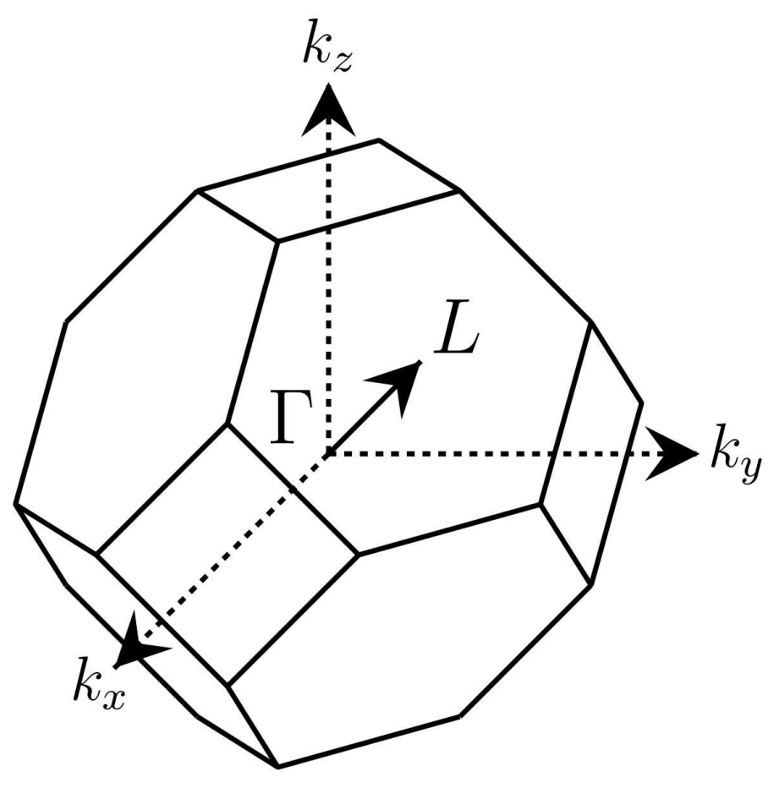
SAND2016-9289C

The Initial Pump-Probe Polarization Anisotropy of Colloidal PbS Quantum Dots

Samuel D. Park, Dmitry Baranov, Jisu Ryu, and David M. Jonas
Department of Chemistry and Biochemistry, University of Colorado

Introduction:

- Bulk lead chalcogenide semiconductors have a rock salt structure and an interesting electronic structure, with their bandgap at the 4-fold degenerate (8-fold including spin) *L*-point of the first Brillouin zone, where $\vec{k} = (\pm\pi/a, \pm\pi/a, \pm\pi/a)$ [1].
- The electronic structure near the bandgap of their quantum dots (QDs) is more complicated than suggested by the particle in a sphere model commonly used to explain quantum confinement [2].
- Theoretical studies report that the splittings of the energy levels in lead chalcogenide QDs due to intervalley coupling are sensitive to the arrangement of atoms having an inversion center, stoichiometry of the QDs, and the surface passivation [3].
- The theoretical results imply that the confinement gives rise to a complex electronic structure, which affects both linear and nonlinear spectroscopic measurements; this naturally leads to question about how the electronic structure in QDs affects the bi-exciton states.



