Matthieu Sala

Quantum Dynamics and Laser Control for Photochemistry

Springer

Matthieu Sala

Quantum Dynamics and Laser Control for Photochemistry

Doctoral Thesis accepted by
Université de Bourgogne Franche-Comté, Dijon, France

Springer

Author
Dr. Matthieu Sala
Laboratoire Interdisciplinaire Carnot de
  Bourgogne
Université de Bourgogne Franche-Comté
Dijon
France

Supervisors
Prof. Stéphane Guérin
Laboratoire Interdisciplinaire Carnot de
  Bourgogne
Université de Bourgogne Franche-Comté
Dijon
France

Prof. Fabien Gatti
Institut Charles GERHARDT—CNRS 5253
Université Montpellier 2
Montpellier
France

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series "Springer Theses" brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student's supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today's younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series at http://www.springer.com/series/8790

Parts of this thesis have been published in the following journal articles:

- M. Sala, F. Gatti, D. Lauvergnat and H.-D. Meyer, "Effect of the overall rotation on the cis-trans isomerization of HONO induced by an external field", *Phys. Chem. Chem. Phys.* **14**, 3791 (2012)

- M. Sala, S. Guérin, F. Gatti, R. Marquardt and H.-D. Meyer, "Laser-induced enhancement of tunneling in NHD_2", *J. Chem. Phys.* **136**, 194308 (2012)

- M. Sala, O. M. Kirkby, S. Guérin and H. H. Fielding, "New insight into the potential energy landscape and relaxation pathways of photoexcited aniline from CASSCF and XMCQDPT2 electronic structure calculations", *Phys. Chem. Chem. Phys.* **16**, 3122 (2014)

- M. Sala, M. Saab, B. Lasorne, F. Gatti and S. Guérin, "Laser control of the radiationless decay in pyrazine using the dynamic Stark effect", *J. Chem. Phys.* **140**, 194309 (2014)

- M. Sala, B. Lasorne, F. Gatti and S. Guérin, "The role of the low-lying dark $n\pi^*$ states on the photophysics of pyrazine: a quantum dynamics study", *Phys. Chem. Chem. Phys.* **16**, 15957 (2014)

- M. Saab, M. Sala, S. Guérin, B. Lasorne and F. Gatti, "Full dimensional control of the radiationless decay in pyrazine using the dynamic Stark effect", *J. Chem. Phys.* **141**, 134114 (2014)

- M. Sala, F. Gatti and S. Guérin, "Coherent destruction of tunneling in a six-dimensional model of NHD_2: a computational study using the multi-configuration time-dependent Hartree method", *J. Chem. Phys.* **141**, 164326 (2014)

- O. M. Kirkby, M. Sala, G. Balerdi, S. Guérin, R. de Nalda, L. Bañares, N. Kaltsoyannis and H. H. Fielding, "Comparing the electronic relaxation dynamics of aniline and d_7-aniline following excitation in the 273–238 nm region", *Phys. Chem. Chem. Phys.* **17**, 16270 (2015)

- M. Sala, S. Guérin and F. Gatti, "Quantum dynamics of the photostability of pyrazine", *Phys. Chem. Chem. Phys.* **17**, 29518 (2015)

Supervisors' Foreword

With the advent of femtosecond laser pulses in the 1990s, real-time imaging of ultrafast molecular phenomena has become possible. They are now used in a systematic manner in pump-probe experiments to map out, in real time, nuclear motion in molecules. In the past two decades, tremendous progress has been achieved on the experimental front with the possibility to align molecules with lasers and the production of attosecond pulses. In particular, the high-harmonic generation technique that is responsible for the formation of attosecond laser pulses has been exploited to image the faster electronic motion. In this context, it becomes conceivable to create a new chemistry where all the different motions (rotational, nuclear and electronic) in a molecular process could be manipulated and controlled by laser pulses. The stakes are high and pose further substantial requirements on the development of suitable theoretical methods. In addition, one important challenge is to transfer to chemistry techniques (experimental and theoretical) that have been developed mainly by physicists and for problems in physics.

