Frontiers of time-resolved spectroscopy and application to quantum dynamics of excitons
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The ultrafast dynamics of excited quantum states in condensed matter present us with a deep challenge to fully comprehend all the complex quantum and classical processes that may occur. On the other hand a fuller understanding will lead to potentially large technological benefits e.g. in optoelectronics of optimized devices for solar energy. A key part of that fuller understanding is to gain an insight into the very fastest timescales of exciton dynamics that hitherto have stayed hidden. We are now applying one of the very latest techniques in attosecond science – time-resolved soft X-ray absorption spectroscopy – with the prospect of returning new understanding of the few-fs dynamics of excitons in matter and the possibilities for their control.

In the case of a condensed phase system or a large molecule, photoexcitation can result in the formation of an excitons, i.e. Coulomb–coupled excited electron and a vacancy (hole). The initial quantum coherence is rapidly damped due to intra- and inter-system interactions. Ultrafast, often sub-10 fs, channels of exciton evolution can be detrimental for the functionality of molecular materials and devices. For this reason, ultrafast dynamics in molecular systems have been extensively studied in the last 20 years including by our collaborators at Imperial Nelson, Durrant, Bakulin. However, most applied spectroscopic techniques cannot resolve dynamics faster than 100 fs, and only a handful of studies have managed to approach 20 fs limit. As a consequence, so far little is known about the initial formation and dynamics of excitons happening on very fast (<10 fs) timescales.

We intend to study these processes in polythiophene films, the base material for many polymer optoelectronic devices. Examples of open questions of clear fundamental and practical importance that we plan to address include: What is the role of electronic coherence and decoherence in exciton transport? Can external laser fields be used to drive excitons to more efficiently follow paths to the charge separation which is required for solar energy conversion? As a first step in this investigation we have recently used a source of soft X-ray (SXR) light from high harmonic generation with a pulse duration less than 1 fs to study the electronic states of these excitons by probing at the carbon K edge (285 eV) (see figure).

6 month project The project would work on our newly developed beamline, which uses high harmonic generation of SXR attosecond pulses for pump-probe transient absorption. The probe pulses are the HHG attosecond pulses mentioned above, the pump pulses (to excite the excitons) lie in the visible. The task in the project will be to study the likely spectrum and factors affecting the quantum dynamics of the excitons to choose appropriate material morphologies to isolate the dynamics. Then to develop and diagnose a source of short pulses of the appropriate wavelength with a duration less than 10 fs for the pump pulse.

PhD project: The main project will build on this by pushing towards a few-femtosecond temporal resolution transient absorption measurement. This would be developed with thin polymer samples and the sub-fs SXR and sub-10 fs optical pulses. The objective would be to measure, for the first time at the femtosecond timescale, the coherent evolution and damping of the exciton state following photoexcitation of the polymer. Methodologies of ultrafast optical pump-probe spectroscopy with additional control laser pulses will then be combined with the SXR probing to build up a complete picture of the underlying dynamics and their quantum control. The possibility to use ultrafast pulses for sub-10-fs optical control of molecular nanodevices will be investigated by this work. We would work closely with experts in optoelectronic materials in the Chemistry Department (Artem Bakulin) and in the Centre for Plastic Electronics.

The project provides a unique opportunity to apply your knowledge of controlled quantum dynamics and training in advanced ultrafast science to a real world technological challenge of high importance.

1 J. Frenkel, Physical Review 37, 17 (1932)
7 A.Johnson et al, Structural Dynamics 3, 062603 (2016)