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Malte Oppermann

**Resolving Strong
Field Dynamics
in Cation States
of CO₂ via Optimised
Molecular Alignment**

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Malte Oppermann

Resolving Strong Field Dynamics in Cation States of CO₂ via Optimised Molecular Alignment

Doctoral Thesis accepted by
Imperial College London, UK

 Springer

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*You can crank up the voltage even more. If
you dare.*

*Leszek Frasiniski about the only available
detector for the experiments.*

London, 2011

Supervisor's Foreword

The behaviour of matter in an intense laser, with electric field strengths near or exceeding 1 V/\AA , is a frontier topic in strong field physics. This high field regime challenges our quantum theoretical and computational methods as the situation is inherently many-bodied and non-perturbative. It is a topic that is fascinating as it may offer new light sources, such as those based on high harmonic generation (HHG) with attosecond temporal structure as discussed by Paul et al. [1] and many other authors. The resulting fragmentation in molecules may also offer new routes to strong field chemical control (see for example Levis et al. [2]) and biomolecular analysis by selective bond cleavage as suggested by Weinkauff et al. [3].

The current experimental approaches concentrate on small gas phase molecules to build up ideas as to how the strong field influences the motion of the electrons and nuclei. It is essential to obtain high quality quantitative experimental data to feed into the advances in establishing theoretically how to understand the dynamics of molecules exposed to strong laser fields. One picture that greatly assists us is the so-called *strong field approximation* as developed formally by Lewenstein et al. [4], which captures the fact that the laser field, rather than the molecular electronic potential, dominates the behaviour of the ionised electron. An important feature of the strong field limit is the existence of laser-driven electron recollision that can lead to HHG and non-sequential double ionisation (NSDI) of an atom or molecule. The extent to which the strong field picture and electron recollision-induced phenomena can be used to understand the results of experiments on simple molecules like CO_2 is the main subject of Malte Oppermann's thesis.

What Malte has achieved is to conduct a series of measurements that explore the dependence of fragmentation and double ionisation on the alignment of the CO_2 molecular axis with respect to the polarisation direction of the strong field. To do this he employed impulsive molecular alignment of CO_2 molecules with a carefully timed pre-pulse of weaker intensity from the same titanium sapphire 800 nm laser used to generate the high intensity pulse (a topic well described by

Stapelfeldt and Seideman [5]). The technique required careful optimisation of the sample cooling and the 800 nm laser beam parameters to implement a high degree of alignment which was achieved by the use of a buffer gas (Ar) that resulted in very high degrees of cooling and thus alignment [6]. A Wiley–McLaren ion time of flight spectrometer was used to measure the fragment yield. Malte utilised the peaks from the Ar buffer gas for in situ monitoring of intensity fluctuations and non-sequential double ionization in the molecule.

Malte's first measurements with 800 nm strong fields showed weak non-sequential double ionisation in CO₂. He identified the higher energy recollision obtained with a longer wavelength field would increase NSDI. He then used an intense short pulse at 1,350 nm to see very clear signatures of NSDI in CO₂. He was able to measure the NSDI yield as a function of laser ellipticity, to confirm the signal came predominately from electron recollision, and then record the yield as a function of molecular alignment. From simple geometrical considerations he then deduced that his measured results could only be explained if the cation intermediate state HOMO and HOMO-1 were involved in the process, a new result published in [7]. His work has gone much further and looked at other zero kinetic energy release fragmentation products (CO⁺ + O and O⁺ + CO) and his results support the idea that laser-driven transitions in the cation state must be invoked to excite the molecular ion to HOMO-2 and HOMO-3 from where it can dissociate.

He has used a high degree of ingenuity to use a simple apparatus to make the first measurements on the angular dependence of NSDI and fragmentation channels in CO₂, which are likely to be of considerable benefit to the theory community trying to develop accurate approaches to molecular strong field processes. Moreover, he has written a clear thesis that succinctly reviews the state-of-the-art in strong field molecular science.