The central subject of the present thesis is the theoretical description of ultrafast dynamical processes in molecular systems of chemical interest and their control by laser pulses. This work, performed in collaboration with experimentalists, can be considered as a decisive step to link and apply quantum physics to chemistry by transferring concepts developed in physics to chemistry such as "wavepackets" or "light dressed states." This is highlighted in Part II, where Dr. M. Sala exploits the "adiabatic Floquet theory" to rationalize the control of several molecular processes. When a molecular system is isolated, its quantum behavior can be described in terms of eigenstates and wavepackets featuring linear combinations of the eigenstates. However, when the system is in interaction with a time-dependent external field, the situation is completely different as the eigenstates are modified by the external fields. The adiabatic Floquet theory provides a quantum mechanical framework for the description of the interaction of quantum systems with light. More precisely, a description in terms of Floquet states or "light dressed states," i.e., quantum states similar to eigenstates that additionally include rigorous quantum-mechanical treatment of the mean frequency of the external fields (like in

the approach of "dressed atoms" in atomic physics). The laser parameters varying slowly in time with respect to the mean frequency (such as the envelope of the pulse and the chirp of the frequency) feature dynamical modification of the Floquet states, topologically represented as dressed surfaces in the parameter space. With adiabatic arguments, one can then characterize the quantum dynamics as trajectories in the parameter space.

Dr. M. Sala's Ph.D. encompasses cutting-edge methods not only for the rigorous description of the interaction of light and matter at the molecular level but also in quantum chemistry and molecular quantum dynamics. Indeed, one important aspect of his work was the exploration of potential energy landscapes for electronic excited states in organic molecules in the vicinity of so-called "conical intersections." At a conical intersection, the potential energy surfaces belonging to different electronic states become degenerate and the Born–Oppenheimer approximation, that separates the nuclear and electronic motions, fails: a nonadiabatic transfer from one electronic state to another can occur. From ab initio electronic structure calculations, Dr. M. Sala could build model Hamiltonians that can be used to solve, in a second step, the Schrödinger equation for the nuclei. For the latter step, he developed his own codes for low-dimensional simulations and exploited the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package otherwise. The MCTDH approach is an efficient tool to solve both the time-dependent and time-independent Schrödinger for relatively large systems. Finally, Dr. M. Sala has highlighted general strategies for the coherent control of strong quantum effects involving the nuclei in chemical process: tunneling and strong nonadiabatic processes.

Altogether, this doctoral thesis lays out important foundations for the quantum mechanical treatment of molecular processes that we anticipate to be very useful in the context of applications of ultrafast laser pulses to chemistry. To conclude, we were impressed by the level of autonomy of Dr. M. Sala and his strong ability to take initiative at all the stages of his Ph.D. work.

<div align="right">
Prof. Fabien Gatti
Prof. Stéphane Guérin
</div>

Acknowledgments

First of all, I am grateful to my supervisor Stéphane Guérin for guiding me through this thesis. His enthusiasm, his encouragement, the constant help and support he provided me with, and the trust he put in me has been instrumental in my development as a scientist. I have learned a lot from him, through numerous hours spent in his office discussing technical details or future projects. I also thank Stéphane for having given me the opportunity to spend six months in the group of Helen Fielding in London, in the middle of this thesis. Finally, I thank him for the wonderful dinner parties at his house with all the colleagues of our team, for the incredible food and wines I had the chance to taste, and the friendly and humorous atmosphere.

I wish to acknowledge Fabien Gatti, who introduced me to research during my master's thesis. His enthusiasm, his energy, and his passion for research are a source of inspiration for me. He has kept a constant interest in my work and has always been available for discussions, providing me with help and support, and giving me many useful advices. Nothing of what is written in this thesis would have happened without him.

I would like to thank Hans-Rudolf Jauslin, head of the quantum and nonlinear dynamics team, for giving me the opportunity to work in such a nice and stimulating environment. I also thank Claude Leroy, Yevgenya Pashayan-Leroy, Dominique Sugny, Vincent Boudon, Béatrice Bussery-Honvault, and Pascal Honvault, who I had the chance to get to know during this thesis, and who greatly contributed to the nice work environment of the first floor of the "Aile de Physique."

I acknowledge Helen Fielding for having made me feel so welcome in her group at the Chemistry Department of University College London, from March to August 2012. This research stay was a great opportunity for me to learn about the experimental point of view on molecular photodynamics. Thanks to her, my stay in London was a rich and rewarding experience. I also thank the students of the Fielding group, Roman Spesyvtsev, Oliver Kirkby, Ciaran Mooney, and Garikoitz Balerdi, who all contributed greatly in making this experience so enjoyable for me.

This thesis has been the opportunity to teach in chemistry and physics lab classes. I thank Frédéric Demoisson, Christine Gautheron-Geraci, Jean Suisse,

Contents

Chapter 1
General Introduction

Light induced chemical transformations, called photochemical reactions, are ubiquitous in nature. These processes are initiated by the absorption of a photon, that promotes the molecule into an excited state, where the reaction takes place. Important examples of photochemical reactions occurring in nature are the photolysis of ozone and molecular oxygen in the stratosphere [1–3], the initial steps of the processes of photosynthesis [4, 5] or of vision [6–9]. In addition, photochemical processes lie at the heart of important emerging technologies, such as 3D optical memories based on photoswitching molecular materials [10], Organic Light-Emitting Diodes (OLED) [11, 12] or organic photovoltaics [13–16]. For these reasons, a detailed understanding of photochemical processes at the molecular level is a major goal of modern physical chemistry.

