

Chapter 1

Introduction

Turning lead into gold or silver was one of the main goals of alchemists by a process known as transmutation. The overall "control" procedure can be summarized in two basic steps: deconstruction, and reconstruction. Their goal was to control a chemical reaction by breaking down a substance into its basic components and then rebuilding it into the substance of their choice. Since the development of chemistry, the successor of alchemy, much has remained the same. Although the main interest of chemistry is not the transmutation of lead into gold or silver, the quest to control chemical reactions remains.

Products formed from chemical reactions can be controlled by varying the parameters that influence it, such as the thermodynamic properties, addition of catalysts, and use of electromagnetic radiation. The radiation produced by lasers is one elegant tool that can alter the outcome of products. Since its development in the early 1960s, its use in controlling chemical reactions has been widespread.

A mode-selective approach to controlling bond breakage was one of the first attempts of applying laser radiation to achieve control, but this approach has had limited success [1, 2, 3, 4, 5]. By tuning the laser radiation to a specific vibrational mode of the molecular system, the corresponding bond was expected to break. However a competing process known as internal vibrational redistribution (IVR) distributes the localized energy over other modes and in most cases limits the success of this method.

In contrast to mode-selective bond breakage, which is a passive control technique, active control methods interact with the system along the reaction pathway to influence its outcome. Quantum interference effects have been exploited to control transitions in which the phase of two laser pulses, each providing a unique pathway to a degenerate state, interact either constructively or destructively [6]. Tannor, Kosloff, and Rice introduced a control scheme based on exploiting the delay time between two laser pulses in a method known as the pump-dump scheme [7, 8]. Other well known schemes which exploit the delay time between two laser pulses are STImulated Raman scattering involving Adiabatic Passage (STIRAP) [9, 10] and a combination of few cycle infrared plus ultraviolet (IR+UV) laser pulses [11, 12, 13, 14, 15]. Another type of control is achieved by optimal control theory (OCT) which designs a control field for a particular molecular system that maximizes a target state [7, 16, 17]. Often these shaped fields are quite complex and are difficult to implement experimentally. Therefore, a closed-loop feedback control mechanism was developed in which an algorithm, typically an evolutionary algorithm, shapes the control field in both amplitude and phase in order to produce the desired products [18]. One of the main advantages of the closed-loop feedback control is its robustness and its applicability to polyatomic molecules. The first application was performed on an organometallic complex [19]. A more detailed review of the control schemes are given in chapter 4.

Transition metals and their complexes are important catalysts for reactions that are used industrially and synthetically [20]. Theoretical studies on this group of molecules has increased significantly in the last few decades and much work has been done to understand the electronic properties of the carbonyl complexes, e.g. [21, 22, 23, 24, 25]. Experimental investigation of dynamics and control scenarios on carbonyl complexes have also been heavily explored, e.g. [19, 26, 27, 28, 29, 30, 31, 32, 33].

Control of molecular dynamics is not limited to single-photon transitions. In fact recently it has been shown that nonresonant multiphoton transitions (NMT) can also be used as a route to achieve control of chemical reactions [27]. Nonresonant multiphoton transitions occur when the electronic excitation requires two or more photons in which no intermediate states exist that facilitate a single-photon transition. The absence of intermediate states indicates that coupling matrix elements to the multitude of high-lying, off-resonant states are very important. Such processes have been extensively considered in the frequency domain but in the femtosecond regime only a few attempts have been made [34, 35, 36, 37].

The main goal of this thesis is to investigate the control of photochemical reactions involving organometallic molecules by either well-timed or optimized shaped ultrashort laser pulses. Figure 1.1 depicts the overall scheme. In general, a well devised laser pulse interacts with the molecule steering the reaction to form one of either two set of products. The first control mechanism that will be investigated in this work is a pump-dump type mechanism in which two pulses are applied to tetracarbonylhydridocobalt, $\text{CH}_3\text{Co}(\text{CO})_4$: the first pulse will create a wavepacket which evolves along an excited electronic potential energy surface and a well-timed second pulse will funnel the wavepacket to an unbound state, thereby changing the branching ratio in favor of one set of products. The second control mechanism will apply OCT within the scope of NMT in order to produce an optimized laser pulse in both shape and amplitude which will steer the system, now tricarbonylcyclopentadienylmanganese, $\text{CpMn}(\text{CO})_3$, to the targeted state.

