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Martin Alex Bjørnholst

# Time-Resolved Photoionisation Studies of Polyatomic Molecules

Exploring the Concept  
of Dynamophores



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Martin Alex Bjørnholst

# Time-Resolved Photoionisation Studies of Polyatomic Molecules

Exploring the Concept of Dynamophores

Doctoral Thesis accepted by  
the University of Copenhagen, Denmark

 Springer

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# Supervisor's Foreword

Femtochemistry brings together researchers from a range of different disciplines; however, those with a strong foundation in fundamental organic chemistry are scarce and this is where the thesis of Dr. Bjørnholst bridges a gap. Organic chemistry is rooted in the functional group, that is, the idea that reactivity can be predicted and utilised based on specific structural units in a molecule. Femtochemistry, on the other hand, is often approached on a case-to-case basis with a slightly more fundamental assessment starting from quantum chemical calculations. The overarching idea behind the dynamophore, a term coined by the Stolow group where Dr. Bjørnholst spent time during his studies, is that functional groups or combinations thereof will determine the initial nuclear motions (the dynamics) of molecules that are electronically excited. These initial motions are predetermining for the chain of events that follow the absorption of a photon, and therefore the aim is to ultimately be able to predict how the nuclei move and what photophysical or photochemical processes these motions trigger simply from a glimpse at the molecular structure—exactly as it is possible for an organic chemist to predict what a carbonyl group will do with an electrophile. The thesis of Dr. Bjørnholst is unique in the sense that it consistently follows this line of thought throughout. By attempting to assess a large range of the possible electronic transitions that can arise from exposing an organic functional group to a photon, the thesis provides a consistent overview of exactly how most functional groups in organic molecules induce specific nuclear motions that potentially lead to specific electronic transitions and eventually selective photoinduced bond breakage—something which has been considered the dream of most photochemists for decades.

Copenhagen, Denmark  
May 2020

Prof. Theis I. Sølling

# Abstract

Non-adiabatic transitions are central in the study of photoinduced dynamics of polyatomic molecules. Time-resolved photoelectron spectroscopy (TRPES) is a technique that is particularly sensitive to the changes in electronic structure, and thus non-adiabatic transitions between electronically excited states have been revealed in a vast number of molecules by TRPES studies.

The non-radiative molecular response to excitation, e.g. internal conversion (IC), is often found to occur on the ultrafast timescale. The associated strong non-adiabatic couplings occur only along a small subset of nuclear degrees of freedom, and few structural changes are inherently responsible for ultrafast IC. The link between molecular structure and the excited state structural changes has previously been conceptualised as ‘dynamophores’.

The VUV photoinduced dynamics of four cyclic ketones and one linear ketone is studied and exhibit qualitatively similar dynamics. The initially excited states have 3d Rydberg character but also display partial ( $\pi, \pi^*$ ) valence character. The observed excited state lifetimes are quantitatively similar, indicating that a common deactivation mechanism is associated with 3d Rydberg excitation in ketones and as such the dynamics are consistent with the dynamophore concept.

The ring-opening and dissociative dynamics of cyclopropane are studied by a joint computational and experimental study. The computational results show that vertical excitation energies are inadequate to predict and assign the experimental absorption spectrum. The explicit inclusion of the electromagnetic field associated with a pump pulse is required to qualitatively reproduce the absorption spectrum. The ensuing dynamics are also simulated and show impressive quantitative agreement with the experimental results.

Model systems for the disulfide bond and the peptide bond, which are both related to the structure of proteins, are additionally investigated. The dynamics are similar in the sense that a dense manifold of Rydberg states is present in both cases,

and these efficiently couple with valence states, ultimately leading to dissociation. Finally, the potential ultrafast intersystem crossing (ISC) in three methylated benzene derivatives is investigated computationally, and the same structural change associated with IC is highlighted as being crucial to the potential ISC as well in all three compounds, consistent with a common dynamophore in the systems.



# Preface

This thesis has been submitted to the Ph.D. School at the Faculty of Science at the University of Copenhagen as partial fulfilment of the requirements to obtain the Ph.D. degree in chemistry. The work has been carried out under the supervision of Prof. Theis I. Sølling at the Department of Chemistry at the University of Copenhagen during a 3-year period from September 2015 to 2018. The majority of this time was spent in the Femtolab at the University of Copenhagen, carrying out experiments and calculations. Part of the work was also carried out during a 7-month visit to the group of Prof. Albert Stolow at the National Research Council of Canada (NRC) and the University of Ottawa in 2016, with an additional 3-week re-visit in March 2018. A purely computational project was carried out during a 6-week visit to the group of Prof. Leticia González at the University of Vienna in late 2017.