Thanks to the development of powerful experimental techniques, tremendous progress in the understanding of photochemical processes have been made in the last few decades. The 1999 Nobel prize in chemistry was awarded to Ahmed Zewail for his seminal work on time-resolved spectroscopy of molecular processes on a femtosecond time scale [17–20]. The characteristic time scale of the vibrational motion of the nuclei in molecule being of the order of the hundred of femtoseconds, experiments with a time resolution of the same order of magnitude or less are able to probe the elementary steps (bond breaking, isomerizations, …) of photochemical reactions. Time-resolved spectroscopic techniques consist in making sequential spectroscopic measurements on a system during a dynamical process, allowing one to record the frames of a "movie" of a chemical transformation. In these techniques, the system is irradiated by two laser pulses delayed in time with respect to each other. The first laser pulse, called pump pulse, triggers a dynamical process via photoexcitation. The second laser pulse, called probe pulse, is then used to monitor the system during its evolution. Different probe techniques are available, such as transient absorption, laser induced fluorescence or photoelectron spectroscopy. This procedure is repeated with different delay times between the two laser pulses, yielding time-resolved spectroscopic data.

Since the first experiments on the I-CN [21] bond cleavage and the wavepacket oscillations between the ionic and covalent potentials in the photodissociation of NaI [22, 23], pump-probe techniques have been applied to a wide range of important photochemical processes. However, the data obtained from such experiments are often difficult to interpret and theoretical modeling is needed to get further insight into the excited state dynamics of the systems of interest at the atomistic level. In this context, the development of efficient and accurate computational methods for the description of ground and excited electronic states of mid-size molecular systems in a balanced way [24, 25], has greatly facilitated the theoretical study of photochemical processes.

During the same period, it became more and more evident that strong non-adiabatic effects, occurring at regions of degeneracy between electronic states, called conical intersections [26, 27], play an important role in a great number of cases. In such situations, associated with a breakdown of the Born–Oppenheimer approximation, the electronic and nuclear motions are strongly coupled, giving rise to non-radiative population transfers between electronic states, i.e population transfers that occur because of the coupling of the electronic and nuclear motions rather than the coupling with the electromagnetic field (Fig. 1.1).

Depending on their position and energetics with respect to the Franck–Condon region of the excited state potential energy surface (the region occupied by the wavepacket on the excited state potential energy surface immediately after a vertical photoexcitation), conical intersections can mediate ultrafast internal conversion processes from the excited state to the photoproducts on the ground state. A systematic exploration of the excited state potential energy surfaces, and their conical intersections with the ground state potential energy surfaces, of the basic organic chromophores using multi-configuration self-consistent field calculations, has been launched in the nineties in the groups of Robb, Bernardi and Olivucci [28, 29]. In most cases, these studies revealed the existence of low-lying conical intersections between the first excited state and the ground state, at geometries consistent with the observed photoproducts. This findings supported the hypothesis that low-lying

Fig. 1.1 Schematic view of an ultrafast radiationless decay process through a conical intersection
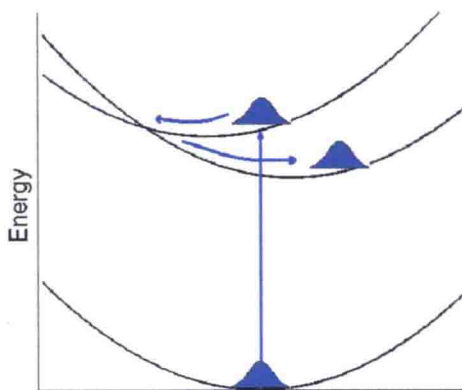
conical intersections are ubiquitous in organic molecules, and act as key mechanistic features in organic photochemistry, similarly to the transition state in thermal reactions occurring on the ground electronic state.

Often, the relaxation of a molecule to its ground electronic state via a conical intersection is associated with a competition between two situations. The molecule can reach a region of the ground state potential energy surface corresponding to a different isomer, or to a repulsive part resulting in a bond breaking process. This situation is called photoreactivity. But the molecule can also reach the ground state potential energy surface in the region of its equilibrium geometry. This situation is called photostability. The competition between photoreactivity and photostability (Fig. 1.2) is directly related to the topography of the potential energy surfaces around the conical intersection [30–32].

