_{g} \rangle 
= \frac{2}{3} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} \right]_{\nu_{g}}^{2} 
= \frac{2}{3} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} + \sum_{a} \frac{\partial \mu^{e}}{\partial \mathbf{Q}_{a}} \mathbf{Q}_{a} \right]^{2} |v_{g}\rangle 
\]

(4.31)

Since expectation values of the linear term $\delta_{\text{OPA}}^{\text{FC}}$ vanish, as well as those of the non-diagonal bilinear terms $\delta_{\text{OPA}}^{\text{HT}}$ with $a \neq b$, leaving under our approximation only expectation value of $\delta_{\text{OPA}}^{\text{HT}}$, for each final electronic state $f$ we can obtain

\[
\sum_{\nu_{g},\nu_{f}} \delta_{\text{OPA}}(\omega) = \frac{2}{3} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} \right]_{\nu_{g}}^{2} + \frac{\hbar}{2\omega_{a}} \left[ 2 \nu_{a} + 1 \right] 
= \delta_{\text{OPA}}^{\text{FC}} + \delta_{\text{OPA}}^{\text{HT}} 
\]

(4.32)

**One-photon circular dichroism:**

Similarly, we can get the expression of the total intensity for ECD

\[
\sum_{\nu_{g},\nu_{f}} \delta_{\text{ECD}}(\omega) = \frac{3}{4} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \langle v_{g} | \mu^{e}(\epsilon) \mathbf{Q} | v_{f} \rangle \langle v_{f} | m^{e}(\epsilon) \mathbf{Q} | v_{g} \rangle 
= \frac{3}{4} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} \right]_{\nu_{g}}^{2} 
= \frac{3}{4} \sum_{a=x,y,z} \sum_{\nu_{g}} p_{\nu_{g}} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} + \sum_{a} \frac{\partial \mu^{e}}{\partial \mathbf{Q}_{a}} \mathbf{Q}_{a} \right]^{2} |v_{g}\rangle 
\]

(4.33)

Analogously to what seen for OPA, also for ECD only expectation values of $\mathbf{Q}_{a}^{2}$ contribute to the analytical sum and, for each final electronic state $f$, we obtain

\[
\sum_{\nu_{g},\nu_{f}} R_{\text{ECD}}^{\nu_{g},\nu_{f}}(\omega) = \frac{3}{4} \sum_{a=x,y,z} \left[ \mu^{e}(\epsilon) \mathbf{Q}_{a} + \sum_{a} \frac{\partial \mu^{e}}{\partial \mathbf{Q}_{a}} \mathbf{Q}_{a} \right] |m^{e}(\epsilon) \mathbf{Q}_{a}| + \sum_{b} \frac{\partial m^{e}}{\partial \mathbf{Q}_{b}} \mathbf{Q}_{b} + \frac{\hbar}{2\omega_{a}} \left[ 2 \nu_{a} + 1 \right] 
= R_{\text{ECD}}^{\text{FC}} + R_{\text{ECD}}^{\text{HT}} 
\]

(4.34)

**Two-photon absorption:**

The corresponding expression for the analytical total intensity for TPA reads as
4 Vibronically resolved spectra

\[
\sum_{\nu_{ij}} S_{\nu_{ij}}^{\nu_{ij}}(\omega_b) = \sum_{\rho\sigma} [F \times S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0) S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0) + G \times S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0) S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0)] + \\
H \times S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0) S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}_0)] + \]  
\sum_{\nu_{ij}} \sum_{\rho\sigma} p_{\nu} \frac{h}{2\omega_a} (2\nu_{\sigma\rho} + 1) [F \times \frac{\delta S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} + \\
G \times \frac{\delta S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} + H \times \frac{\delta S_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta S_{\nu_{ij}}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a}] = \delta_{\nu_{ij}}^{FC} + \delta_{\nu_{ij}}^{HT}
\]

Macák et al.\textsuperscript{51} has reported the 0 Kelvin expression obtained for linear polarized light. The above equation generalizes it for finite temperature and both linear and circular polarized lights.

**Two-photon circular dichroism:**

In this section we derive analytical sum rules for the total intensity of TPCD. We neglect the frequency-dependence and to that end, for each transition \(|g\nu_{\rho} \rightarrow f\nu_{\sigma}\)
, we define three terms \(B_{ii}^{HT}(\omega_b) = \omega^3 B_{ii}^{HT}(\omega_b)\), where \(i = 1, 2, 3\) and the quantities \(B_{ii}^{HT}(\omega)\) are given in Eqs. (3.21)-(3.23). In the limit of first order expansions of the three tensors defined in Eqs. (4.28), (4.29) and (4.30) and assuming completeness of the vibrational state manifold we have

\[
\sum_{\nu_{ij}} B_{ii}^{HT}(\omega_b) = \sum_{\rho\sigma} \sum_{\nu_{ij}} p_{\nu} \langle \nu_i | M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) | \nu_j \rangle \langle \nu_i | P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) | \nu_j \rangle 
\]

\[
= \sum_{\rho\sigma} \sum_{\nu_{ij}} p_{\nu} \langle \nu_i | M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) | \nu_j \rangle \sum_{\nu_{\sigma\rho}} p_{\nu_{\sigma\rho}} \langle \nu_{\sigma\rho} | P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) | \nu_{\sigma\rho} \rangle 
\]

\[
= \sum_{\rho\sigma} \sum_{\nu_{ij}} M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) + \sum_{\nu_{ij}} p_{\nu} \sum_{\rho\sigma} \sum_{\nu_{\sigma\rho}} \frac{\delta M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} h \frac{2\omega_a}{2\omega_{\sigma\rho}} (2\nu_{\sigma\rho} + 1) \]

\[
= B_{ii}^{HT, FC} + B_{ii}^{HT, HT}
\]

