

Understanding the reaction kernel of ring-closing reaction through broadband transient absorption spectroscopy

Prof. R. J. Dwayne Miller
<https://lphys.chem.utoronto.ca>

USRA program 2023

An electrocyclic ring-closing reaction is a prototypically classic example of a bond-making process. Following the atoms while bonds are being formed, is the ultimate magnum opus of chemistry and understanding the spatial correlations of the reactants in solution versus lattice will open up new research possibilities and may revolutionize new ways of carrying out reactions. In this regard, the conquest of comprehending the reaction mechanism through the barrier-crossing process becomes imperative because of the enormous reduction of dimensionality during a chemical reaction which still eludes chemists and physicists all around the world. The idea of only a few key reactive modes out of $3N-6$ degrees of freedom (N being the number of atoms) driving a chemical reaction through the transition state is still an open quest yet fully to conquer. Ultrafast broadband transient absorption spectroscopy gives information on the timescales of ultrafast electronic evolution while careful engineering of the femtosecond optical pulses forces the molecular vibrations to pack together to form a wavepacket. This allows us to elucidate the key reactive modes ultimately defining the reactive kernel in the photoinduced ring-closing processes. These studies are the precursor to ultrafast electron diffraction experiments which gives the direct observation of atomic motions along the barrier-crossing process with a previously unimaginable sub-Angström resolution ($< 1/100$ th of typical bond lengths) to bring the chemists' 'Gedanken' experiment for conceptualizing chemical reactions to reality.

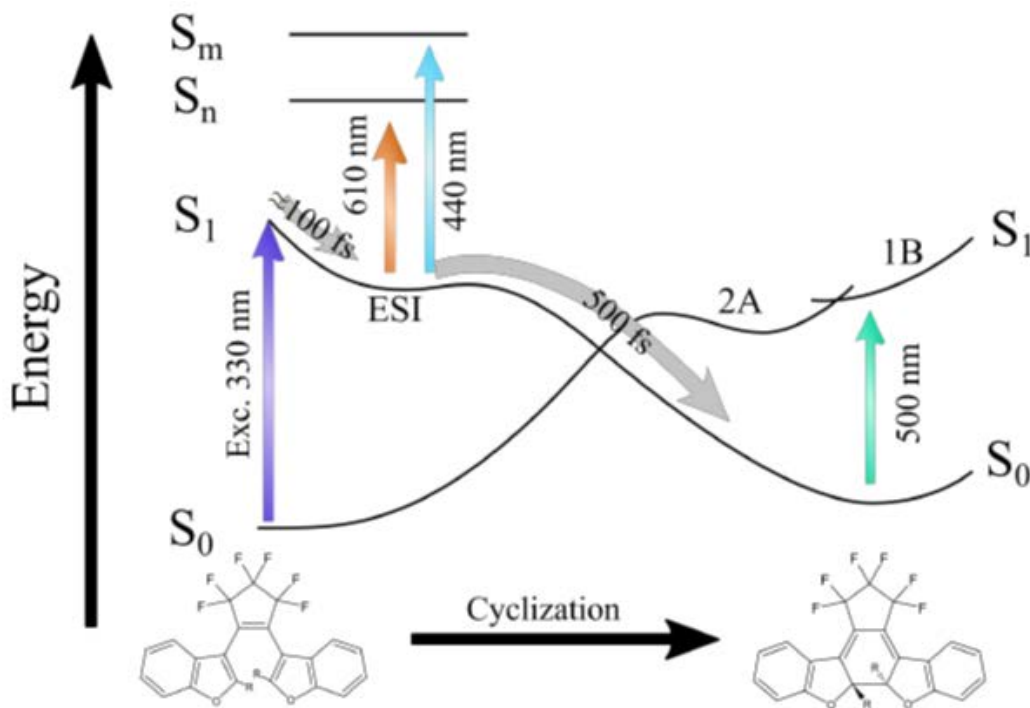


Fig 1. Scheme of events in the cyclization process of DFE (Difurylene derivative). The image is taken from Dr Simon Bittmann's thesis.

The goal of this project is to work with the available experimental transient absorption datasets in single crystal and solution phase of Difurylene derivative of different substituents to analyze the timescales of electronic evolution and perform time-frequency analysis to figure out the key reactive modes driving the ring-closing reaction. The project will also involve carrying out quantum chemical calculations (DFT/TDDFT in gaussian) to elucidate the nature of the excited and ground state vibrations, and possibly assigning them to the experimental findings. It is an exciting and challenging project, and enthusiastic students are encouraged to join the program. The student will work with a senior graduate student in a dynamic interdisciplinary environment. Prior knowledge in quantum mechanics and scientific programming is required for the project (preferably MATLAB or Python).

For more information please contact Soumyajit Mitra, soumyajit.mitra@mail.utoronto.ca

References

1. Bittmann, S. F. *et al.* Ultrafast ring-opening and solvent-dependent product relaxation of photochromic spironaphthopyran. *Phys. Chem. Chem. Phys.* **21**, 18119–18127 (2019).
2. Johnson, P. J. M. *et al.* Local vibrational coherences drive the primary photochemistry of vision. *Nat. Chem.* **7**, 980–986 (2015).
3. Kuramochi, H. & Tahara, T. Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy. *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).