Multi-dimensional terahertz spectroscopy of organic semiconductors

Supervisor: Prof. James Lloyd-Hughes. Email: j.lloyd-hughes@warwick.ac.uk

Molecular organic semiconductors are stable and easily processed, making them excellent materials for some advanced optoelectronic devices and display technologies, but their range of scope is limited by their low electrical mobility. The THz frequency vibrational modes of crystalline molecular organic semiconductors have been suggested to critically limit their mobility [**1**]: with low enough energy to be highly active at room temperature, these intermolecular vibrational modes can modify the overlap of electronic states from molecule to molecule, changing the ease with which electrons flow through the crystal. Linear THz spectroscopy, with low electric field strengths, can struggle to distinguish the many vibrational modes in the complex spectra of molecular organic semiconductors.

In this project, the student will therefore develop a new experimental capability: a multi-dimensional coherent THz spectrometer, which they will use to investigate the vibrational and conductive properties of organic semiconductors. Multi-dimensional nonlinear spectroscopy methods are well-known in the visible and infrared wavelength ranges [**2,3**] and are analogous to established 2D NMR methods. In the simplest schemes, a sequence of pulses initialise and then probe quantum coherent states, creating 2D spectrograms that contain information about coupling between modes, and about dynamic changes in electronic and atomic structure. Although nonlinear spectroscopy provides a wealth of useful information beyond that of linear spectroscopy, and experimental techniques are well established in the visible and infrared ranges [**2,3**], multi-dimensional spectroscopy in the THz range is in its infancy [**4**].

In this project, the student will build a new multi-dimensional THz spectrometer (MDTS) capable of examining the nonlinear optical properties of materials at THz frequencies via 2 pulse and 3 pulse schemes. This will build on experience and advances in the research group and WCUS RTP [**5**] in generating and detecting intense (MV/cm) THz pulses, and in quantum coherent vibrational processes [**6**]. The student will then use MDTS to probe how different vibrational modes are coupled in organic semiconductors, examine their anharmonicity, and investigate electron-phonon coupling. The fundamental insights gained into the structure and dynamics of organic semiconductors will enable the development of the next generation of materials, with higher mobility. The student will gain excellent training in cutting-edge experimental methods, and be part of an international collaboration with industrial and academic partners.

References

1. G. Schweicher *et al.,* Advanced Materials **31** 1902407 (2019).
2. S. Mukamel. "*Principles of Nonlinear Optical Spectroscopy*", Oxford Series on Optical and Imaging Sciences. Oxford University Press, New York, 1995.
3. P. Hamm, M. Zanni, "*Concepts and Methods of 2D Infrared Spectroscopy*", Cambridge University Press, 2011.
4. K. Reimann, M. Woarner and T. Elsaesser, J. Chem. Phys. **154** 120901 (2021).
5. The Warwick Centre for Ultrafast Spectroscopy is a laser facility used by researchers from across the UK, and is one of the University's research technology platforms. go.warwick.ac.uk/WCUS
6. J. Keat *et al.*, Phys. Rev. Lett. **129** 237401 (2022).