Analogously, we can prove that the following hold

\[
\sum_{\nu_{ij}} B_{ii}^{HT}(\omega_b) = \frac{1}{2} \sum_{\rho\sigma} M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) + \sum_{\nu_{ij}} p_{\nu} \sum_{\rho\sigma} \sum_{\nu_{\sigma\rho}} \frac{\delta T_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} h \frac{2\omega_a}{2\omega_{\sigma\rho}} (2\nu_{\sigma\rho} + 1) \]

\[
= B_{ii}^{HT, FC} + B_{ii}^{HT, HT}
\]

\[
\sum_{\nu_{ij}} B_{ii}^{HT}(\omega_b) = \sum_{\rho\sigma} M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q}) + \sum_{\nu_{ij}} p_{\nu} \sum_{\rho\sigma} \sum_{\nu_{\sigma\rho}} \frac{\delta M_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} \frac{\delta P_{\rho\sigma}^{\nu_{ij}}(\omega_b, ^{s}\mathcal{Q})}{\delta^s\mathcal{Q}_a} h \frac{2\omega_a}{2\omega_{\sigma\rho}} (2\nu_{\sigma\rho} + 1) \]

\[
= B_{ii}^{HT, FC} + B_{ii}^{HT, HT}
\]
Therefore, the total intensity of the TPCD rotatory strength can be written as

\[
\sum_{v_{g,v_f}} R_{\text{TPCD}}^{\nu_{g,v_f}} = (-b_1 B_1^{\text{HT}} - b_2 B_2^{\text{HT}} - b_3 B_3^{\text{HT}}) + (-b_1 B_1^{\text{HT}} - b_2 B_2^{\text{HT}} - b_3 B_3^{\text{HT}})
\]

(4.39)

\[
R_{\text{TPCD}} = R_{\text{TPCD}}^{\text{FC}} + R_{\text{TPCD}}^{\text{HT}}
\]

### 4.3.3 Adiabatic harmonic Franck-Condon model

The simplest way to introduce vibrational effects in electronic spectra is at the level of FC approximation, where the vibrational structure of a spectrum depends only on the square overlap between vibrational states, the so-called FC factors. At the FC level, different properties of the same system are predicted to have superimposed line shapes (not the intensity). The non-Condon effect, with the first order known as the so-called HT term, can modulate the spectral line shape. The general idea to calculate the FC factors is to approximate the complicated multidimensional potential energy surfaces associated with the states with model surfaces. The difference between the various vibronic models lies in the use of different model representations of the potential.

**Adiabatic harmonic FC (AFC) model** involves optimizing the ground- and excited-state geometries, making a harmonic approximation (second-order Taylor expansion) of the ground- and excited-state potential energy surfaces at their respective minimum energy geometries and evaluating the FC factors between the ground- and excited-states to construct the spectrum.

In the Duschinsky formulism,\(^{52}\) the assumption of a general linear transformation holds among the normal coordinates of the initial and final states, as

\[
\begin{align*}
\tilde{Q} &= J/Q + K \\
J &= L^{e^{-1}}L' \\
K &= L^{e^{-1}}(q^{f,\text{eq}} - q^{g,\text{eq}})
\end{align*}
\]

(4.40)\-(4.42)

where the Duschinsky matrix \(J\) and the equilibrium displacement vector \(K\) can be easily obtained by the normal output of a frequency calculation

where \(L'\) and \(L'\) are respectively the normal coordinates matrix, \(q^{e,\text{eq}}\) and \(q^{f,\text{eq}}\) respectively the mass-weighted Cartesian coordinates of the equilibrium positions of the initial and final states. The linear transformation in Eq 4.40 is, in general, non-diagonal, thus preventing the calculation of the multidimensional FC overlaps to be separated in a
product of mono-dimensional integrals.

As mentioned, molecular motion involves simultaneous translation, rotation and vibration. For the interpretation of the vibronically resolved spectra discussed in the present thesis, we are only interested in the vibrational motions. While the three translational coordinates can be exactly separated, and therefore do not deserve further discussion, this is not completely possible in general for the rotational coordinates. Nonetheless, their mixing with the vibrational coordinates can be minimized according to different procedures. According the approach followed in this thesis, this is done by imposing the irrotational condition between the two equilibrium geometries, i.e. minimizing the root-mean-square distance (RMSD) of the molecule nuclei in the two equilibrium positions, through a suitable rotation of one of the two equilibrium structures.

\[ q^{\text{eq}}_{\text{eq}} = R(q^{\text{eq}}_{\text{eq}}) \]  

\[ \text{RMSD}^2 = \frac{1}{N} \sum_{k=1}^{N} (q^{\text{eq}}_{k} - q^{\text{eq}}_{k})^2 \]

where the rotation matrix \( R \) which minimizes RMSD can be efficiently obtained by adopting the quaternion formulism.

