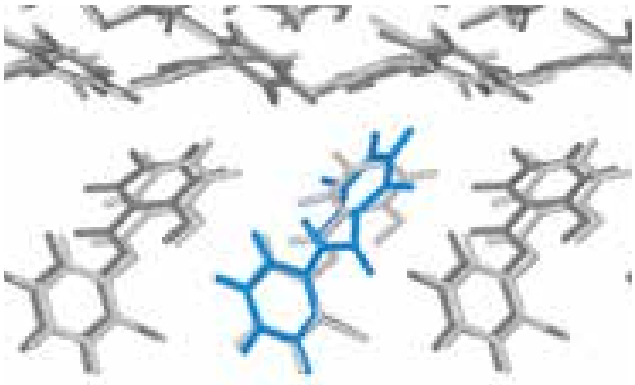
[MS31 - 02] Exciting 'stuff': modelling photochemical reactions in the condensed phase. Applications in time-resolved diffraction. Carole A. Morrison, Michal A. Kochman,

School of Chemistry and EaSTCHEM Research School, University of Edinburgh, EH9 3JJ, UK. Email: c.morrison@ed.ac.uk

Interpreting the data obtained from time-resolved pump/probe electron diffraction experiments is challenging, so we have been looking to develop computational methods to help with this process. For the solid state, we know that laser-induced photo-excitation will affect a subset of molecules randomly distributed in the crystal while the remainder stay in a non-reactive ground state. From a modelling perspective the problem is therefore how to treat one molecule in a crystal lattice differently to the rest.

We have achieved this aim by adopting a novel implementation of the QM/QM subtractive paradigm, whereby the reactive molecule is treated using an excited-state quantum mechanical procedure, such as CASSCF or TD-DFT coupled to a localised basis set, while the rest of the system is modelled at the DFT level with a localised basis set. [1,2] In this way we can calculate and extract the forces on the atoms. From here we can run molecular dynamics simulations to model the timescales for photochemical events, or follow geometry optimisation procedures to obtain the reactive intermediate embedded in a crystal lattice.

As an illustration of the predictive power of this simulation method, in this talk we will discuss its application to the test system N-saliclidene-2-chloroaniline (shown in Figure), which undergoes a pedal-motion following photoexcitation. We will also discuss the predicted photocyclisation dynamics of a diarylethene derivative, where structures obtained by our QM/QM method are compared to time-resolved electron diffraction data.



[1] M. A. Kochman and C. A. Morrison, *J. Chem. Theory Comput*., (2013), **9**, 1182-1192.

[2] M. A. Kochman and C. A. Morrison, Phys. Chem. *Chem. Phys, in press.*

[3] H. Jean-Ruel, R. Cooney, M. Gao, L. Meng, M. A. Kochman, C. A. Morrison and R.J. D. Miller, *J. Phys. Chem. A*. (2011), **115**, 13158.

Keywords: photochemical reactions, time-resolved diffraction, ab initio calculations.