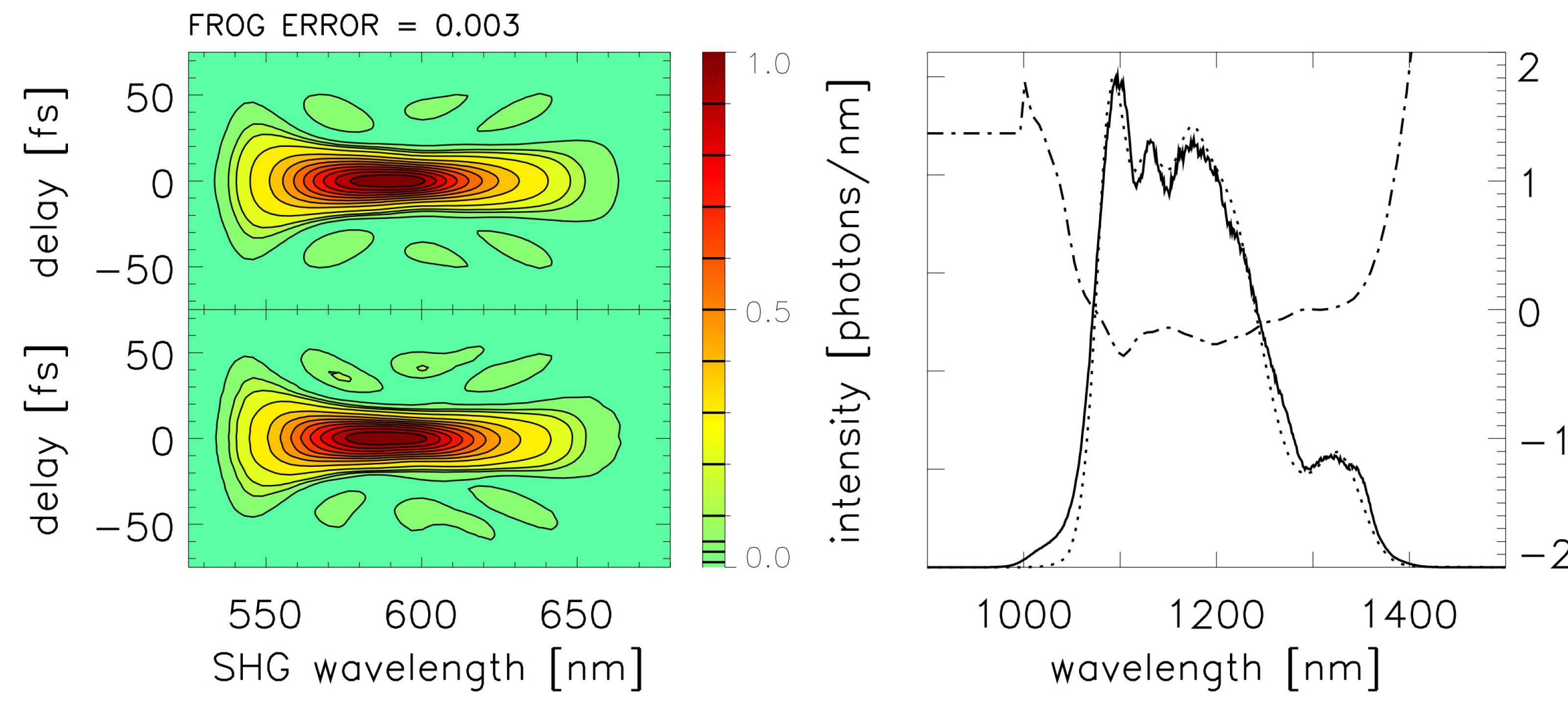
- The pump-probe polarization anisotropy is a valuable technique for probing the electronic structure of QDs because it can provide structural information on the angles between transition dipoles.
- The polarization anisotropy is obtained by taking the difference between parallel and perpendicular pump-probe signals and dividing by the isotropic signal (the division by the isotropic signal removes common factors, such as lifetime decay, so that the anisotropy purely reflects the change in dipole alignment), given by the equation:

$$r(\omega,T) = \frac{S_\parallel(\omega,T) - S_\perp(\omega,T)}{S_\parallel(\omega,T) + 2S_\perp(\omega,T)},$$