In the frame of AFC, because of the Duschinsky rotation, the calculation of FC overlaps involves evaluating multidimensional integrals. Several approaches have been pursued in literature starting from two equivalent routes: the generating function of Sharp and Rosenstock and the coherent state approach of Doktorov et al. According to Sharp and Rosenstock approach, since the 0-0 integral is analytical, the integrals \( I_{0,0} = \langle 0 | w \rangle \) can be evaluated through the following recursion formula:

\[ I_{0,w} = I \begin{pmatrix} 0 & \ldots & \ldots & \ldots & 0 \\ w_1 & w_1' & \ldots & w_k & w_N \end{pmatrix} = \left( \frac{1}{2w_k} \right)^{1/2} A_k I \begin{pmatrix} 0 & \ldots & \ldots & \ldots & 0 \\ w_1 & w_1' & \ldots & w_k & w_N - 1 \ldots w_N \end{pmatrix} + \left( \frac{w_k - 1}{w_k} \right)^{1/2} D_{k,l} I \begin{pmatrix} 0 & \ldots & \ldots & \ldots & 0 \\ w_1 & \ldots & w_k & w_N - 2 \ldots w_N \end{pmatrix} + \sum_{l \neq k} \left( \frac{w_l}{w_k} \right)^{1/2} D_{k,l} I \begin{pmatrix} 0 & \ldots & \ldots & \ldots & 0 \\ w_1 & \ldots & w_l - 1 \ldots w_k - 1 \ldots w_N \end{pmatrix} \]
4.3 Theory for vibronically resolved spectra

\( \omega_k^g / h \) and \( \omega_k^e / h \); and \( \mathbf{I} \) the identity matrix; the vectors and matrices that appear in previous equations are

\[
\mathbf{X} = \mathbf{J}^\dagger \Gamma^g \mathbf{J} + \Gamma^f
\]
\[
\mathbf{A} = -2 \mathbf{K}^\dagger \Gamma^e \mathbf{J} \mathbf{X}^{-1} (\Gamma^f)^{1/2}
\]
\[
\mathbf{D} = 2 (\Gamma^f)^{1/2} \mathbf{X}^{-1/2} (\Gamma^f)^{1/2} - \mathbf{I}
\]

(4.46)
(4.47)
(4.48)

It has been noticed that the first and second terms in the right-hand side of Eq. (4.45) generalize the effect on the vibrational progressions due to the shift in equilibrium positions and frequencies, respectively.\(^{58}\) When considering sizeable molecules, a huge number of vibronic transitions should be considered in principle, making a brute force calculation unfeasible. In these cases, the adoption of efficient pre-screening techniques able to select a priori the relevant vibronic transitions is mandatory. In recent years different methods have been proposed for FC spectra at 0 Kelvin.\(^{59-61}\) In this thesis we adopt the method proposed by Santoro et al.\(^{58,62}\) based on a partition of the manifold of the final vibronic states in classes \( C_n \) depending on the number \( n \) of simultaneously excited modes, and on effective selection schemes. The method has been extended to compute finite temperature spectra\(^{63}\) and to Herzberg-Teller transitions.\(^{64}\) In this respect, it is noteworthy that in harmonic approximation HT integrals \( \langle \nu_q | Q_o | \nu_f \rangle \) can be traced back to the FC integrals with the help of raising and lowering operators (see Eq. (4.55)).

4.3.4 Linear coupling model

At variance with the AFC model, requiring the optimization of the excited state geometry, different methods for the computation of vibronic spectra are based on the expansion of the difference between the two sets of potential energy surfaces in a Taylor series around the equilibrium geometry of the ground state.

**Linear coupling model (LCM, shown in Fig. 4.1),\(^{65}\)** which is also known as gradient FC model, only keeps the linear term of the expansion. The multi-dimensional vibronic coupling constants are obtained from ground-state frequencies and normal coordinates, whereas excited state energy gradients are evaluated numerically, also at the ground state equilibrium geometry. This approach probes only the effect of totally
symmetric normal modes, neglecting the possible frequency changes of different electronic states and furthermore Duschinsky effect. Nonetheless, it avoids the often cumbersome excited-state geometry optimizations, and was proven to provide very often a simple and reliable treatment, capturing the most important features of the vibrational structures of one- and two-photon absorption and emission spectra of several systems.\textsuperscript{51-70} LCM assumes that the excited and ground electronic states have the same harmonic potential energy surface (PES) curvatures but differ only by small displacements $\Delta Q_a$ along the directions of the normal coordinates $Q_a$. In this framework, the displacements can be simply derived from the numerical excited PES gradients

$$
\Delta Q_a = \frac{G_a}{\omega_a^2} \quad G_a = \frac{\partial E^f}{\partial Q_a}
$$

where $\omega_a$ is the vibrational frequency of normal mode $a$.