Copenhagen, Denmark

Martin Alex Bjørnholst

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- **Coherent Motion of Excited State Cyclic Ketones: The Have and The Have-Nots**, M.A.B. Larsen, A.B. Stephansen, T.I. Sølling, *Chem. Phys. Lett.*, (683), 495–499, **2017**
- **Vacuum Ultraviolet Excited State Dynamics of the Smallest Ring, Cyclopropane. II. Time-Resolved Photoelectron Spectroscopy and Ab Initio Dynamics**, M.R. Coates, M.A.B. Larsen, R. Forbes, S.P. Neville, A.E. Boguslavskiy, I. Wilkinson, T.I. Sølling, R. Lausten, A. Stolow, M.S. Schuurman, *J. Chem. Phys.*, (149), 144311, **2018**
- **Putting the Disulfide Bridge at Risk: How UV-C Radiation Leads to Ultrafast Rupture of the S-S Bond**, M.A.B. Larsen, A.B. Skov, C.M. Clausen, J. Ruddock, B. Stankus, P.M. Weber, T.I. Sølling, *ChemPhysChem*, (19), 2829–2834, **2018**
- **Vacuum Ultraviolet Excited State Dynamics of Small Amides**, M.A.B. Larsen<sup>a</sup>, T.I. Sølling, R. Forbes<sup>a</sup>, A.E. Boguslavskiy, V. Makhija, K. Veyrinas, R. Lausten, A. Stolow, M.M. Zawadski<sup>a</sup>, L. Saalbach<sup>a</sup>, N. Kotsina, M.J. Patersen, D. Townsend *J. Chem. Phys.*, (150), 054301, **2019** (<sup>a</sup>joint lead investigators)

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I am sincerely grateful to Prof. Albert Stolow for letting me visit his group and thereby giving me the possibility to learn from all the amazing people at the NRC. The many discussions on diverse subjects and field trips made my stay absolutely joyous thanks to excellent people like Andrey, Coates, Hockett, Kévin, Ruaridh, Rune, Ryan, Schuurman, Simon, Spanner, Varun and many more. I must especially thank Andrey for his ability to accommodate a solution to almost any technical request and Varun for his patient manners and his attempts to teach me some physics. I am also grateful to Spanner for breaking his own promise of never again spending time with temporary visitors to make friends and to Rune for providing opportunities to enjoy Danish liquorice, cross-country running, skiing and sailing. Last but not least, I probably spent the majority of my time in Ottawa in the company of Ruaridh and even late nights collecting data became tolerable (if not habit) in his dedicated and humorous company.

I am also grateful to Prof. Leticia González and her friendly group for showing me the computational chemists' perspective and I in particular owe thanks to Clemens, Maximilian, Nico, Patrick, Pedro and Sebastian for doing their best to teach me the basics of multi-reference quantum chemistry and their use in

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# Abbreviations

B.O.	Born-Oppenheimer
BBO	$\beta$ -barium borate
CCD	Charge-coupled device
CH	Cyclohexanone
CI	Conical intersection
CP	Cyclopentanone
DEDS	Diethyldisulfide
DMA	<i>N,N</i> -Dimethylacetamide
DMF	<i>N,N</i> -Dimethylformamide
E-L	Even-Lavie
FC	Franck-Condon
fs/ps/ns/ $\mu$ s	Femto-/pico-/nano-/microsecond
FOR	Formamide
FWHM	Full-width at half-maximum
IC	Internal conversion
IE	Ionisation energy
ISC	Intersystem crossing
MCP	Multi-channel plate
MECP	Minimum energy crossing point
PAD	Photoelectron angular distribution
PEL	Potential energy landscape
PEC	Potential energy curve
REMPI	Resonance-enhanced multi-photon ionisation
SOC	Spin-orbit coupling
TRPES	Time-resolved photoelectron spectroscopy
TRMS	Time-resolved mass spectrometry
VMI	Velocity map imaging
VUV	Vacuum ultraviolet

1,2-DT	1,2-dithiane
2-MCP	2-Methylcyclopentanone
2-MCP	3-Methylcyclopentanone
3P	3-Pentanone