

# Exciton-Phonon Spectroscopy of Quantum Dots Below the Single-Particle Homogeneous Line Width

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**Supporting Information** 

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**ABSTRACT:** We demonstrate that high-dimensionality coherent spectroscopy yields "superresolved" spectra whereby peaks may be localized far below their homogeneous line width by resolving them across multiple, coherently coupled dimensions. We implement this technique using a fifth-order photon-echo spectroscopy called Gradient-Assisted Multidimensional Electronic–Raman Spectroscopy (GAMERS) that combines resonant and nonresonant excitation to disperse the optical response across three spectral dimensions: two involving excitonic transitions and one that encodes phonon energies. In analogy to super-resolution localization microscopies, which separate spatially overlapping signals in time, GAMERS isolates signals spectrally using combined electronic and nuclear resolution. Optical phonon lines in a colloidal solution of CdSe quantum dots at room temperature separated by less than  $150 \ \mu eV$  are resolved despite the homogeneous line width of these transitions being nearly an order of magnitude broader. The frequency difference between these phonon modes is attributed to softening of the longitudinal phonon mode upon excitation to the lowest exciton state. Further, such phonon mode selectivity yields spectra with electronic line widths that



approach the single particle limit. Through this enhanced spectral resolution, the GAMERS method yields insights into the nature of coupling between longitudinal optical and acoustic phonons and specific excitonic transitions that were previously hidden.

 $\mathbf{M}$  ultidimensional Fourier-transform electronic spectros-copy<sup>1</sup> is a class of powerful methods that disentangle the congested spectra of proteins<sup>2-5</sup> and nanostructured materials<sup>6–8</sup> by separating spectral features across multiple correlated dimensions. Among the many advantages of these techniques, their ability to resolve the homogeneous peak shapes of heterogeneous samples and to separate independent signal pathways that otherwise overlap in lower dimensionality spectra make them effective tools for studying the electronic and vibrational structure and dynamics of complex chemical systems. Analogous to how super-resolution localization microscopy<sup>9</sup> resolves overlapping features by separating their signals in time, we show that high-order coherent spectroscopy offers additional spectral dimensions along which overlapping homogeneous lines may be separated (Figure 1a). Specifically, in a colloidal solution of quantum dots (QDs), we demonstrate that phonon peaks separated by 130  $\mu$ eV may be distinguished even at room temperature where the homogeneous line width is ~1 meV or greater, representing an improvement in functional resolution of nearly an order of magnitude. This dramatic resolution improvement enables identification of features in the electronic and phonon structure of the ubiquitously studied cadmium selenide QD that are vitally relevant to charge carrier relaxation and exciton-phonon coupling.

Colloidal semiconductor nanocrystals, or quantum dots, exhibit confinement of the charge carrier wave function along one or more spatial dimensions of the particle.<sup>10</sup> A remarkable property of QDs is that their exceptionally narrow luminescent

emission is tunable across a wide spectral range,<sup>11,12</sup> making them attractive targets for a wide range of applications from lasing<sup>13</sup> to biological imaging.<sup>14</sup> Yet, despite decades of steady progress in the synthesis of semiconductor QDs<sup>15–18</sup> as well as a myriad of optical studies, a comprehensive understanding of their photophysical properties has proven elusive.

Not unlike many other complex chemical systems in solution, a fundamental limit to studying the electronic structure and carrier dynamics of QDs is their relatively broad absorption and emission line widths owing to interactions of carriers with the environment, particularly optical phonons.<sup>19–23</sup> In addition to this source of homogeneous line broadening, inhomogeneous broadening is also present—a result of static particle-to-particle variations (e.g., size, shape, ligand coverage, etc.).<sup>24,25</sup> These compounding layers of broadening lead to severe spectral congestion (Figure 1c), hindering investigations into the detailed electronic structure.

There have been many important methods developed that separate homogeneous and inhomogeneous effects in order to characterize the underlying single-molecule states. Notably, photon-correlation Fourier spectroscopy (PCFS) has been utilized to study single-QD emission line shapes in solution at room temperature.<sup>24</sup> The line shapes of single-QDs in films