Before quantum dynamic simulations can be performed on the photochemical control of $\text{CH}_3\text{Co}(\text{CO})_4$, the potential energy surfaces (PES) must be calculated. The quantum chemical theory pertaining to these calculations is therefore described first in chapter 2, in which the Schrödinger equation is separated into its electronic and nuclear components by applying the Born-Oppenheimer approximation [38]. Solving the electronic Schrödinger equation supplies the surfaces on which the subsequent nuclear wavepacket dynamics will take place. The solution to the nuclear Schrödinger equation provides the eigenfunctions and eigenvalues, including the ground state vibrational eigenfunction (wave function) that is used in the quantum dynamic simulations.

Analysis of the field-free wavepacket dynamics is essential in determining possible control mechanisms. Therefore chapter 3 investigates the field-free dynamics, and presents the theoretical UV absorption spectrum for $\text{CH}_3\text{Co}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$. Although control mechanisms will only be discussed for $\text{CH}_3\text{Co}(\text{CO})_4$, quantum chemical investigations as well as quantum dynamic simulations will also be performed on its chemical analogue, the tetracarbonylhydridocobalt complex $\text{HCo}(\text{CO})_4$. Chapter 4 presents a thorough overview of different control mechanisms.

The formulation of the theory to NMT will be developed by deriving an effective time-dependent Schrödinger equation which describes these processes, as suggested by Faisal [39]. Solving the effective time-dependent Schrödinger equation exactly circumvents the time integrals that appear in the perturbational treatment of NMT. The exact solution of the effective TDSE is also well suited for application in optimal control theory, and is presented in chapter 5.

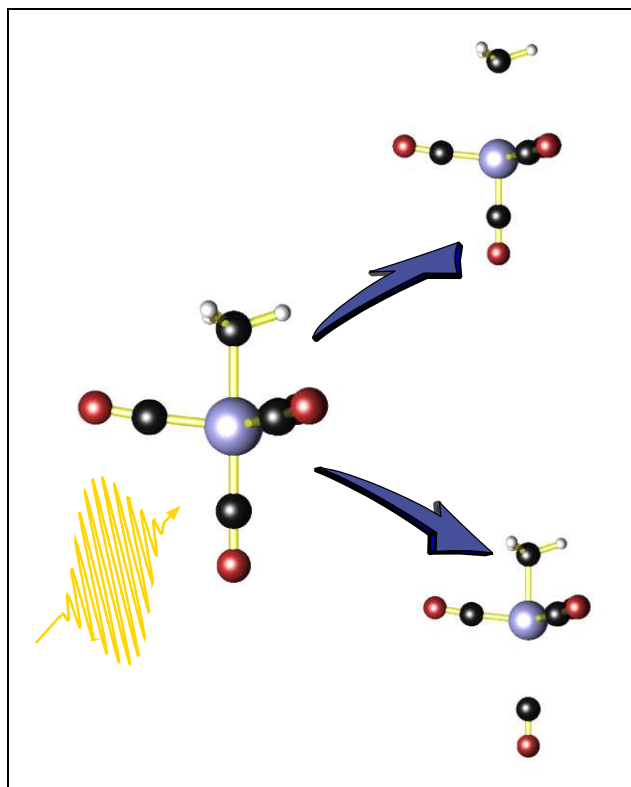


Figure 1.1: The photochemical reaction of a polyatomic molecule is depicted in which the breakage of two bonds is investigated. By applying tailored, i.e. either well-timed or phase-shaped, laser pulses to a molecular system, control over the two possible reaction pathways may be achieved by steering the reaction to favor one set of products.

The organometallic complex, $\text{CpMn}(\text{CO})_3$, has been selected as the model system for the development of NMT and its implementation into OCT. This selection is based on two reasons. First, the mechanism of the feedback-loop control in which the parent ion $\text{CpMn}(\text{CO})_3^+$ is optimized with respect to its fragment $\text{CpMn}(\text{CO})_2^+$, was successfully deciphered assuming resonant single-photon transitions [27]. Second, *ab initio* electronic calculations indicate that for certain wavelengths the control route occurs via nonresonant multiphoton transitions [40]. Combining OCT with NMT presents a valuable tool for elucidating laser fields which successfully and optimally achieve the control task via nonresonant multiphoton transitions.

The results of investigated control mechanisms are presented in chapter 6. The structure of this chapter follows the same structure as the body of this work. Specifically the results are presented first for the quantum chemical calculations, section 6.1. In this section the focus

is on the comparison of the two analogue organometallic molecules $\text{CH}_3\text{Co}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$; their respective electronic spectra, state correlation diagrams and potential energy surfaces are presented. An analysis of the quantum dynamics accompanying a transition induced by a delta pulse is presented in section 6.2. The field-free evolution of the wavepackets are discussed and the theoretical absorption spectra are presented. Section 6.3 discusses the results of the investigated pump-dump control mechanism, and the final section 6.4 presents the application of NMT to femtosecond spectroscopy as well as results from its application to OCT.