Understanding Coherent Microscopic Spin Processes via Macroscopic Transport Measurements on Organic Photovoltaic Devices

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Organic semiconductors are a complex material system – chemical and conformational changes may influence electronic structure, and temperature and voltage can impact transport properties [1]. Spin also plays a crucial role, impacting a wide range of physical processes including recombination and dissociation of charge pairs, and also in magnetoresistive effects [2,3]. Interestingly, however, relatively little study on the effect of such parameters on coherent spin processes has been undertaken, particularly for organic semiconductors included in devices. One reason for this may be the difficulty in undertaking spin resonance on thin films in device geometries. In this talk, I will discuss recent advances in measuring coherent spin effects in organic semiconductor devices, what we have learnt about spins in these materials and the impact similar techniques have had in other material systems.

Coherent spin processes involving electronic spins have been investigated in bulk semiconductors for over 60 years. Traditionally, electron spin resonance has been the method of choice for investigating such effects – time varying magnetic fields are used to manipulate spin ensembles, and the subsequent decay of the ensemble magnetization is monitored to infer resulting dynamics. Whilst powerful and widely utilized, this technique is impeded by a detection limit when the number of spins in a sample is small – such as in thin-film or nanoscale electronic devices.

Alternative detection techniques allow this problem to be overcome. For example, if spin dependent electronic transport processes exist, monitoring the change in current through a thin-film device when spins are manipulated can prove a much more sensitive way to detect spin resonance. Thankfully, many spin dependent processes exist in semiconductors, including spin-dependent scattering, trapping, hopping and recombination, as do a number of optical processes including photoluminescence. If these processes can be independently monitored, only those spins which impact the specific process will be observed, providing a powerful tool to distinguish between sub-ensembles of spins, which would be much more difficult with conventional spin resonance techniques.

In this talk, I will discuss the application of electrically detected spin resonance techniques to organic semiconductors. Particular attention will be given to organic light emitting diodes, as such devices provides a wide level of control as well as the ability to investigate both electronic and optical spin dependent processes. The main focus of the talk will be extending electrically detected spin resonance in organic materials to the detection and investigation of *coherent* spin motion, and related effects.

Initially, the technical requirements for coherent spin manipulation and electronic measurement will be discussed. A novel device architecture will be presented which allows the application of the homogeneous high power microwave pulses required for controllable spin manipulation [4].

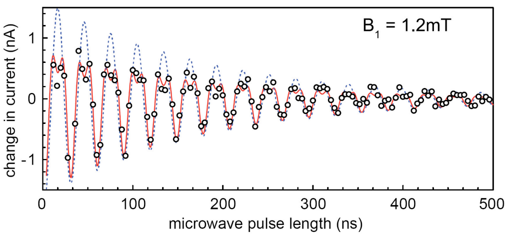

Figure 1: Coherent spin Rabi oscillations of the carriers in MEH-PPV OLEDs leads to a change in the current through the device. From [7].

The resulting change in the current will be considered theoretically [2], and compared to experiment.

With the ability to manipulate and detect spins, more complicated coherent experiments can be undertaken. Rabi oscillations demonstrate that truly coherent effects are visible [5]. Hahn echoes allow phase coherence times to be obtained. Since most electrical spin processes depend on permutation symmetry within spin pairs rather than simply ensemble polarization, coherent spin processes can be observed even at high temperatures. Spin coherence times exceeding 0.5 μs have been observed at room temperature [6].

Novel effects are seen, including spin beating with carrier pairs, resulting from the local spatial variations in the Overhauser field of the hydrogen nuclei which make up the organic semiconductor. We are able to use these processes to measure the difference in Overhauser field felt within an electron-hole pair, on the scale of ~2 nm [7].

The final section of the talk will provide a brief overview of the range of application that the techniques presented here have found in inorganic semiconductors devices, and how these may be used to increase our understanding of electronic and optical processes in organic semiconductors.

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