\[ Fig. 4.1 \text{ graphical illustration of linear coupling model } \]

For normal mode $a$, a general expression for the overlap integral between two displaced vibrational states with occupation quantum numbers $v_{a,g} \leq v_{a,f}$ can be written as

$$
\langle v_{a,g} | v_{a,f} \rangle = (-1)^{v_{a,f} - v_{a,g}} e^{\frac{x_a^2}{2}} \sum_{\nu} \frac{\Gamma_{v_{a,f} - v_{a,g}}}{\sqrt{v_{a,f}!}} \langle v_{a,g} | \Gamma_{v_{a,f} - v_{a,g}} (x_a) \rangle
$$

where $x_a$ is a dimensionless factor and relates with the displacement $\Delta Q_a$ and
4.3 Theory for vibronically resolved spectra

vibrational frequency $\omega_a$ as

$$x_a = \sqrt{\frac{\omega_a}{2\hbar}} \Delta Q_a$$  \hspace{1cm} (4.51)

$L^{v_a}_{m_a}(x_a)$ is the associated Laguerre polynomial

$$L^{v_a}_{m_a}(x_a) = \frac{\exp(-x^2)}{2^m a^m} \frac{d^m}{dx^m} \left( x^2 a^2 \right)$$ \hspace{1cm} (4.52)

If $v_{a,g} > v_{a,f}$, we have

$$\langle v_{a,g} | v_{a,f} \rangle = (-1)^{v_{a,g} - v_{a,f}} \langle v_{a,f} | v_{a,g} \rangle$$ \hspace{1cm} (4.53)

The normal coordinates can be related with the raising and lowering operators,

$$Q_a = \sqrt{\frac{\hbar}{2\omega_a}} (a^+ a)$$ \hspace{1cm} (4.54)

And the integral $\langle v_{a,g} | Q_a | v_{a,f} \rangle$ can be traced back to FC integrals as

$$\langle v_{a,g} | Q_a | v_{a,f} \rangle = \sqrt{\frac{\hbar}{2\omega_a}} \left( \sqrt{v_{a,g} + 1} \langle v_{a,g} + 1 | v_{a,f} \rangle + \sqrt{v_{a,g} - 1} \langle v_{a,g} - 1 | v_{a,f} \rangle \right)$$ \hspace{1cm} (4.55)

For a polyatomic molecular system which has more than one normal mode, we need to evaluate the product of the single displaced harmonic oscillator overlap integrals

$$\langle v_{a} | v_{f} \rangle = \prod_a \langle v_{a,g} | v_{a,f} \rangle$$ \hspace{1cm} (4.56)

$$\langle v_{a} | Q_a | v_{f} \rangle = \langle v_{a,g} | Q_a | v_{a,f} \rangle \prod_{b \neq a} \langle v_{b,g} | v_{b,f} \rangle$$ \hspace{1cm} (4.57)

In the frame of LCM, one can get the final expressions of the tensors of interest, here for example the electric dipole moment

$$\mu_{a}^{(\nu_c, \nu_f)} = \mu_a^{(\xi \xi)} \prod_a \langle v_{a,g} | v_{a,f} \rangle + \sum_a \frac{\partial \mu_a^{(\xi)}}{\partial Q_a} \langle v_{a,g} | Q_a | v_{a,f} \rangle \prod_{b \neq a} \langle v_{b,g} | v_{b,f} \rangle$$ \hspace{1cm} (4.58)

Since LCM assumes the same set of normal modes and frequencies of the initial and final electronic states of the transition, the effect from the translation and rotation has already been eliminated automatically. Different situation occurs for AFC approach where both the equilibrium geometries of the initial and final states are applied.

An alternative vibronic model, known as the **Vertical FC (VFC) model**, can be by considering also the second-order terms in the Taylor expansion. Specifically, according
4 Vibronically resolved spectra

to this approach, the excited-state potential energy surface is approximated by a quadratic function of the normal coordinates on the base of energy, gradient and Hessian computed at the ground state equilibrium geometry. VFC retains some of the simplicity of the LCM approximation (avoids the optimization the excited-state geometry), while introducing also the Duschinsky rotation effect. VFC and AFC models share the difficulties coming from the non-separability of multidimensional FC overlaps.

![Graphical representation of three different vibronic models.](image)

Fig. 4.2 Graphical representation of three different vibronic models.

