Modelling the impact of vibrational modes on electronic dynamics and transport in molecular electronic materials and devices

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**Abstract**
Molecular electronic materials have attracted intense interest for applications in low-energy electronics and energy conversion. Whilst these materials benefit from facile processing and extensive control of properties by tuning molecular structure, they suffer from intrinsic energy losses through the strong coupling of electronic and vibrational states. This electronic-vibrational coupling limits charge-carrier mobility via the reorganisation of the molecular environment to localise charges and the resulting energetic cost of mobilising the charge. Vibrational relaxation of excited states was recently identified as the primary pathway for non-radiative potential losses in molecular solar cells, limiting photovoltaic efficiency [1]. Whilst vibrational loss pathways limit device performance in general, little attention has been paid to the effects of specific vibrational modes. Recent experimental reports demonstrate that exciting specific modes could enhance charge transport [2] or charge separation [3], motivating the development of relevant computational models. In this project we will build simple models of the role of vibrational modes in charge transport, first by incorporating vibrational states explicitly into the dynamic dielectric response of the molecular environment during charge propagation, building directly on a recent TSM CDT PhD [4]; and second by calculating the electronic-vibrational coupling terms to simulate the effect of exciting specific vibrational modes on charge carrier mobility. The final (PhD) phase will address the impact of specific vibrational modes on the generation and decay of charge transfer excited states at donor:acceptor interfaces, to move beyond simple models [5] and improve materials for solar energy conversion.


**What is the multi-scale nature of the project?**
Performance of electronic devices and solar cells is determined by macroscopic (device-level) properties such as charge-carrier mobility, photoconductivity and photovoltage. The underlying electronic states, and the vibrational modes with which they couple, extend over molecular (few nm) length scales, with charge transfer processes occurring on ~picosecond time scales. These microscopic processes contribute to the net conduction of charges and energy over 100s of nm and microsecond time scales in devices. Whilst multi-scale models exist to relate electronic transfer at molecular level to macroscopic properties, these generally do not include vibrational states or if so, only without chemical specificity. The multi-scale nature of the project lies in the use of molecular vibrational and electronic calculations to determine parameters for charge and energy transfer that can be incorporated into Monte-Carlo or rate-equation models of devices.
In the MSc phase, the multi-scale nature of the proposed approach lies in the use of molecular-scale information on the energy, intensity and nature of the vibrational modes to develop a coarse-grained treatment of polaron states, and to construct a dielectric response function to describe the polaronic electron-phonon coupling. The time scale of the dominant vibrational modes will be used in the simulation of non-adiabatic polaron detrapping and transport. The model for polaron dynamics is based on direct propagation of the electronic wavefunction, coupled with a classical response of the dominant vibrational modes in the coarse grained molecular assembly. Direct Master equation solutions and/or kinetic Monte Carlo models will be used to propagate the charges within the coarse grained assembly.

In the PhD phase, the energies and strengths of the vibrational modes of the donor: acceptor complex will be used to parametrise a model predicting rates of radiative and non-radiative decay of the charge-transfer excited states, which can then be used in a macroscopic model of non-radiative losses and their impact on device performance. For the macroscopic scale work, we will use simple one-dimensional models of solar cell device performance, and Monte Carlo models of charge generation and survival to compare with transient spectroscopic measurements.

How do the expertise of the supervisors complement each other?

Nelson is an expert in the science and application of molecular electronic materials who brings oversight of experimental and applications aspects as well as the theory of electronic materials and devices. She has developed multi-scale approaches to the properties of nanostructured and molecular semiconductor materials and response of devices, for almost 20 years. The second supervisor, Dr Bakulin, is a leader in the design and implementation of experimental electronic and vibrational spectroscopic methods to probe charge dynamics in novel semiconductor systems. In particular, he has developed techniques to probe the impact of vibrational excitation on electron dynamics. Although primarily an experimental spectroscopist, Dr Bakulin brings a profound understanding of the nature of vibrational-electronic interactions in molecular semiconductors and the relevant theoretical descriptions. Moreover he is currently developing experimental measurements which will be essential for validation of the theoretical work. The third supervisor, Dr Frost, has over ten years’ experience in the in development and application of efficient computational methods to simulate the electronic properties of materials, including the development of coarse-grained models that span the length scales between atoms and molecular subunits. Importantly, he has recently developed an exceptional understanding of the nature of polarons in soft electronic materials, along with recent code development in solving the path-integral variational model of the Frohlich polaron, which he brings to this project. Together with a previous TSM student Frost and Nelson developed a coarse-grained approach to model polaron formation in molecular systems, which underpins part of the proposed study.

Note:
(i) Nelson and Bakulin have not previously collaborated
(ii) Although this is not a cluster project, the project promises teamwork, as the proposed work is well aligned to that of Bakulin’s PhD student, Nathaniel Gallop, 2017-20, on experimental measurement of vibrational excitations on charge transport, and to a physics DTP student Mohammed Azzouzi, 2016-20, who has developed device-scale models of the contribution of vibrational modes to losses in solar cells.

Literature Review
Title: *How does the excitation of vibrational modes in molecular electronic systems influence the rate of intermolecular and intramolecular charge transfer?*
MSc Project

The first stage will implement an approach to polaron transport in molecular materials where we evolve the electronic wavefunction in its dielectric environment whilst allowing the polarisable molecular environment to respond classically. A 1D code has already been developed. We will construct the dielectric function with chemically specific calculation of the optically active vibrational states of the system and allow the dynamic reorganisation of molecular dipoles during and in response to charge movement. A critical parameter will be the length scale over which the charge is localised in different systems, as this determines which approximations to charge transport (e.g. hopping transport) are valid. Detrapping of the localised polarons will use a stochastic surface-hopping approach. The method will be applied first to C60 as an isotropic system of simple vibrational structure and then to a more anisotropic but well studied system such as pentacene. The second stage will address how excitation of a specific vibrational mode, in each test system, influences charge transport. This will include the impact of the mode on transfer integral via intermolecular (non-local) coupling and on site energy via the local deformation potential, and possibly on localised heating. A key question is whether excitation of a specific vibrational state will then enhance polaron transport via detrapping, or inhibit it. These studies will be developed to align with experimental measurements.

In the PhD stage the work will address charge transfer between different (donor and acceptor) molecules, in the processes of interfacial charge separation, back transfer, and non-radiative charge recombination. As above, we will scrutinise the role of particular modes in the intermolecular coupling and the local potential energy. A particular goal is to advance on existing frameworks [1,5] that describe non-radiative recombination quantitatively in terms of simultaneous excitation of several vibrational modes, but neglect the chemical nature of those modes and their specific different impacts. This stage will address the key limits to power conversion efficiency in molecular photovoltaic systems and guide materials design.