London, January 2014

Jonathan Marangos

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Abstract

In this thesis, the role of the molecular structure in strong field induced processes in CO_2 is resolved by the use of optimised impulsive molecular alignment. Two processes were investigated: recollision induced ionisation and the dissociation of the molecular ion CO_2^+ . Both processes are driven by the initial tunneling ionisation of CO_2 . Through the use of molecular alignment, the orbital symmetries of the involved molecular ionic states were resolved, revealing the internal molecular dynamics in the form of ionisation and excitation pathways.

A novel data analysis procedure was developed to extract the alignment distribution and rotational temperature of the impulsively aligned molecular ensemble. This facilitated the optimisation of molecular alignment in mixed gas samples and was demonstrated for N_2 , O_2 and CO_2 seeded in Ar.

The recollision induced or non-sequential double ionisation (NSDI) of CO_2 was then studied in the molecular frame. The process was fully characterised by measuring the shape of the recolliding electron wavepacket and the angularly resolved inelastic electron ion recollision cross-section. The results reveal the contribution from both the ionic ground and first excited state of CO_2^+ to the NSDI mechanism.

This study was extended to the strong field induced dissociation of impulsively aligned CO_2^+ . It was found that dissociation is driven by a parallel dipole transition from the second excited ionic state B to the predissociating state C, whilst recollision excitation was shown to not play a role. The strong field induced coupling of the ionic states B and C could thus be controlled by the laser polarisation.

The results obtained in this thesis further the understanding of population dynamics of cation states in strong field processes. This is of special interest for extending molecular strong field physics to the study of electronic degrees of freedom and their coupling to the nuclear motion.

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This Ph.D. project would have never been possible without the massive support, advice and motivational speeches that I received on the way.

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Chapter 1

Introduction

Molecular physicists face a dilemma. They'd love to study the microscopic world inside molecules and shed light onto the fundamental dynamics that drive chemical and biological processes. Unfortunately they live in a macroscopic world. Because of this, molecular physicists need suitable experimental tools to access and manipulate the molecular properties they are interested in.

In this introduction I will provide a first glimpse at those molecular properties that are of interest for this thesis and the chosen experimental tools to access them. This should provide the reader with a roadmap that marks the most important points of departure for the conducted research.

Molecular physicists typically approach their work with a so-called bottom-up approach. This means that they attempt to understand the behaviour of molecules by investigating the properties and interactions of the components that comprise them. These components are the positively charged nuclei and negatively charged electrons that make up the individual atoms that in turn are bound together to form the molecule. Here, Sect. 2.2.1 provides a brief introduction to molecular physics with all basic terms and mechanisms relevant to this thesis.

Research in molecular physics can then be divided into two strands: structural and dynamical. The first studies the specific properties of a given molecule, for instance the geometric arrangement of its atomic nuclei and electron distribution (which is directly linked to the molecule's so-called *orbital*) and the resulting electronic, vibrational and rotational energy levels (which are associated with the molecule's so-called *quantum states*). The second strand investigates how these properties change in time; as part of a chemical reaction for example. The relevant time scales of such molecular dynamics are essentially determined by the motion of the involved molecular components. Due to the comparatively large mass of the atomic nuclei the associated dynamics such as vibrations, rotations or changes of the molecular structure typically cover durations from hundreds of picoseconds ($1 \text{ ps} = 10^{-12} \text{ s}$) down to a few femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$). Here, the fastest vibrational period can be found in an H_2 with about 8 fs. Due to these extremely short time scales, the associated field of research is often called *ultrafast molecular dynamics*.

However, as an electron is about a thousand times lighter than the lightest atomic nucleus (a proton), the associated dynamics are accordingly faster. The molecule's internal electron motions thus take place on the attosecond time scale ($1 \text{ as} = 10^{-18} \text{ s}$) and is related to phenomena such as electron charge migration in molecules and orbital changes during a molecular energy level transition, for example (for a review of the emerging field of attosecond physics see [1]).