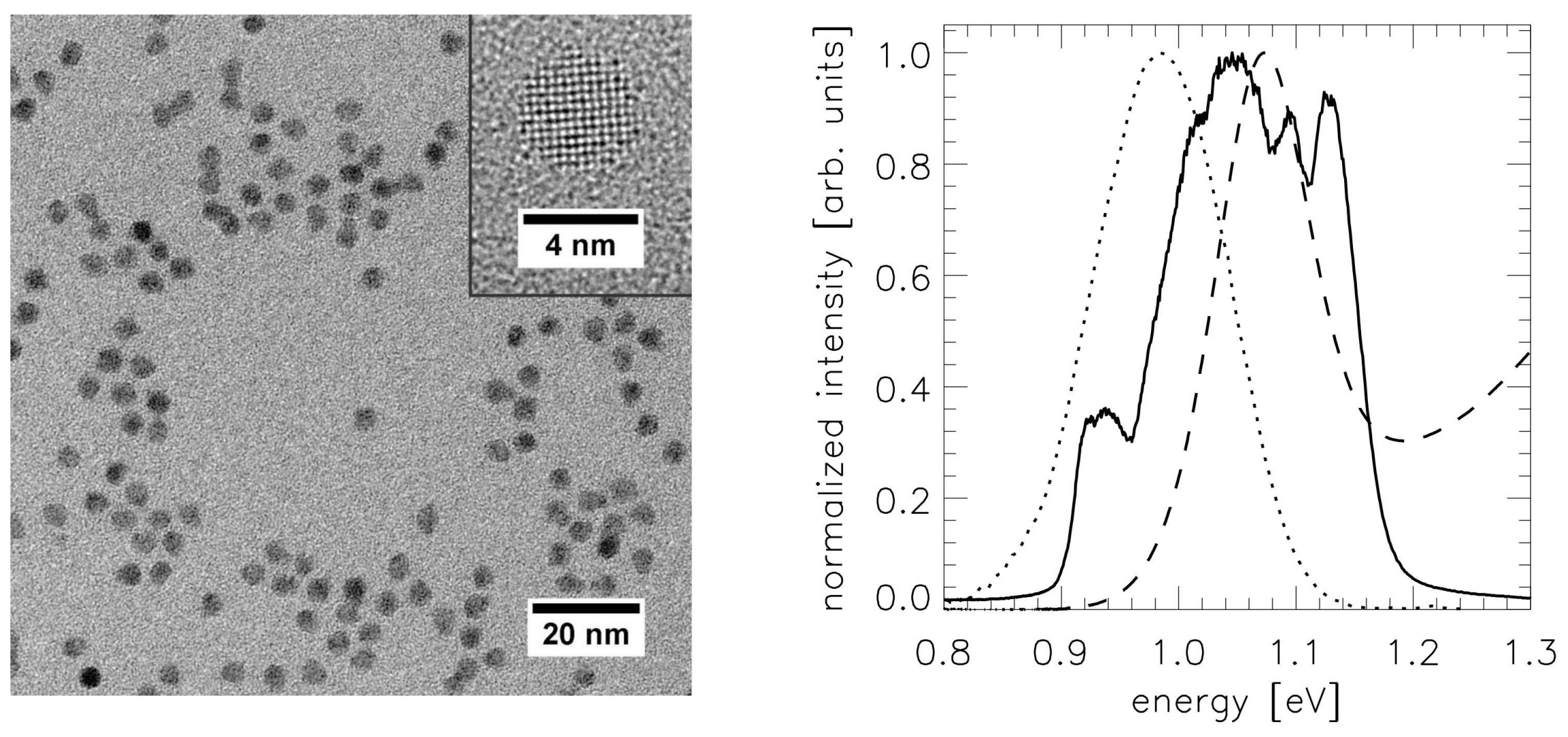
  where $S_\parallel(\omega,T)$ and $S_\perp(\omega,T)$ are the spectrally resolved pump-probe (SRPP) signals with probe polarization parallel and perpendicular with respect to the pump at a time delay, *T*.
- In an orientationally isotropic ensemble of molecules with non-degenerate transitions, the initial anisotropy should be 2/5, because the $\cos^2(\theta)$ dipolar excitation probability gives rise to a 3:1 signal strength ratio between parallel and perpendicular polarization geometries.
- If the coupling between degenerate or quasi-degenerate transitions is weak enough such that all of the single excitations remain within the pulse bandwidth, the initial anisotropy of 2/5 is recovered in pump-probe signals from degenerate transitions.

Experimental methods:

- Pulses from a 1 kHz Ti:Sapphire regenerative amplifier pump a single-pass, short-wave IR non-collinear optical parametric amplifier with a PPSLT crystal, and compressed using a deformable mirror to pulse durations of 15 fs [4].