Fig. 4.2 is the graphical comparison of the three different vibronic models. In the limit of an exactly harmonic excited PES, VFC and AFC are equivalent, whereas in all the realistic cases where anharmonicities exist they are different. In the latter case, VFC motivated by the short-time picture of spectroscopy, gives a better description of the broad features (position of intensity maximum, overall width, and envelope) of the spectrum rather than the accurate calculation of specific low lying vibrational lines. On the other hand, specific low-lying vibrational lines in the spectrum, in particular the 0-0 transition may be better described by AFC, which thus provides a better description and assignment of high-resolution spectra. The two approaches may yield sensibly different predictions when relevant anharmonicities play a role. Only the reliable treatment of these anharmonicities, which is hardly feasible for sizeable molecule, can provide a clear cut improvement of the spectrum description. In these cases, remaining within the
realm of harmonic models, only an ad hoc study on the specific system can tell which of AFC and VFC approaches performs better. VFC has already been successfully applied to linear absorption and circular dichroism spectra by Nooijen and coworkers\textsuperscript{71-74}.
4 Vibronically resolved spectra
5. Summary of papers

5.1 Electronic spectra

Linear and nonlinear optical properties of molecules in gas phase and in solution have been studied in terms of the state-of-the-art response theory. The results reported in the present section focus on the ‘vertical-transition’ approach, which only takes electronic transitions into account, without considering the contribution from vibrational states. The vibronically resolved properties will be discussed in the next section.

5.1.1 Three-photon absorption, paper I

![Molecular structure of FLU. The torsion angles are labeled as $\theta_1 : 1-2-5-6$ and $\theta_2 : 7-8-9-10$.](image)

Three-photon absorption, is a fifth-order nonlinear optical property which, however, can be evaluated from the third-order transition matrix elements obtainable from the
single residue of the appropriate cubic response function. Since the measurements are conducted for solvated species, the consideration of the influence from the solvent medium becomes relevant for comparisons with experiment.

In paper I we present a theoretical study of the solvent-induced three-photon absorption cross-section of a highly conjugated fluorene derivative (labelled as FLU, see Fig. 5.1), performed using density functional cubic response theory in combination with the polarizable continuum model.

![Graph](https://via.placeholder.com/150)

*Fig. 5.2 Changes with respect to optimized geometry in the total energy ΔE (upper panel), in the wavelength of the excitation to the first excited state, Δλ (middle panel), and corresponding cross section σ₃P (bottom panel), are presented as functions of torsion angles θ₁=θ₂. All results are obtained from B3LYP/6-31G calculations in gas phase starting from both HF (diamonds) and B3LYP (triangles) optimized geometries.*

It is found that the molecular geometry is very sensitive to the choice of the computational method, with B3LYP predicting a more planar structure and HF larger torsion angles. Although there are evidences showing that HF agrees better with the
5.1 Electronic spectra

For both geometries, the dielectric medium enhances the three-photon absorption cross section remarkably and it is also clear that the 3PA cross section is strongly dependent on the geometrical structure of the molecule. The effects of geometrical distortions have been carefully examined, see Fig. 5.2. It is found that the change of torsion angle is thermodynamically possible, which implies that at room temperature in solution one might expect to observe a rather wide distribution of structures with different torsion angles rather than a unique equilibrium structure.

For sizable molecules, the full response calculations often become really expensive. The applicability of the often used two-state model, which is less computational intensive, is examined by comparison against the full response theory results. It is found that the simplified model performs poorly for the three-photon absorption properties of our symmetric charge transfer molecule. A detailed comparison with experiment is also presented.

5.1.2 One- and two-photon circular dichroism, paper II, III

![Fig. 5.3 The structures of both the equatorial-methyl (Eq) and axial-methyl (Ax) conformers of R-(+)-3-methyl-cyclopentanone.](image)

Both one- and two-photon circular dichroism spectra, which are highly related with chirality, have been proved to be very promising tools for fingerprint applications, and can be calculated at *ab initio* level by applying response theory.
In paper II, motivated by a recent experimental study\textsuperscript{78} of the (2+1) resonance enhanced multi-photon ionization circular dichroism (REMPICD) on a typical chiral molecule, R-(+)-3-methyl-cyclopentanone (R\textsubscript{3}MCP), we have calculated the one- and two-photon circular dichroism spectra of the same system with an origin-invariant density functional theory approximation in the region of the lowest electronic excited states, both for the gas phase and for a selection of solvents. A polarizable continuum model is used in the calculations performed on the solvated system. Two low-lying conformers, whose structures are sketched in Fig. 5.3, are analyzed, and a comparison of the intensities and characteristic features is made with the corresponding two-photon absorption for each species, also for the Boltzmann-averaged spectra. The effect of the choice of geometry, basis set and exchange-correlation functional is carefully analyzed. As one can see in Fig. 5.4, it is found that the recently developed CAMB3LYP functional can describe the Rydberg-state characteristics more appropriately than the popular B3LYP functional. With the combination with the correlation-consistent basis sets of double-zeta quality, we can reproduce the experimental electronic circular dichroism spectrum of R-(+)-3-methyl-cyclopentanone recorded by Li et al. in the gas phase (Ref. 78) with our calculated results (Boltzmann averaged at 298.15 K and 1 atm).

![Graph comparing ECD spectra](image_url)
5.1 Electronic spectra
dichroism spectra very well.