Here, one should also note that there is an intermediate regime in molecular dynamics, where the motion of the nuclei and electrons cannot be studied separately. This is the case, when these molecular components interact with each other and is often referred to as a coupling of the molecule's nuclear and electronic degrees of freedom. Here, energy can be transferred between the interacting particles, such that a molecular vibration may enable an internal electronic excitation. However, the interaction of the particles increases the complexity of such phenomena and makes their investigation and description very challenging.

It is at this point, where the current frontier of ultrafast molecular dynamics research becomes apparent: the description and control of ever faster molecular phenomena in increasingly complex molecules. Throughout Chap. 2, it will become clear that this not only requires the development of novel theoretical and numerical tools, but also new experimental techniques and high quality data for benchmarking the theory. This thesis is based on this latter experimental perspective.

In this context, lasers have become a popular and equally successful experimental tool for molecular physicists. This is because lasers are an astonishingly precise macroscopic tool for inducing and manipulating microscopic quantum state distributions, due to their coherent, collimated, intense and potentially frequency-tunable flux of photons. This is outlined in more detail in Sects. 2.1 and 2.2, which discuss the basic mechanisms underlying light-matter interactions. Their study using lasers as light sources is called *laser spectroscopy*. Chapter 3 then provides a basic introduction to laser physics and presents the basic architecture and working principle of the laser systems employed for this thesis. Whilst the basic properties of laser light are thus at the heart of molecular laser spectroscopy, three further developments in this field form the context of this thesis.

The first development is the application of pulsed lasers for the time resolution of laser spectroscopy techniques. The use of laser pulses enables a time-sequencing of the induced dynamics within so-called pump-probe setups. Here, a first laser pulse (the pump) triggers a molecular process, like a photoexcitation to a so-called repulsive molecular state that leads to the breaking of a molecular bond. A second laser pulse (the probe) then probes the molecular properties as a function of time delay after the pump pulse, for instance the distance of the molecular fragments as a function of time after the pump. In this example, the nuclear motion during a chemical reaction is mapped out as a function of time. However, this requires that the probe pulse is shorter than the typical time scale of the motion of the atoms in a molecule. The application of femtosecond laser pulses with durations around 20 fs thus created the field of femtochemistry, aiming at the time-resolution of the nuclear motion in molecules [2].

The second development is the use of high power femtosecond laser pulses for entering a new regime of light-molecule interaction, the so-called strong field regime (see Sect. 2.2.1). It is marked by the onset of optical field ionisation, which takes place when the laser electric field becomes comparable in strength to the binding Coulomb field in the molecule. The Coulomb potential of the molecule is thus suppressed and a finite potential barrier formed that allows an electron to escape from the molecule via tunneling (see Sect. 2.2.1). This ionisation event is the fundamental process in strong field physics. Whilst being a research topic in its own right, tunneling ionisation also represents an ultrafast (less than a few tens of attoseconds [3, 4]), highly nonlinear response of the molecule to an electric field and can thus be used as a probing process for molecular properties. At the same time, the ionisation step triggers molecular dynamics that can be studied and controlled through the driving laser field. This approach has become an excellent tool for imaging molecular structure and internal dynamics. It is built on the high degree of control of the driving laser field parameters achieved over the last two decades [1, 5]. Pulse durations in the near-infrared (NIR) from 30 fs down to below 4 fs [6] now routinely provide electric field gradients steep enough to achieve the peak intensities on the order of 10^{14} Wcm⁻² that are required for observing strong field phenomena.

This development has informed the application of ultrafast strong field processes for probing molecular dynamics, with the aim to extend this study to the investigation of the electronic degrees of freedom and their coupling to the nuclear degrees of freedom. Recent examples for achieving this include the use of high harmonic generation [7], time-resolved photoelectron spectroscopy [8] and strong field ionisation [9], to name but a few highlights from the last two years. Rather recently, the control of the carrier envelope phase and the production of pulse durations in the attosecond regime (for a recent review of the required experimental tools see for example [10]) have even opened routes towards imaging the internal electron dynamics in molecules in a weak field regime [1]. Here, Sects. 2.3, 2.4 and 2.5 provide a review of those parts of molecular strong field physics relevant to this thesis.