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Figure 1. (a) Principle of super-resolution localization spectroscopy. As with super-resolution localization microscopy, the signals are separated along some additional dimension, enabling the peak positions to be definitively isolated in a more sparse domain. (b) Energy ladder (or wave-mixing) diagram demonstrates an example of a coherence pathway that is detected in Gradient Assisted Multidimensional Electronic-Raman Spectroscopy. Excitation pulses are labeled 0, 0', 1, 2, and 3 and are separated by the time delays labeled  $T_0$ ,  $\tau$ , and T, with t denoting the time axis for signal radiation. (c) Intensity spectra of the preresonant prepump pulses 0 and 0' (red dashed line) and the resonant excitation pulses 1, 2, and 3 (blue dashed line) overlaid on the absorption spectrum of the CdSe quantum dot sample (red asterisks). The lowest four excitonic transitions were fit to a sum of Gaussians model, yielding peak centers of 1.934  $\pm$  0.002 eV and  $2.01 \pm 0.01$  eV (vertical dashed lines) and peak widths (fwhm) of 79.1 and 155 meV, respectively, for the two lowest energy peaks. (d) A 2D electronic slice of the GAMERS spectrum of CdSe quantum dots at  $(T_0 = 50 \text{ fs}, T = 4.1 \text{ ps}).$ 

have also been investigated at cryogenic temperatures where homogeneous effects are minimized.<sup>26</sup> In another study, Norris and Bawendi<sup>27</sup> modeled transient absorption spectra to extract the single-QD line shape. Yet, while these single-particle methods help recover the homogeneous line widths under some circumstances, spectral congestion caused by overlapping homogeneous lines in room temperature measurements continues to obscure the underlying electronic structure.

Here, we demonstrate separation of naturally broad electronic and phonon transitions *beyond* the single-particle line width. These advances are made possible by a coherent, fifth-order spectroscopy that was recently developed by the authors<sup>28–30</sup> called Gradient Assisted Multidimensional Electronic–Raman Spectroscopy (GAMERS). This method has two essential ingredients that are critical in achieving super-resolution. First, as a type of photon-echo spectroscopy, GAMERS separates line shapes into their homogeneous and inhomogeneous components. Second, and most importantly, by dispersing the sample's optical response across up to two electronic and two Raman-like dimensions, homogeneous transitions that overlap in lower-dimensional experiments can be readily isolated (Figure 1a). The key idea, then, is that one or more frequency dimensions may act to separate homoge-

neous contributions to the line shape in much the same way that stochastic processes separate the emission from single fluorophores in localization microscopy. While homogeneous broadening in semiconductor QDs has been studied by lower-order photon echo methods before,  $^{25,31}$  the fifth-order GAMERS method isolates coherence pathways to a degree that allows separation of extremely congested spectral lines. Combined with the ability to remove inhomogeneous broadening in ensemble measurements, this results in subhomogeneous (analogous to subdiffraction) line width resolution.

GAMERS is a time-resolved, Fourier transform spectroscopy that exposes four-dimensional frequency-frequency correlations between vibronic transitions using a sequence of five excitation pulses (Figure 1b). Details of the GAMERS method can be found in the SI. Of the four time-frequency dimensions in GAMERS, two encode electronic transitions and two encode vibrational (e.g., phonon) modes. As the two electronic dimensions ( $\omega_{\tau}$  and  $\omega_{t}$ ) are acquired in a spatially multiplexed fashion with each laser shot, only two temporal axes (T and  $T_0$ ) must be sequentially scanned to generate the full 4D correlation spectrum,  $\hat{S}^{(5)}(\omega_{T,t}\omega_{\tau}\omega_{\tau}\omega_{t})$ . An advantage of GAMERS is that the resonance conditions of the prepump and pump can be controlled independently in order to selectively excite ground state or ground and excited state vibrational coherences along the  $T_0$  and T dimensions, respectively. This ability to definitively isolate and distinguish ground and excited state processes provides an important handle for dissecting congested spectral features. Related methods have been employed in third-order spectroscopies to help determine the source of coherences based on their dependence on excitation pulse spectrum.<sup>32,33</sup> In the present study, we focus on "T-scan",  $\hat{S}_T^{(5)} \equiv \hat{S}^{(5)}(\omega_{\tau}\omega_T,\omega_t,T_0)$ , data sets in which the  $T_0$  delay is held constant at 50 fs. By setting  $T_0$  outside of pulse overlap, we are able to track coherent dynamics while minimizing pathways involving the solution's instantaneous response. Comparison to the complementary " $T_0$ -scan"  $\hat{S}_{T_0}^{(5)} \equiv \hat{S}^{(5)}(\omega_{T,j}\omega_{\prime j}\omega_{\prime j}T)$  experiment will be the subject of future study.