An analysis, performed on the basis of the major contributions to the excitation TDDFT vectors and on the visual appearance of the Kohn-Sham molecular orbitals, allows us to determine the character of each state in terms of the dominating single excitations. The features appearing in experiment are characterized in terms of molecular excitations, and the differences in the response of each state in the one- and two-photon processes are also highlighted. The difference in the relative intensities and shapes of the ECD and TPCD signals of the different states of R3MCP provides a nice example of the complementary fingerprinting capability of TPCD spectroscopy with respect to ECD.

Fig. 5.5 Left panels report the polarization dependent two-photon absorption cross-section spectra for SBN and RBN. The spectra for linear (LPL), left (LCPL) and right (RCPL) polarized electromagnetic field are depicted. Right panels present the experimental (upper panel) and theoretical (lower panel) two-photon circular dichroism.

In Paper III the first experimental measurement of TPCD spectra is given on an axial chiral system, R-(+)-1,1′-bi(2-naphtol) (RBN) and its enantiomer S-(−)-1,1′-bi(2-naphtol) (SBN), in tetrahydrofuran. The double L-scan technique is applied. The corresponding theoretical efforts are also given.
From the left panels of Fig. 5.5, one can identify the differences in TPA between left and right circularly polarized lights. Moreover, the dominant contribution TPA from left and right circularly polarized light is reversed for RBN and SBN, as expected for enantiomers. Right panels of Fig. 5.5 report the difference between left and right circularly polarized light in TPA, which determines TPCD. It is clearly indicated that the spectrum of one enantiomer is the specular image of the other as expected. It is worth to stress that the spectral features obtained by TPCD are different from those reported by ECD,\textsuperscript{79} which provides a nice example of the complementary fingerprinting capability of TPCD with respect to ECD.

Fig. 5.6 Two-photon circular dichroism both in gas phase (upper panel) and in tetrahydrofuran (lower panel) of RBN in the region of the first 25 excited states, computed at B3LYP/aug-cc-pVDZ level. Both the stick and convoluted (with Lorentzian lifetime of 0.3 eV) are given.

The calculated TPCD result at the B3LYP/PCM level well reproduces the experimental shapes. Due to the weak interaction between the two single naphthols,
5.1 Electronic spectra

many near-degenerated states have been explored, and the first 25 states have to be included in the calculation in order to cover the experimental frequency range of 200-350 nm. Fig. 5.6 shows the comparison between calculated results in gas phase and in solution, which indicates that TPCD is very sensitive to the solvent environment, accompanying with sign changes of the signals. A detailed analysis of the stick bands reveals that each experimental band results from a complicated balance of contributions, of opposite sign, from several electronic excited states.

5.2 Vibronically resolved spectra

The present section focuses on the discussion of vibronically resolved spectra, where contributions from both electronic and vibrational states are taken into account. Our study focuses on the one- and two-photon absorption and circular dichroism properties of molecules. The state-of-the-art response theory has been applied throughout the calculations.

5.2.1 One- and two-photon absorption, paper IV, V

In paper IV, both the electronic and the vibronic contributions to one-, and two-photon absorption of a D-π-D charge-transfer molecule (DMTS, shown in Fig. 5.7) are studied by means of density functional response theory combined with LCM vibronic model. In Fig. 5.8 the vibronic TPA profiles of the first four excited states are fully explored.
Fig. 5.8 Vibronic two-photon absorption spectra of the first four excited states S1 (1a-1f), S2 (2a-2f), S3 (3a-3f), and S4 (4a-4f) of DMTS. Franck-Condon contribution, Herzberg-Teller contribution and total spectra are shown for lifetime broadenings of 0.10 eV (left panels) and 0.01 eV (right panels), respectively. The dashed line corresponds to the vertical transition.

For allowed transitions (here S4 for TPA), FC term dominates the spectra, with, on the other hand, rather negligible HT contribution. In the present case, FC introduces a red-shift of the main absorption peak position with respect to the corresponding vertical-transition value, resulting from the fact that the 0-0 integral is in all cases very close to 1. It is also clear that vibrational levels with quantum number higher than 2 can be safely neglected. For forbidden transitions, the role of HT will become apparent with the intensity become comparable or even larger than the FC part. The ‘borrowing mechanism’ of HT contribution, whose general behavior can be rationalized by inspecting the layout of the excited state manifold, has been analyzed in detail. In general, the HT is small whenever the energy separation between the interacting states is large, like S1 for TPA here, since large energy separations hamper the coupling between states. The necessary precondition for a strong HT of a given excited state is the presence of other strong states close by in energy, for instance S3 for TPA in our case.
5.2 Vibronically resolved spectra

A similar vibronic coupling behavior is found for both one- and two-photon absorptions. The dominating vibrational modes for both Franck-Condon and Herzberg-Teller contributions are also identified.

Fig. 5.9 Molecular structure of MH101

Fig. 5.10 (a) Calculated and (b) experimental OPA (green line) and TPA (blue line) spectra of MH101 in DCM for the first (S1, upper panels) and second (S2, lower panels) excited states.

At Franck-Condon level, both one- and two-photon absorption spectra of the same molecule should have the same shape whose vibrational progressions are uniquely
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determined by the so-called FC factors. However, the experiments\textsuperscript{80-86} often show a strong violation of this statement, with differences being detected between the experimental OPA and TPA spectra.