The third development is the introduction of laser induced impulsive molecular alignment to resolve the molecular structure in strong field processes (for a review see [11]). Molecules in gas phase are randomly aligned within the laboratory frame of reference. This implies that the interaction of the molecular ensemble with a linearly polarised laser field is averaged over all possible orientations of the molecule with respect to the laser polarisation. This makes it impossible to resolve the effect of the molecular structure on the studied laser induced processes.

However, with the use of laser induced impulsive alignment, one may impose a preferred direction of alignment on the molecular ensemble within the laboratory frame. In this way its interaction with the laser takes place in the molecular frame of reference and the role of the molecular structure may be resolved. As an example, one may now record the ionisation rate in a given linear molecule as a function of the angle between the linear probe laser polarisation and the molecular axis. Here, the angular distribution of photoelectrons would be a direct mapping of the ionised orbital of the probed molecule.

Impulsive molecular alignment is presented in full detail in Chap. 5. Briefly, a relatively weak (10^{13} Wcm^{-2}) femtosecond laser pulse kicks a linear molecule and forces it to rotate. Typical small diatomic molecules like N_2 have rotational periods of several picoseconds, so the interaction of the laser pulse is much shorter than the time-scale of the induced rotation. The laser pulse thus induces a coherent superposition of rotational states of the molecule creating a rotational wavepacket that is initially aligned along the laser pulse polarisation. Due to the imposed phase relationships between the coupled rotational states, the wavepacket subsequently de- and rephases periodically at times that are characteristic to the molecule. Constructive interference of the rotational states is associated with alignment of the wavepacket along the initial laser pulse polarisation and thus allows the probing of a molecular ensemble fixed in the laboratory frame of reference under field free conditions.

Through the above developments, the control of strong field induced dynamics in small molecules on the femtosecond time scale continues to be a fruitful branch of research; also for establishing the experimental and theoretical tools required to go towards ever faster molecular dynamics and more complex molecular systems. This is the context of the experiments presented in this thesis. They aim at resolving the role of the molecular structure in strong field induced processes in CO_2 by the use of optimised impulsive molecular alignment.

CO_2 was chosen as a target molecule for several reasons. It is a triatomic molecule and thus the smallest possible polyatomic system. This implies that all fundamental molecular processes, such as vibration, bending and internal couplings can play a role in the probed dynamics, whilst the complexity of the molecule is kept as small as possible. Therefore CO_2 is a suitable model system to study ultrafast dynamics in the presence of a strong laser field.

Additionally, the choice of CO_2 also offers advantages from a practical point of view. Firstly a rather large body of work is available on the tunneling ionisation of CO_2 [12–14]. Secondly, the dissociation of the molecular ion CO_2^+ is relatively well understood [15]. Thirdly, the resulting fragmentation channels could be identified and isolated rather easily in the used experimental setup due to their lack of kinetic energy release [16]. Two processes were then investigated: the second ionisation and the dissociation mechanism of the molecular ion CO_2^+ . Both processes are driven by the initial tunneling ionisation of the neutral molecule. Through the use of molecular alignment, the orbital symmetries of the involved molecular ionic states could be resolved, such that the internal dynamics in the form of ionisation and excitation pathways were tracked down.

