Semiconductor nanocrystal quantum dots (QDs) have received considerable attention in recent years because they lie in the intermediate regime between atoms and bulk semiconductors.\textsuperscript{1} Despite containing hundreds or even thousands of individual atoms, these materials exhibit highly tunable optical properties such as photoluminescence (PL) arising from quantum mechanical effects of spatial confinement.\textsuperscript{2} In lead chalcogenide QDs, strong-confinement effects are readily observed because of the relatively large electron and hole Bohr radii (e.g., \(\sim 10\) nm in PbS), compared, for example, to CdSe (\(a_h \sim 1\) nm and \(a_e \sim 3\) nm). This confinement gives rise to complex electronic structure, which manifests itself in both the linear and the nonlinear optical response. As a consequence of these novel and tunable optical and electronic properties, QDs are now being explored for a host of applications from solar cells\textsuperscript{3} to optical gain media.\textsuperscript{4} A key to exploiting the electronic properties of QDs is a detailed, molecular-level understanding of their dynamics across all relevant time scales. In particular, changes in electronic structure that occur in the coherent regime—tens to hundreds of femtoseconds after excitation—reveal the nature of the quantum, rather than classical, features of these systems. However, the ultrafast dynamics after optical excitation are still poorly understood compared to bulk semiconductors because of the complexity of the interactions among excitons and the interactions between excitons and phonons. Understanding interactions among excitons has proven especially difficult because the states of the QDs are often degenerate or nearly so. In lead-salt QDs, the direct-band gap lies at four equivalent \(L\) points in the Brillouin zone, creating a 64-dimensional excitonic manifold when spin is included.\textsuperscript{5} At the band edge, minor deviations from spherical symmetry as well as band anisotropy\textsuperscript{6,7} may give rise to splitting of degenerate energy levels, especially for small QDs. Intervalley and interband coupling\textsuperscript{6} as well as electron-hole Coulomb and exchange interactions\textsuperscript{9} can further split the excitonic energy levels. None of these interactions can be resolved in the linear absorption spectrum because inhomogeneous broadening caused by the finite size distribution of the QD ensembles hides the signal. At present, a gap exists in our ability to probe simultaneously the nonlinear optical properties and fast dynamics of highly degenerate systems.

In this letter, we exploit spectrally resolved ultrabroadband continuum excitation coupled with femtosecond temporal resolution to reveal new details of the electronic structure of 2–3 nm colloidal PbS QDs at room temperature. Using multidimensional optical spectroscopy,\textsuperscript{10} we reveal that beneath the seemingly featureless absorption spectrum lies rich and complex electronic structure with dynamics on an ultrafast timescale. Additionally, we find that the observed energy level structure and ensuing dynamics are highly sensitive to excitation intensity. This work required a new approach for facile collection of 2D spectra of PbS QDs using a novel single-shot spectrometer because instability in white-light continuum excitation sources would preclude the measurements with point-by-point implementations of two-dimensional electronic spectroscopy (2D ES).\textsuperscript{11–13} Our results demonstrate the need for new theoretical models that properly incorporate static as well as dynamic properties of these nanostructures resulting from exciton-phonon coupling and many-body exciton interactions to explain the observed nonlinear optical response on an ultrafast time scale. The linear absorption spectrum of 2–3 nm PbS QDs is shown in Fig. 1. At the band edge, near 1.55 eV, only a single broad absorption band is visible. The distribution of dot sizes as determined by transmission electron microscopy (TEM) measurements [Fig. 1(b)] shows significant inhomogeneous broadening in accordance with the known band gap dependence on dot size.\textsuperscript{14} The broad (>300 meV) inhomogeneous absorption line width at the band edge completely masks...
smaller splittings of the excitonic energy levels (<100 meV) or exciton-biexciton transitions (<50 meV red shift).3 This inhomogeneity also precludes state-resolved transient absorption measurements [Fig. 1(c)] of excitonic fine structure or intraband dynamics.

To simultaneously eliminate the effects of inhomogeneous broadening as well as to obtain sufficient bandwidth to observe level splitting resulting from exciton-exciton interactions, we employed a new method that combines 2D photon echo spectroscopy with a white light continuum source. Conventional multidimensional optical experiments are unable to incorporate continuum excitation because of the stringent stability requirements. Such laser power stability requirements are inherent to all Fourier experiments that rely on indirect sampling such as that employed by conventional multiscan 2D photon echo spectroscopy. In multiscan spectroscopies, small fluctuations in laser power create noise across the entire spectrum when sampled in the Fourier domain. As the bandwidth of excitation increases, so do the demands placed on phase stability. Changes in the index of refraction due to eddies in air lead to frequency-dependent changes in the effective path length and phase between pairs of pulses used to excite the system. To circumvent these limitations, we have employed a new single-shot approach, which we call gradient-assisted photon echo spectroscopy (GRAPES), which relaxes both the phase and power stability requirements by 2–3 orders of magnitude with respect to that of the final rephasing period, Τ, with that of the initial rephasing period, τ, for each waiting time, T. The shapes of peaks appearing on the diagonal provide a measure of the “memory” of the system, while cross-peaks provide information on electronic coupling. As a function of the waiting time, 2D spectra measure system relaxation such as energy transfer or spectral diffusion originating, for example, from exciton-phonon interactions.