The QD solution was delivered as 25 mg of octadecylaminecapped, wurtzite CdSe QDs dispersed in ~5 mL of toluene (NN-Laboratories, PN: CSE640-25). No additional purification was performed. For GAMERS experiments, 1 mL of the QD solution was diluted with 1 mL of toluene (Alpha-Aesar) to yield an experimental sample with an absorbance of approximately 0.2 at 640 nm in a 200  $\mu$ m path length cuvette and a concentration of 2.5  $\mu$ M. Over the course of the experiment, the sample was flowed through a 200  $\mu$ m path length cuvette within a closed loop by a peristaltic pump to minimize repetitive excitation. The total sample volume was ~2 mL, which was large enough to prevent substantial photodegradation over the course of ~4 h of data collection.

Our experiments utilize a third-harmonic–pumped, noncollinear optical parametric amplifier (ORPHEUS-N 3H, Light Conversion), or NOPA, that produces ~30 fs pulses with a spectrum centered at a wavelength of 640 nm. This NOPA was pumped by the output of a 1028 nm wavelength, 200 kHz repetition rate, Yb:KGW laser system (PHAROS, Light Conversion). The NOPA output is routed into a passively phase-stable GRAPES apparatus where it is split evenly into three excitation pulses, each measuring 15 nJ (~3  $\mu$ J/cm<sup>2</sup>) at the sample. Passive phase stabilization of the delays between GRAPES excitation pulses is utilized as described in previous GRAPES and GAMERS work.<sup>28,29</sup>



**Figure 2.** Raman-like spectrum of CdSe quantum dots generated by integrating the GAMERS spectrum over the electronic dimensions  $E_{\tau} \equiv \hbar \omega_{\tau}$  and  $E_t \equiv \hbar \omega_t$  2D beating map (2DBM) spectra of longitudinal optical phonon modes activated by resonant excitation during *T* are shown in panels a and c. (b) Diagonal (blue) and antidiagonal (red) projections of the upper peak in panel a (circles) exhibit much narrower widths compared to the same projections of the overall GAMERS 2D electronic slice spectrum (asterisks). Each beating map peak is labeled by a symbol ( $\bullet$ ,  $\blacktriangle$ , or  $\blacksquare$ ) for cross referencing to Figure 3.

The previous GAMERS setup<sup>28</sup> was modified by splitting the nonresonant prepump into two noncollinear beams in order to alter the emission direction of the detected 6WM signal such that it does not spatially overlap with other 4WM signals. The prepump pulses are generated by a second-harmonic-pumped NOPA (ORPHEUS-N 2H, Light Conversion), pumped by the same aforementioned Yb:KGW laser system, that produces ~25 fs pulses with a spectrum centered at 680 nm. The secondharmonic-pumped NOPA's output is split into two coincident, noncollinear pulses, denoted 0 and 0', using a Sagnac interferometer. Within the interferometer, pulse 0' passes through a pair of glass wedges, and beam 0 passes through a compensating block (1 mm thick glass window). One of the beam wedges is mounted on a motorized translation stage (MTS50-Z8, Thorlabs) so that the relative delay of pulse 0' with respect to pulse 0 can be finely controlled. Pulses 0 and 0' each had a pulse energy of 100 nJ ( $\sim 20 \,\mu$ J/cm<sup>2</sup>) at the sample. The beam geometry is set such that pulses 0 and 0' have the same wavefront tilt at the sample as pulse 1, thereby ensuring that there is no spatial-temporal gradient between pulses 0, 0', and 1. All five excitation pulses (0, 0', 1, 2, and 3) plus a reference, or local oscillator, pulse (4) are focused to an approximately 5 mm tall by ~100  $\mu$ m wide vertical line in the sample by a 20 cm focal length cylindrical mirror.

The desired fifth-order GAMERS signal is generated by one light-matter interaction from each of the five excitation pulses. The resulting 6WM signal is emitted in the phase-matched directions defined by  $\hat{k}_{6WM} = \hat{k}_0(-\omega_0) + \hat{k}_{0'}(\omega_{0'}) + \hat{k}_1(-\omega_1) + \hat{k}_2(\omega_2) + \hat{k}_3(\omega_3)$ . Since pulses 0 and 0' are equidistantly displaced horizontally on either side of beam 1, the emitted sixwave mixing (6WM) signal is emitted in a unique direction (i.e., background-free) that is displaced by  $\hat{k}_0 - \hat{k}_{0'}$  from the four-wave mixing (4WM) signal emitted in the  $\hat{k}_{4WM} = \hat{k}_1(-\omega_1) + \hat{k}_2(\omega_2) + \hat{k}_3(\omega_3)$  direction. This change in geometry relative to previous GAMERS experiments<sup>28,29</sup> improves the dynamic range and sensitivity of the measurements by eliminating the strong 4WM background. After the sample cuvette, the 6WM signal and collinear local oscillator were spatially filtered from all other excitation beams. The signal and local oscillator were

reimaged from the focal line in the sample onto the slit of a spectrograph (TRIAX 320, ISA), and acquired by an sCMOS image sensor (Zyla 5.5 sCMOS 10-tap, Andor). Additional details regarding experimental methods and data analysis are found in the SI.

