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Malte Oppermann

# Resolving Strong Field Dynamics in Cation States of CO<sub>2</sub> via Optimised Molecular Alignment

Doctoral Thesis accepted by  
Imperial College London, UK

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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  $1 \text{ V/\AA}$ , 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  $\text{CO}_2$  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  $\text{CO}_2$  molecular axis with respect to the polarisation direction of the strong field. To do this he employed impulsive molecular alignment of  $\text{CO}_2$  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 CO<sub>2</sub>. 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 CO<sub>2</sub>. 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<sup>+</sup> + O and O<sup>+</sup> + 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 CO<sub>2</sub>, 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  $\text{CO}_2$  is resolved by the use of optimised impulsive molecular alignment. Two processes were investigated: recollision induced ionisation and the dissociation of the molecular ion  $\text{CO}_2^+$ . Both processes are driven by the initial tunneling ionisation of  $\text{CO}_2$ . 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  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  seeded in Ar.

The recollision induced or non-sequential double ionisation (NSDI) of  $\text{CO}_2$  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  $\text{CO}_2^+$  to the NSDI mechanism.

This study was extended to the strong field induced dissociation of impulsively aligned  $\text{CO}_2^+$ . 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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However, the fact that my experiments got done and even lead to some meaningful results is mostly due to a group of heroic postdocs from the Red Dragon Lab. They taught me everything I know. Omair Ghafur showed me how cool molecules are (oh yes, molecular-beam-pun intended) and that you need to put on the ‘Mission Impossible’ theme when you handle the most expensive equipment. I cannot thank Thomas Siegel enough for all his hohehoheho (French for ‘awesomeness’). He taught me how to use and (most importantly) fix the laser and his pragmatic approach and incredible talent at planning and building experimental setups were a massive help and inspiration. Amelle Zaïr was the best lab boss/mum I could have asked for. Whenever I got stuck in my project she was there to support me and her trust was invaluable for the progress of my work. Last but not least, I would like to thank Sébastien Weber for being the most awesome

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