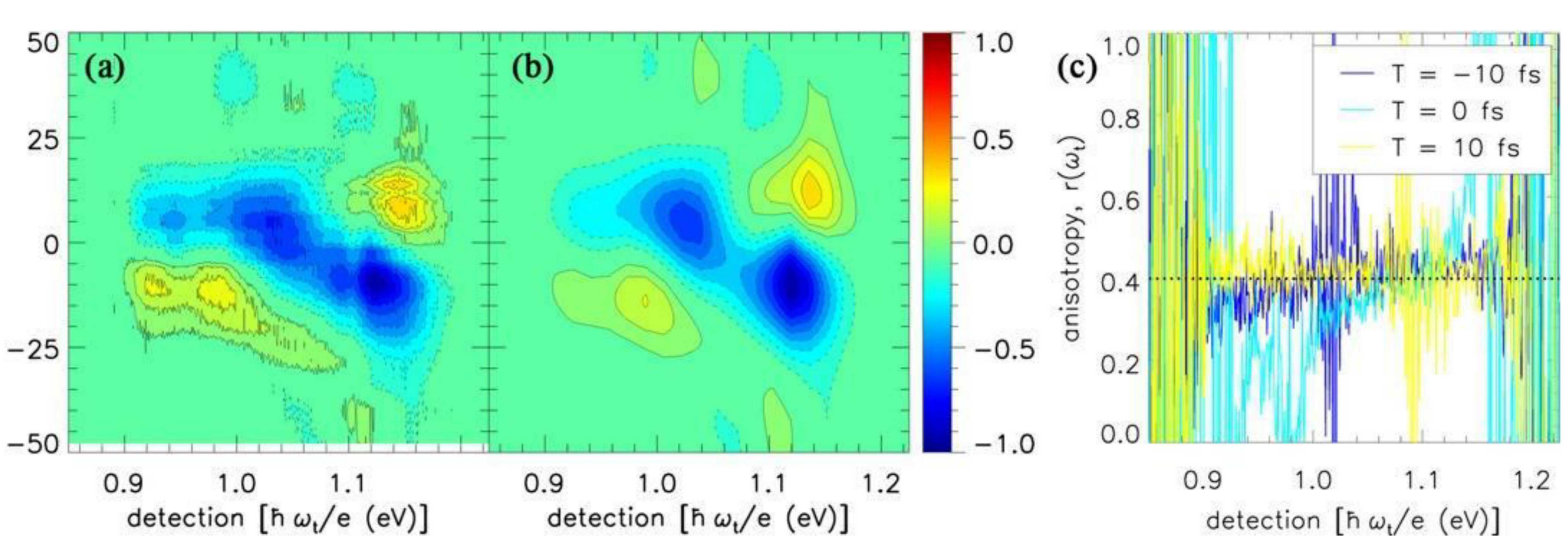
- A sample of PbS QDs with a bandgap of 1.074 eV and ~101 meV FWHM of the first absorption peak was synthesized from lead chloride and elemental sulfur in oleylamine following the hot injection procedure reported by the Tisdale group [5] with modifications in the washing procedure.



- Nonlinear optical experiments on the sample of PbS QDs were performed using a custom built ultra high vacuum compatible spinning sample cell [6].