As shown in Figure 1c, the absorption spectrum of the CdSe QDs sample is broad and relatively featureless. Excitonic transitions were identified by fitting the absorption spectrum to a sum of Gaussians to estimate their peak centers (vertical dashed lines) and widths (horizontal solid lines). The prepump pulses (red dashed line) were tuned to a photon energy of 1.83 eV (680 nm), just to the red of the lowest excitonic transition  $(X_1)$ , to take advantage of the increased signal strength afforded by preresonance. The subsequent pump pulse pair and probe pulse spectra (blue dashed line) were centered at 1.94 eV (640 nm), directly on the first exciton peak but with some overlap of the second exciton peak  $(X_2)$ . The 6WM 2D electronic spectrum at  $(T_0 = 50 \text{ fs}, T = 4.1 \text{ ps})$  in Figure 1d portrays little structure due to the overlapping, broadened excitonic transitions visible in the absorption spectrum. This spectrum illustrates that photon-echo spectroscopy alone (e.g., 2D electronic spectroscopy of any order) does not effectively separate the homogeneous contributions from one another.

Unlike the 2D spectrum, the 3D GAMERS spectrum is rich in features, encoding frequency correlations between multiple excitonic states and phonon modes. We note at this point that a complete analysis and assignment of all observed peaks is beyond the scope of this work and instead we will focus on the most prominent features, leaving additional details to the SI. The 3D spectrum may be projected (i.e., integrated) along one or more axes to approximate lower-order spectra. For instance, projecting the T-scan spectrum along both electronic frequency coordinates results in the 1D Raman-like spectrum,  $\hat{S}_T^{(5)}$  shown in Figure 2. The most intense peaks include a longitudinal optical (LO) phonon mode at  $\pm 25.8 \text{ meV} (\approx \pm 208 \text{ cm}^{-1})$  and a series of acoustic phonon modes below 2 meV ( $\approx 16 \text{ cm}^{-1}$ ). We will focus most of our analysis on the LO phonon modes, which are believed to couple strongly to the excitonic transitions through the Fröhlich mechanism. 34-36

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In order to correlate these phonon modes with the excitonic transitions to which they are coupled, 2D Beating Map (2DBM) spectra<sup>28</sup> were constructed by taking the  $\hat{S}_T^{(5)}(\omega_n \omega_T)$ =  $a_i \omega_i$ ) slice of the 6WM 3D spectrum, where a is the frequency of a prominent phonon mode. These beating maps are analogous to 4WM beating maps generated from 2DFT electronic spectra<sup>8,37</sup> and may be thought of as "super-resolved" 2D electronic spectra which only involve specific phonon transitions. Although related to 4WM beating maps, the initial preresonant pulses 0 and 0' in GAMERS select for pathways that start from a ground-state vibrational coherence. The additional vibrational energy imparted by the prepump pulses alters the resonance conditions for subsequent transitions, potentially enabling access to higher-lying states. Select slices are depicted in the insets (a,c) of Figure 2. The most striking observation is the substantial reduction in electronic peak widths compared to the total 6WM 2D electronic spectrum (overlaid as contours in the insets of Figure 2). For comparison, in Figure 2b, the diagonal (blue) and antidiagonal (red) projections of the upper peak ( $\blacktriangle$ ) of the 2DBM in Figure 2a are plotted against the same projections of the 6WM 2D electronic spectrum. The antidiagonal line width of the 2DBM peak (47 meV) is less than half that of the total spectrum (101 meV), approximately matching the emission line widths reported for single-QDs and QD ensembles, respectively.<sup>24</sup> This demonstrates that detection of a highdimensionality photon echo signal enables GAMERS to resolve the single-QD absorption line width.

Well-resolved 2DBM spectra reveal electronic structure that is otherwise hidden within the total 2D spectrum. In Figure 2a, the 2DBM  $\hat{S}_T^{(5)}(\hbar\omega_T = -25.8 \text{ meV})$  exhibits two peaks ( and •) whose locations along the  $\omega_\tau$  dimension are consistent with signal pathways involving excitation of the X<sub>1</sub> (dashed blue line) and X<sub>2</sub> (dashed orange line) excitons, indicating that both excitonic transitions are coupled to the LO phonon mode. Interestingly, the same X<sub>2</sub> feature is not present in  $\hat{S}_T^{(5)}(\omega_T =$ +25.8 meV) (Figure 2c) due to differences in accessible coherence pathways (see SI).