Two-dimensional spectroscopy is advantageous over continuous wave (CW) methods for studying highly quantum-confined systems because it achieves high spectral resolution and high temporal resolution simultaneously from a large population of absorbers.19,20 CW methods achieve high...
FIG. 3. (Color online) Ultrafast dynamics of PbS quantum dots at low excitation power. Absolute value of rephasing part of two-dimensional photon echo spectrum at \( T = 25, 50, 75, \) and 100 fs at 40 \( \mu J/cm^2 \) per pulse. Dotted line shows the diagonal of the 2D spectrum in which absorption and stimulated emission/excited state absorption are identical. Note that the coherence frequency, \( E_c \), recorded in the rotating frame, includes the contribution from the carrier frequency in the plot. The color bar is identical for each 2D spectrum.

The sub-100 femtosecond nonlinear dynamics of PbS quantum dots in pure decane (see Supplementary Material for synthetic methods)\(^{18}\) observed at low excitation intensities are shown in Fig. 3. These spectra correspond to less than a single exciton per QD per pulse (\( \langle N \rangle_{\text{pulse}} < 1 \)). The \( T = 0 \) spectrum was discarded due to inadequate temporal resolution needed to see the ultrafast (subpicosecond) relaxation dynamics in these systems. Such CW approaches, therefore, lead to a time-averaged spectrum, which as we show below, obscures many of the features in the electronic structure.

The physical mechanism leading to the ultrafast initial decay of the TG signal was attributed to phonon-assisted optical transitions. The cross-peak appearing at \( [1.60, 1.55] \) eV is consistent with transfer of energy from the higher energy level to a lower energy band resulting from intervalley splitting. The higher energy band undergoes rapid relaxation likely because it couples to the band-edge state, which facilitates ultrafast energy dissipation. Another cross-peak at \( [1.59, 1.51] \) eV appears to form between the original position of the lowest energy peak and both high energy peaks. Meanwhile, the low-energy peak itself appears to shift vertically to lower energy. By 100 fs, the new cross peak also relaxes to lower stimulated emission energy supporting our assignment. After 100 fs, the 2D spectrum does not show significant changes for at least 3 ps, the maximum population time measured. This timescale is consistent with recent exciton-dephasing measurements of 4- to 6-nm-diameter PbS quantum dots at 5 K using heterodyne-detected transient grating (TG).\(^{22}\)

The electronic structure of quantum dots is highly sensitive to the number of excitons per particle because the confined nature of the nanostructure results in strong Coulomb interactions between excitons.\(^{23,24}\) Figure 4 shows 2D spectra at a population time of 200 fs for different excitation intensities corresponding to between 0.08 and 1.5 excitations per pulse (\( \langle N \rangle_{\text{pulse}} = 0.08-1.5 \)). We see significant qualitative differences as a function of excitation intensity. The spectra appear to evolve in a quasicontinuous fashion from sharp stimulated
emission features at low excitation probability to well-resolved absorptive bands at high exciton densities. At low pulse powers, the 2D spectra consist of several well-resolved peaks as discussed above. The narrow stimulated emission bands result from relatively long-lived single-quantum coherences for a single excitation. As the excitation density is increased, the band-edge peak begins to disappear and, remarkably, by \( \langle N \rangle = 0.6 \), little absorption is seen except for a broad feature at low energy. As the pulse power is increased further toward \( \langle N \rangle = 1.49 \), new absorption bands emerge. Although we cannot definitively assign these bands without new theory, the data would suggest that the transition frequency of one exciton experiences perturbations arising from the field created by another, separate exciton. This interaction apparently causes an energy splitting during the coherence period of the 2D pulse sequence. Coulomb interactions between excitons in PbS are expected to be on the order of meV to tens of meV, depending on particle size, within the range of the observed splitting in the absorption band of 36 meV. We also observe that structure exists along the emission axis. Figure 4 compares cuts of the 2D spectra at different coherence frequency values for \( \langle N \rangle = 1.49 \). Each trace shows four or five peaks separated by 22–35 meV. The two absorption bands near 1.57 and 1.61 eV show nearly identical structure, again consistent with the splitting of a degenerate exciton state. We do not yet understand the origin of the fine features in the 2D spectrum at high excitation fluence. Not surprisingly, the emission is significantly broadened from rapid decoherence (\(<50 \text{ fs}\)) during the rephasing time compared to the low exciton density data.

In conclusion, we demonstrate that beneath the broad, featureless absorption spectrum of PbS nanostructures lies rich electronic structure. In qualitative agreement with a large body of theoretical work on the electronic structure of quantum confined nanostructures, the fine structure of both excitons and biexcitons governs the system’s nonlinear optical response. Here, we probe the fine structure of nearly degenerate systems with spectra dominated by inhomogeneous broadening. To measure these spectra, we utilize continuum generation coupled to single-shot 2D photon echo spectroscopy. This novel approach allows us to probe a sufficiently broad spectral range to capture the exciton dynamics without losing the requisite temporal resolution. Furthermore, the use of single-shot 2D spectroscopy allows us to capture snapshots of the electronic structure with well-defined mean exciton occupancy for the first time. While we cannot assign all the features in the 2D
spectrum because of the complexity of the electronic structure of PbS quantum dots, we believe that this data will motivate and guide new theoretical efforts toward this goal. The authors thank the NSF MRSEC (Grant No. DMR 08-00254), AFOSR (Grant No. FA9550-09-1-0117), DARPA (Grant No. N66001-10-1-4022), and the Searle Foundation for Support. E.H. acknowledges support from the National Science Foundation (Grant No. DMR-0844115) and the Institute for Complex Adaptive Matter Branches Cost-Sharing Fund. R.S. and D.V.T. acknowledge support by the University of Chicago and the Department of Energy under Section H.35 of U.S. Department of Energy Contract No. DE-AC02-06CH11357 awarded to UChicago Argonne, LLC, operator of Argonne National Laboratory. This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357.

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