The notion of photostability is very important in the field of molecular biology. The molecular "building blocks of life", such as the DNA bases or the amino acids, often absorb in the ultra violet (UV) region of the electromagnetic spectrum. A UV photon carries an energy which is of the same order of magnitude as the binding energy associated with the weakest bonds of these molecules. Therefore, UV light is potentially harmful for these compounds and, by extension, for life. This is, however, in contradiction with the exceptional photostability observed experimentally for these molecules and their complexes. A large number of theoretical and experimental investigations, performed over the last two decades, have established that this exceptional photostability is related with the existence of conical intersections providing extremely efficient radiationless decay channels leading the molecules back to their ground state [33–37].

Nevertheless, although the characterization of the topography of potential energy surfaces using electronic structure calculations often provides a qualitative understanding of the mechanisms of photochemical transformations, a deeper insight into such processes often requires simulating the dynamics of the nuclei. For instance, it is known that the existence of conical intersections is often reflected in the absorption
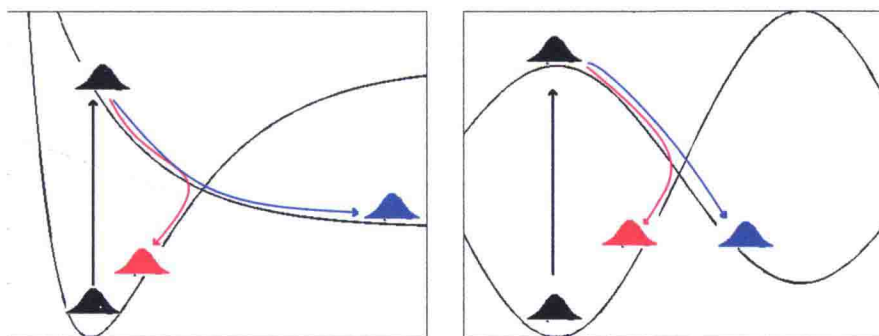
Fig. 1.2 Illustration of the competition between photostability (featured in *red*) and photoreactivity (featured in *blue*) in two different situations: a non-adiabatic photodissociation process (*left panel*) and a non-adiabatic photoisomerization process (*right panel*)

Fig. 1.3 Structure of the butatriene molecule
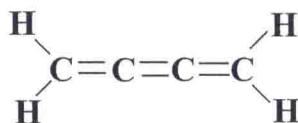
spectra through the presence of unexpected bands or of bands presenting an unusually complicated and broad profile. An interesting and historically important example is provided by the photoelectron spectrum of the butatriene molecule (see Fig. 1.3).

Despite the fact that butatriene is a quite exotic molecule, it has attracted a considerable attention in the spectroscopy community in the 70s because of the unusual structure of its photoelectron spectrum in the region between 9 and 11 eV [38]. It was known that the butatriene radical cation has only two electronic states in this energy range, corresponding to the bands centered around 9.3 and 10.0 eV (bands noted 1 and 2 in the left panel of Fig. 1.4). However, the photoelectron spectrum presents a third, broad feature (noted 1′ in the left panel of Fig. 1.4) between these two bands that cannot be directly assigned to a given electronic state, and was termed the "mystery band". It was shown later by Cederbaum et al. [39] that this "mystery band" was a direct signature of the existence of a strong vibronic coupling between the two lowest excited electronic states of the cation, manifested by a conical intersection of the two corresponding potential energy surfaces. They constructed a model potential including the two most important vibrational modes and taking into account the vibronic couplings and could reproduce the photoelectron spectrum, including the "mystery band", as seen in Fig. 1.4. Since then, thanks to the enormous progress made in the methodology of molecular quantum dynamics calculations, absorption and photoelectron spectra of molecular systems of increasing complexity showing signatures of strong vibronic couplings have been simulated (see e.g. Chap. 7 in ref. [26] and Chap. 6 in ref. [27]).

Beyond the computation of spectra, the simulation of the dynamics of the nuclei has proven to be necessary for a proper understanding of a number of photochemical processes. Indeed, in most systems, the excited state dynamics is governed by the competition between several dynamical processes including several electronic states. These processes can correspond to channels with similar energies and in this case, it is difficult to predict the dynamics of the molecule using only the static information that can be obtained from electronic structure calculations. However, the simulation of such photochemical processes, which often involve large amplitude nuclear motions and complicated potential energy surfaces, using quantum dynamics techniques, remains a formidable challenge from the numerical point of view. For this reason, a variety of computational techniques based on a mixed quantum-classical formalism have been developed and used to study the excited state dynamics of mid-size molecular systems such as, for instance, the DNA bases [40–42]. The most popular family of such techniques is the trajectory surface-hopping method (see Chaps. 11–13 in ref. [27] and references therein). Other important methods in this category are the ab initio multiple spawning method (see Chap. 9 in ref. [27] and references therein) or the methods based on the Herman-Kluk semi-classical propagator combined with