Fig. 5.11 Vibronically resolved OPA (upper panels) and TPA (lower panels) spectra of MH101 in DCM for the first (S1, left panels) and second (S2, right panels) excited states. Both FC (red dashed lines) and HT (green solid lines) contributions are given. Dashed vertical lines in gray show the vertical excitation energies of S1 (408 nm) and S2 (332 nm) states.

In paper V, we choose a heterocyclic molecule MH101 as our model system, whose structure can be found in Fig. 5.9. It is shown that the unexpected shift between one- and two-photon absorption in experiment (see bottom panels in Fig. 5.10) is due to the Herzberg-Teller effect. The study applies density functional response theory in combination with Linear Coupling Model, which is good enough to find the physics behind the phenomenon. It is worth to mention that paper V is the first study to take both the vibronic contribution and solvent effect into the two-photon absorption spectrum. The Polarizable Continuum Model is applied for the solvent effect.

As we can see in Fig. 5.10, our calculation reproduces well the experimental findings, with in the S1 region the OPA spectrum redshifted with respect to TPA and
5.2 Vibronically resolved spectra

opposite in the S2 region. One can understand the intrinsic physics better by inspecting the different mechanisms of FC and HT, as shown in Fig. 5.11. For the case under study, the 0-0 transition contributes the most in FC spectra, resulting a red-shift with respect to the vertical excitation energy (VEE). On the contrary, HT, lying in the well known “borrowing mechanism”, in most cases introduces a blue shift. OPA in S1 is mainly from FC with negligible HT, thus with the total spectrum redshifted with respect to the VEE. The opposite holds for TPA in the same region, with its HT contribution even larger than the FC counterpart, resulting a blue-shift of the total spectrum with respect to VEE. Similar mechanism can be used to explain the phenomenon in the S2 region.

It is worth to stress that the proposed theoretical mechanism can go far beyond the specific molecule studied here and be extended to general cases for molecules possessing different strong one- and two-photon absorption states.

5.2.2 One-photon circular dichroism, paper VI, VII

![Fig. 5.12 Stick spectra (left panels) for the vibronically resolved ECD of the Ax conformer of R3MCP, in the second excited state region. Both the FC and the total (TOT = FC + HT) contributions are shown. Convoluted spectra (Lorenzian lifetime 0.01 eV) applying both LCM and AFC (data from paper VIII) are shown in right panels, with the AFC spectrum blue-shifted by 1.6 nm for a better comparison with the LCM one.](image)
Motivated by a recent experiment which gives the vibronically resolved ECD spectra of R3MCP, a corresponding computational study by use of LCM vibronic model is performed in paper VI, including both Franck-Condon and Herzberg-Teller contributions. It shows that Herzberg-Teller can introduce a change of sign on the chiral response of an electronic excited state (cf. Fig. 5.12), which breaks the usual belief that the sign reversion only occurs with the involvement of different electronic states. As we all know that the enantiomers show exactly the opposite ECD signals, therefore, this sign inversion within the vibronically resolved electronic band, which can be interpreted as a change of the chirality of the system, has in principle important consequences in comparisons of theoretical and experimental ECD spectra employed for the assignment of absolute configurations.

Fig. 5.13 Comparison of the experimental (Exp) ECD spectra of R3MCP in the S1 and S2 region with the Boltzmann averaged (T=298.15 K, P=1 atm) spectra computed at LCM and AFC (Harm) levels. For a better comparison, the spectra were normalized to a maximum (minimum) intensity of 1 (-1) for S1 (S2) state, respectively, and the computed spectra were shifted on the energy axis by the amount reported in the insets.

In order to perform a confident assignment of the experimental peaks, in paper VII we applied the more accurate but also more computational intensive AFC model, which can give high-resolution spectra, on the same system, taking into account Duschinsky rotation effect and possible frequency changes between the normal modes of the initial and final states at the harmonic level. The CAM-B3LYP functional reproduces both the position and the intensity of the experimental peaks, providing a remarkable improvement over the spectra obtained with the popular hybrid B3LYP functional, which is consistent with the conclusion of the ‘vertical-transition’ result (paper II). As
5.2 Vibronically resolved spectra

one can see from Fig. 5.13, the AFC calculation shows a better agreement with the experiment than LCM, particularly for the relative heights between vibrational peaks in the S1 region. Its high-resolution capability allows a confident assignment of the fine vibrational structures. It is worth to mention that the AFC result confirms the sign-reversion observed with LCM (cf. Fig. 5.12). The fact that the change of sign occurs in the axial-methyl conformer of R3MCP, which is in ratio of 1:9 with respect to the predominant equatorial-methyl conformer, limits the chance that our theoretical prediction might be easily confirmed by experiment.