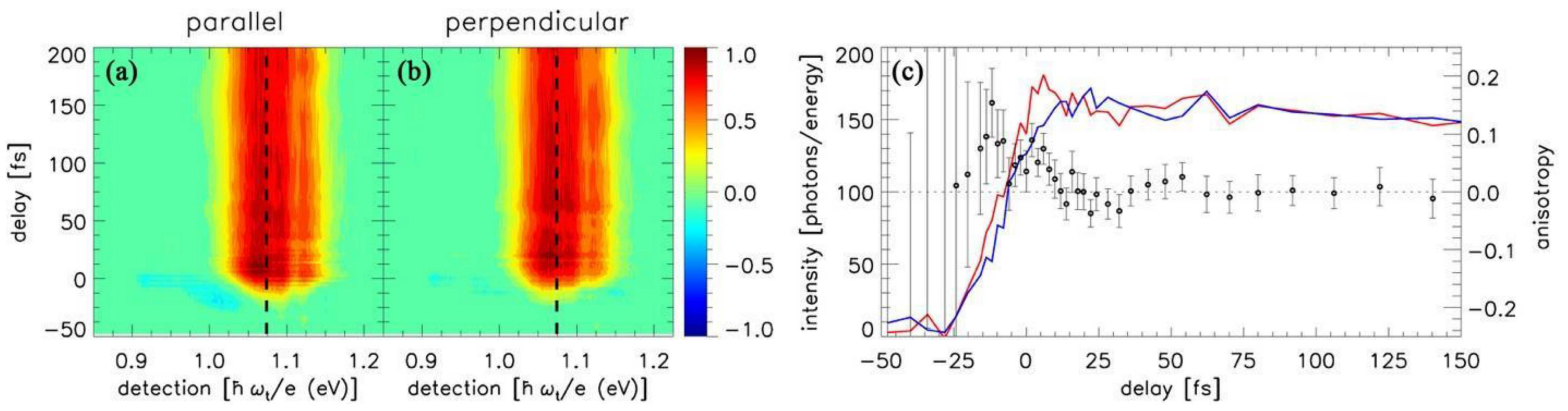
Cross Phase Modulation (XPM):

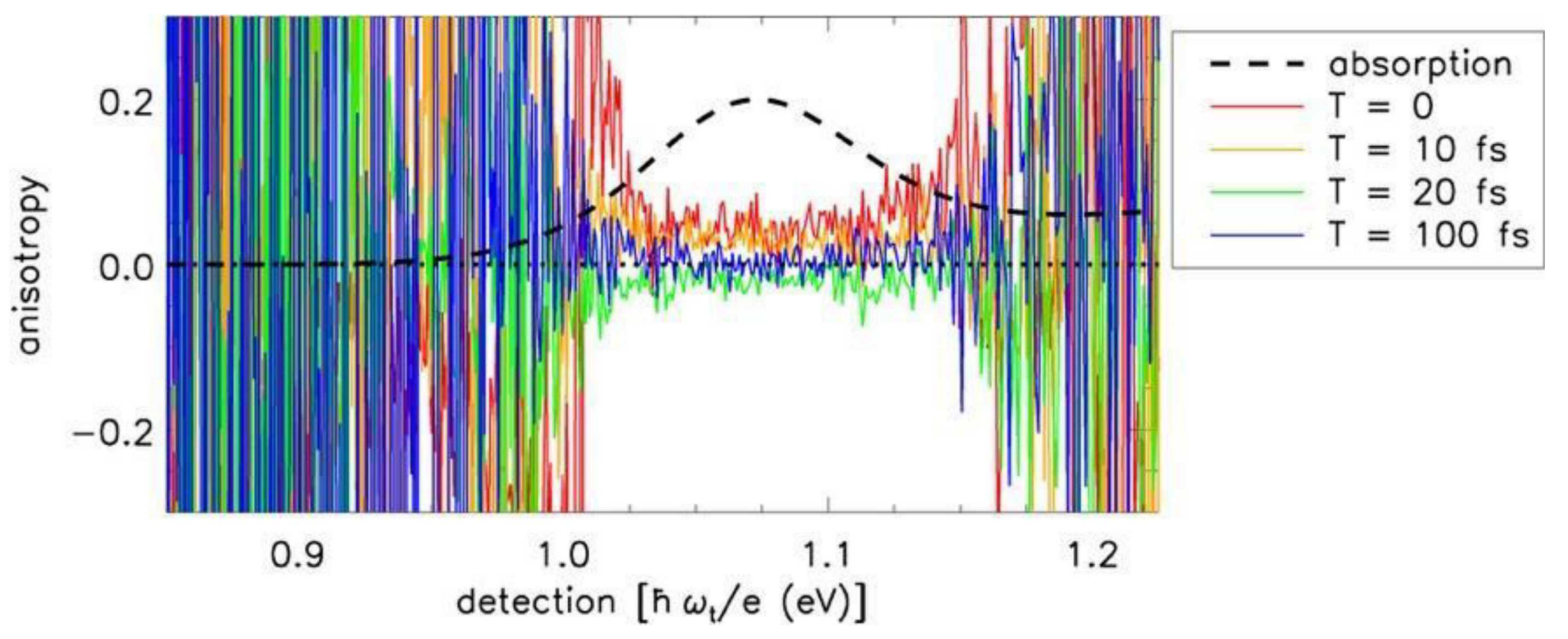
- The SRPP signal at early times (during pulse overlap) is dominated by XPM originating from solvent/glass.
- The XPM signal is proportional to the square of the peak intensity, and therefore, becomes more apparent with shorter pulses.
- Because the initial anisotropy contains information about the bi-exciton states, an XPM subtraction scheme is used to reveal the dynamics of the PbS QDs during pulse overlap.
- The XPM signal can be approximately simulated assuming a delta function response with the pulse phase and amplitude retrieved from FROG.
- The XPM signal also serves as a check on the polarized measurements. The anisotropy of the XPM where there is signal is ~2/5, which is consistent with previous reports on the signal strength ratio of 3:1 in XPM with parallel and perpendicular polarization geometries [7]. For each delay, the anisotropy diverges in regions where there is no XPM signal.
- The XPM was calculated including absorptive and dispersive propagation effects to account for pulse attenuation from absorption by the QDs [8].