Complementary electronic-Raman slices of the 3D GAMERS spectrum taken at specific electronic frequencies reveal the correlation between exciton and phonon modes. In Figure 3, the  $\omega_t$ -slice of the 3D GAMERS spectrum given by  $\hat{S}_T^{(5)}(\omega_{\tau}\omega_{T'}\hbar\omega_t = 1.91 \text{ eV})$  reveals coupling of the -25.8 meVphonon mode to distinct  $X_1$  ( $\bullet$ ) and  $X_2$  ( $\blacktriangle$ ) transitions. Slices through the maxima of these peaks as a function of  $\omega_T$ (blue and red lines at top of enlarged panel) indicate an energy difference of 130  $\pm$  30  $\mu$ eV (1.0  $\pm$  0.2 cm<sup>-1</sup>) between X<sub>1</sub>- and X<sub>2</sub>-coupled LO phonons, centered at -25.79 meV and -25.92 meV, respectively. To our knowledge, this marks the first time that two distinct LO phonons (i.e., phonons coupled to two different excitonic transitions) have been identified in multidimensional spectra of CdSe QDs. The features described here are distinct from the LO phonon peak structure reported elsewhere<sup>38</sup> that is often attributed to the surface-optical phonon;<sup>39</sup> the electronic correlation information afforded by GAMERS is necessary to isolate these transitions. Based on an analysis of the available coherence pathways (see SI), we note that the X1-coupled LO peak includes contributions from both ground and excited electronic state pathways during T, while the X<sub>2</sub>-coupled LO peak exclusively contains ground state pathways. Therefore, the X<sub>2</sub>-coupled LO peak is expected to be located at the frequency of the ground-state phonon mode while the X<sub>1</sub>-coupled LO peak contains a mix of both ground-



**Figure 3.** Electronic–Raman slices of the GAMERS spectrum at  $E_t \equiv \hbar \omega_t = 1.91$  eV as a function of  $E_T \equiv \hbar \omega_T$  and  $E_\tau \equiv \hbar \omega_\tau$ . To the right is an enlarged view of the LO phonon peak at  $\hbar \omega_T = -25.8$  meV, along with slices through the peak centers plotted above. Each beating map peak is labeled by a symbol ( $\bullet$ ,  $\blacktriangle$ , or  $\blacksquare$ ) for cross referencing to Figure 2 and associated coherence pathways (see SI for details).

and  $X_1$ -state LO phonon contributions. This implies that upon excitation from the ground state to the  $X_1$  state, the LO frequency red shifts by at least 130  $\mu$ eV (1.0 cm<sup>-1</sup>) due to softening of the phonon mode in the electronic excited state. Since the  $X_1$ -coupled phonon peak is thought to contain both ground- and  $X_1$ -state contributions, 130  $\mu$ eV is a lower bound on the LO phonon red shift in the  $X_1$  state. This result is in good agreement with the ~1 cm<sup>-1</sup> shift reported by Hannah et al.<sup>40</sup> in a femtosecond stimulated Raman spectroscopy study on CdSe QDs of similar size (estimated from Figure S5 of ref 40).

In conclusion, we have demonstrated that GAMERS represents a "super-resolution" approach to spectroscopy that enables the complex vibronic structure of CdSe nanoparticles in solution to be measured with unprecedented detail. By separating signals based on their coupling to specific excitonic and phonon transitions, we identify two independent LO phonon modes whose separation is nearly an order of magnitude less than their individual homogeneous line widths. We attribute their 130  $\mu$ eV frequency different to softening of the LO phonon mode upon excitation to the X<sub>1</sub> state. While our focus here was on QDs, we note that this approach can be applied to any system with accessible optical transitions. Unlike fluorescence detection in single-molecule spectroscopies, GAMERS accesses both absorptive and emissive transitions to provide a much broader view of the vibronic landscape. Future work will be directed toward achieving even higher spectral resolution by capitalizing on all four frequency dimensions, and using these capabilities to study the electronic, vibrational, and phonon structure and dynamics of highly coupled biological and nanostructured materials.

# ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b00065.

Description of GAMERS technique, experimental methods, and detailed coherence pathway analysis (PDF)

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#### Notes

The authors declare no competing financial interest.

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