Ultrafast Optical Studies of Electron Spin Coherence in CdSe Nanocrystals

Rice,W.D. (NHMFL-LANL); Liu, W.; Baker, T.A.; Chen, G.; Pietryga, J.M.; Klimov, V.I. (CPCS-LANL); Crooker, S.A. (NHMFL-LANL)

Introduction: Colloidal semiconductor nanocrystals exhibit sharp, atomic-like absorption and emission spectra that are blue-shifted from their bulk analog by the strong confinement of the exciton wavefunction. Large efforts worldwide have focused on utilizing the size-dependent optical properties of nanocrystals, along with their strong emission efficiencies, to produce photon-harvesting devices. However, less attention has been paid to the spin properties of confined electrons and holes in semiconducting nanocrystals. Previous efforts that have examined this aspect used either magnetic circular dichroism and/or electron spin resonance measurements to measure Zeeman splitting in both undoped and doped semiconducting nanocrystals (see, for example, Refs. [1] and [2]). While electron spin resonance can probe embedded magnetic moments, it is not a good tool for measuring transient electrons and holes. Conversely, magnetic circular dichroism measures Zeeman splittings of excitons, but it cannot extract their dephasing time. Motivated by earlier work [3], we therefore constructed a time-resolved Faraday rotation (TRFR) setup based on a wavelength-tunable optical parametric oscillator, to directly and simultaneously investigate both the Zeeman splitting and spin dynamics of electrons in colloidal nanocrystals.

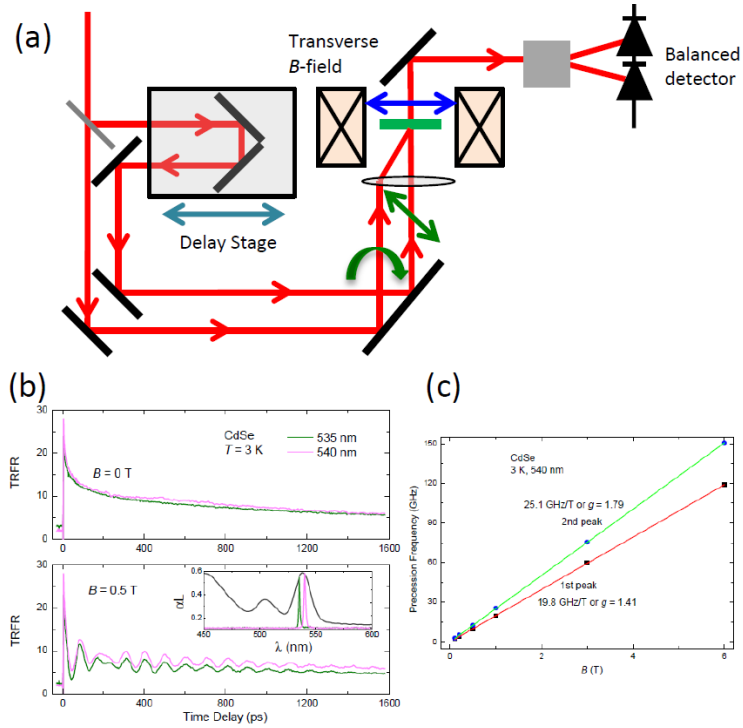

Figure 1: (a) Experimental schematic of the TRFR setup. (b) Wavelength-dependent TRFR traces at 3 K for two different applied magnetic fields. (c) Magnetic field dependence on the two precession frequencies observed in CdSe. As expected, the linear dependence follows from simple Zeeman splitting of the lowest exciton transitions.

Experiment: In the TRFR technique, a circularly-polarized pump pulse optically orients electrons and holes in an ensemble of colloidal nanocrystals. Spin dynamics are then interrogated via the Faraday rotation (optical polarization rotation) that is imparted on a time-delayed and linearly-polarized probe pulse (Fig. 1a). Because of the transversely applied magnetic field, the linear polarization is Faraday rotated by the presence of spin-polarized, coherently precessing excitons. Typically, because of strong valence band mixing, the hole dephases very rapidly after the pump pulse, leaving only a coherent electron that is observable in TRFR.

Figure 1b shows that the long-lasting (~1 ns) electron dephasing envelope in CdSe does not significantly change when we investigate different subsets of nanocrystals by changing the laser wavelength. When a finite field is turned on, electron precession is clearly observed over 1 ns. Interestingly, this precession shows a beating pattern from two resolvable frequencies. By changing magnetic field, B, we find that both of these precession frequencies follow a linear dependence on B (Fig. 1c). This linear behavior confirms our expectations that we are probing the Zeeman splitting, $\Delta E = g\mu B$ (where μ is the Bohr magneton), of the CdSe 1S exciton. Indeed, the g-factor of 1.4 that we obtain from our data agrees very well with magnetic circular dichroism data obtained on similar samples [1]. The higher precession frequency, g = 1.8, may be related to unpaired electrons from surface traps or free-radicals from ligands. For temperatures below 100 K, we see little change of the precession frequencies. Future work may include investigating similar binary colloidal nanocrystals, like ZnSe.

This work was supported by the Los Alamos National Laboratory LDRD program.

[1] M. Kuno *et al. J. Chem. Phys.* **108**, 4242 (1998).
[2] P. I. Archer *et al. Nano Lett.* **7**, 1037 (2007).
[3] J. A. Gupta *et al.*, *Phys. Rev. B* **59**, 10421 (1999)