Results:

- Our result shows a nominally zero anisotropy, but may be compatible with a small initial anisotropy of up to ~0.1. The initial anisotropy needs to be carefully considered because it can arise from an imperfect XPM subtraction or errors in time delay.

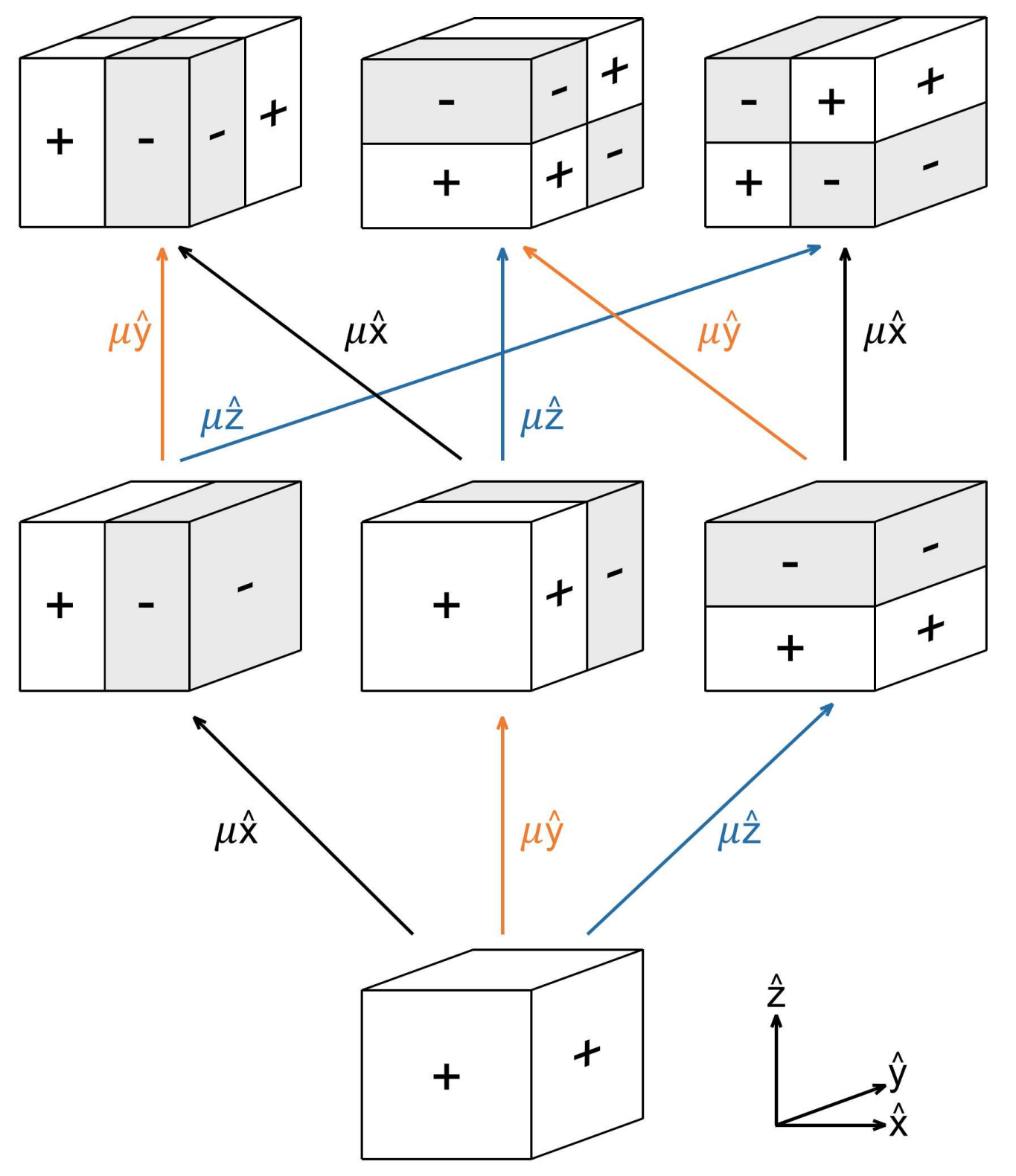




- The polarization anisotropy as a function of the detection frequency at different time delays, *T*, shows a nominally uniform anisotropy inside the first exciton peak. (The anisotropy diverges where there is no signal, which is all outside of the first exciton peak).
- Two possibilities can explain this anomalous initial anisotropy: either a near zero bi-exciton binding energy for the excited state absorption spectrum so that it lies on top of the ground state absorption spectrum, or a very large bi-exciton binding energy for the excited state absorption spectrum so that it lies outside of the laser bandwidth.