The ionisation of CO_2^+ —or double ionisation of CO_2 —can proceed in two ways. Firstly, the ion can be field-ionised. Here, the first and second ionisation event are independent of each other. In the second mechanism, CO_2 is ionised and the ejected electron driven into the continuum by the strong laser field. Due to its oscillatory motion, the free electron can be driven back to the parent ion and may excite or impact ionise it when they collide. This process is called laser driven electron recollision [17] and is attracting wide attention from strong field physicists as it represents an ultrafast process that can be fully controlled by the driving laser field parameters (see Sect. 2.1.3). In fact, the excursion time of the recolliding electron is about 3/4

of the laser field's oscillation period and can thus be tuned by its wavelength. The impact energy is given by the electric field strength and total acceleration time and hence can be tuned by the intensity and wavelength, respectively. Furthermore, the electron trajectory is confined to the plane of polarisation of the laser field. Using molecular alignment, the electron's recollision angle with respect to the molecular axis can thus be controlled by the laser polarisation.

This control perspective is especially interesting as electron recollision allows for inducing and probing ultrafast molecular dynamics combining sub-Ångstrom spatial with sub-femtosecond time resolution [18]. Here, the spatial resolution is related to the wavelength of the electron that is on the order of hundreds of picometers ($1 \text{ pm} = 10^{-12} \text{ m}$), whereas the time resolution is rooted in the excursion time of the electron in the continuum. This allows to time-resolve the sub-cycle dynamics in the molecule that take place between the initial tunneling ionisation and recollision event. These aspects have led to milestone experiments tracking down the nuclear motion in molecules [19, 20], structural changes during chemical reactions [21] or the tomographical imaging of molecular orbitals [22], to name but a few examples. In the experiment presented in this thesis, recollision induced double ionisation was controlled via increasing the driving laser wavelength and impulsive molecular alignment to angularly resolve the mechanism. This allowed for the identification of the intermediate ionic states involved in the double ionisation mechanism of CO_2 and thus suggests a novel way for employing inelastic electron recollisions as an ultrafast spectroscopy technique.

The dissociation of CO_2^+ requires its excitation to a repulsive state. In the strong field regime, this is possible via several pathways. Firstly, the tunneling ionisation of CO_2 may take place from a low lying orbital, which would leave the parent ion in an excited electronic state. In addition, inelastic recollisions [16] and laser induced photo-excitation may facilitate the population of excited ionic states. The experiments presented in this thesis firstly aim at identifying the contributions from the above channels to the dissociation mechanism by recording the resulting fragmentation yield as a function of different laser parameters such as intensity, ellipticity and polarisation. As the above excitation pathways proceed via different ionic states, their angular dependence in the molecular frame is related to the associated molecular orbitals. It was found that the fragmentation mechanism of CO_2^+ is dominated by a strong field induced coupling between its second and third excited state. This coupling and thus the fragmentation yield could be controlled by the laser polarisation with respect to the molecular axis and a signal suppression of up to 70% was achieved. This result is especially interesting from a theoretical point of view as it offers the possibility to study the ultrafast population transfer between electronically coupled states in the strong field regime. Theoretical tools that successfully describe such complex scenarios are needed for extending strong field spectroscopy to even more challenging processes such as charge migration or the coupling of electronic and nuclear degrees of freedom in biological systems.

In order to contextualise the research conducted for this thesis, I have structured its contents as follows. In Chap. 2, the strong field regime and its associated phenomena are introduced and applied to the case of small linear molecules. This includes a

brief introduction to molecular physics and the discussion of previous experimental research on double ionisation and strong field induced dissociation relevant to this thesis. In Chaps. 3 and 4, the laser system and the experimental setup employed for the experiments are presented and discussed in detail. Chapter 5 then introduces the technique of laser induced impulsive molecular alignment from a theoretical and experimental perspective. In particular, a novel procedure for characterising the quality of the resulting molecular alignment distribution in the used experimental setup was developed. This was applied to optimise molecular alignment in mixed gas samples that could then be used in the strong field experiments. Chapter 6 then presents the experiment on recollision induced double ionisation in CO_2 , whilst Chap. 7 focusses on strong field induced dissociation of CO_2^+ . In the last chapter, the results presented in this thesis are summarised. This leads to the discussion of their contribution to the scientific community, possible improvements and the motivation of new experiments.

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