5.2.3 Two-photon circular dichroism, paper VIII

Fig. 5.14 Assignments of the main stick bands of the FC, HT and total (TOT=FC+HT) vibronic spectra for the Eq conformer of R3MCP in the S1 region, as obtained with the AFC model. The spectra are convoluted with a Lorentzian spectral shape function with a broadening of 0.05 eV. The Boltzmann-averaged spectrum is also shown in red.
**5 Summary of papers**

Very recently, the experimentalists have made very striking progress on the measurement of TPCD responses on chiral species. This progress, together with the fact that TPCD combines the advantages of both ECD and TPA, makes TPCD a possibly very promising tool for fingerprinting applications and also evokes our theoretical study on the vibronically resolved TPCD spectra.

In *paper VIII*, the AFC vibronic model in combination with density functional response theory for computing two-photon vibronically resolved circular dichroism spectra of chiral molecules is presented. It includes both Franck-Condon and Herzberg-Teller contributions and it takes fully into account frequency changes and Duschinsky effects. Model calculations have been performed for two dominant conformers of R3MCP in the gas phase.

It is found that the change of sign can also occur in TPCD responses, introduced by the Herzberg-Teller contribution. As one can see from Fig. 5.14, different from ECD, the sign-reversion survives even after Boltzmann averaging which might make it be amenable to experimental verification.

*Table 5.1* The FC, HT and total (TOT) intensities of some selected vibronic transitions for TPCD responses of both the Equatorial conformer of R3MCP, for the first excited state, calculated with the AFC vibronic model. Atomic units ($10^{-3} \text{ au}$) are given.

<table>
<thead>
<tr>
<th></th>
<th>FC</th>
<th>HT</th>
<th>TOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>-0.242</td>
<td>0.959</td>
<td>-0.136</td>
</tr>
<tr>
<td>10^1</td>
<td>-0.048</td>
<td>0.059</td>
<td>-0.445</td>
</tr>
<tr>
<td>30^1</td>
<td>-0.283</td>
<td>0.094</td>
<td>0.148</td>
</tr>
<tr>
<td>10^130^1</td>
<td>-0.053</td>
<td>-0.046</td>
<td>-0.351</td>
</tr>
<tr>
<td>30^2</td>
<td>-0.141</td>
<td>0.030</td>
<td>0.827</td>
</tr>
<tr>
<td>30^3</td>
<td>-0.038</td>
<td>0.232</td>
<td>0.705</td>
</tr>
<tr>
<td>30^4</td>
<td>-0.006</td>
<td>0.143</td>
<td>0.270</td>
</tr>
</tbody>
</table>

It is found that the interesting interference effects between Franck-Condon and Herzberg-Teller contributions play an important role for the TOT intensity, especially in the region where the sign reversal appears. *Table 5.1*, reporting the FC, HT, and TOT intensities for some selected vibronic transitions, highlights such a role.
5.2 Vibronically resolved spectra

Fig. 5.15 Comparison between TPCD spectrum for the first excited state computed by AFC and by an independent-mode model as LCM. The green curve “DISP” in the middle panel reports the independent-mode prediction employing the AFC displacements and the LCM values for excited-state frequencies; the blue curve “DISP+FREQ” in the bottom panel is obtained with the independent-mode model adopting AFC values both for the frequencies and the displacements. The spectrum is given as a function of \((E-E_{0,0})\), unit of eV, where \(E\) is the excitation energy and \(E_{0,0}\) is the 0-0 transition energy.

A detailed comparison between the results obtained within AFC and the more approximate and less computationally intensive LCM is presented in Fig. 5.15. The top panel of Fig. 5.15 shows that LCM predicts a significantly different vibrational structure with respect to AFC, especially in the region where the sign reversion takes place. To rationalize the role played by displacements, frequencies, and Duschinsky mixings in determining the LCM/AFC difference, we performed a step-by-step comparison considering a harmonic independent-mode model as LCM and modifying progressively its parameters, displacements, and excited-state frequencies, setting them equal to those adopted by AFC. Inspection of the middle panel indicates that the displacements
account for part of the differences. Nonetheless, the spacings between the peaks are still different, as well as their relative intensities. The bottom panel shows that the difference can be further decreased after also removing the effect of the frequencies. The residual difference, still evident, is due to the Duschinsky mixing effect.
References

14 Peach, M. J. G., Helgaker, T., Salek, P., Keal, T. W., Lutnaes, O. B., Tozer, D. J.;
15 DALTON, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html.
References

52 Duschinsky, F. Acta Physicochim. 1937, URSS 7, 551.
57 Doktorov, E. V.; Malkin, I. A.; Man’ko, V. I. J. Mol. Spectrosc. 1977, 64, 302.
References

65 Y. -H. Wang, Theoretical Design of Molecular Photonic Materials, PhD thesis, Royal Institute of Technology, Sweden,
69 Gierschner, J.; Mack, H.-G.; Egelhaaf, H.-J.; Schweizer, S.; Doser, B.; Oelkrug, D.
    122, 234305.
    122, 224505.
    2006, 125, 144304.
81 He, G. S.; Lin, T.-C.; Dai, J.; Prasad, P. N.; Kannan, R.; Dombroskie, A. G.; Vaia, R.
    W.; Marder, S. R. Science 2002, 296, 1106.
83 Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z.; Vogel, H.; Pond, S. J. K.; Perry, J.