- In addition, the anisotropy as a function of the detection energy shows that there is no contribution from the red-shifted photoluminescence spectrum. This is consistent with the hypothesis that the red-shifted photoluminescence signal arises from lower fine structure states with long radiative lifetimes. Such states would not be populated immediately after excitation and would have low stimulated emission cross sections [9].

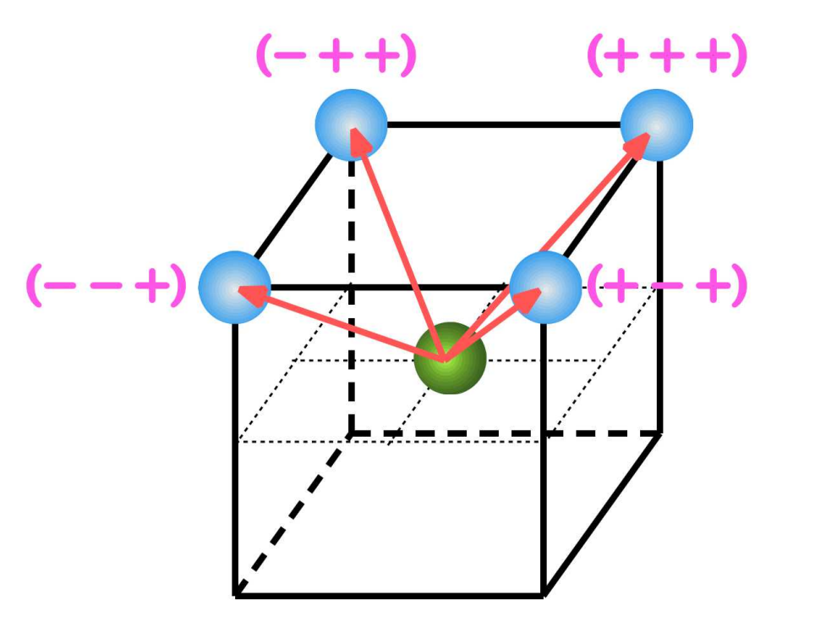
Initial polarization anisotropy using simple models:

Two-electron in a 3D Box



- When coherence and both one-electron and two-electron doubly excited states are considered, the initial anisotropy is 2/5, the standard dipole result.
- Hot single exciton states may play a key role in the initial anisotropy. For example, if we remove the doubly excited single electron contribution, the initial anisotropy is lowered to 1/4.

Effective Mass Approximation



- Transition dipole vectors are aligned along the four degenerate *L*-points of the first Brillouin zone. (The crystal structure has a threefold symmetry around the (1,1,1) axis, so a non-degenerate transition must have a transition dipole that points along the (1,1,1) threefold symmetry axis.)
- If each valley is an independent, uncoupled, absorber, the initial anisotropy is 2/5.
- An effective mass approximation shows that an anisotropy of 2/5 can be recovered without the single electron state.
- The calculation assumes that both valley-splitting and spin-orbit splitting of singly-excited states do not move transitions outside of the pulse spectrum.

Conclusions:

- Accurate subtraction of the XPM signal was required to reveal the initial anisotropy of PbS QDs.
- The initial anisotropy we report for PbS QDs at the bandgap is nominally zero, which is anomalous and suggests a complicated electronic structure.
- The fastest dephasing time allowed by the width of the first exciton peak is ~8 fs, meaning the initial dynamics should have been captured with the time resolution in the experiment.
- We show through calculations, using a 3D particle in a box and an effective mass approximation, that the expected initial anisotropy is 2/5.
- Some considerations may result in a departure from the initial anisotropy of 2/5: spin-orbit coupling, intervalley coupling, and the hot one-electron states must be explored further.
- For considerations of spin-orbit coupling and intervalley coupling, our results suggest that one or both of these values must be larger than previous calculations indicate. The calculation of the initial anisotropy assumes these states are near degenerate.
- To explain the initial anisotropy, large couplings are needed to push some of these states outside of our pulse bandwidth. Considering the bandwidth of our pulses, these values would have to be larger than ~200 meV, which is significantly greater than theoretical predictions.

References:

1. I. U. I. Ravich, B. A. Efimova, and I. A. Smirnov, *Semiconducting lead chalcogenides* (Plenum Press, 1970).
2. A. L. Efros, and A. L. Efros, "Interband Absorption of Light in a Semiconductor Sphere," Sov Phys Semicond. **16**, 772-775 (1982).
3. A. N. Poddubny, M. O. Nestoklon, and S. V. Goupalov, "Anomalous suppression of valley splittings in lead salt nanocrystals without inversion center," Phys Rev B **86** (2012).
4. D. Brida, S. Bonora, C. Manzoni, M. Marangoni, P. Villoresi, S. De Silvestri, and G. Cerullo, "Generation of 8.5-fs pulses at 1.3 mu m for ultrabroadband pump-probe spectroscopy," Opt Express **17**, 12510-12515 (2009).
5. M. C. Weidman, M. E. Beck, R. S. Hoffman, F. Prins, and W. A. Tisdale, "Monodisperse, Air-Stable PbS Nanocrystals via Precursor Stoichiometry Control," Acs Nano **8**, 6363-6371 (2014).
6. D. Baranov, R. J. Hill, J. Ryu, S. D. Park, and D. M. Jonas, (submitted).
7. Q. Lin, and G. P. Agrawal, "Vector theory of cross-phase modulation: Role of nonlinear polarization rotation," Ieee J Quantum Elect **40**, 958-964 (2004).
8. M. K. Yetzbacher, N. Belabas, K. A. Kitney, and D. M. Jonas, "Propagation, beam geometry, and detection distortions of peak shapes in two-dimensional Fourier transform spectra," J Chem Phys **126** (2007).
9. M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, A. L. Efros, and M. Rosen, "Observation of the Dark Exciton in Cdse Quantum Dots," Phys Rev Lett **75**, 3728-3731 (1995).

Acknowledgments:

This material is based upon work supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FG02-07ER15912.