

Ultrafast electronic structures and dynamics of CdSe nanocrystals revealed by gas phase time-resolved photoelectron spectroscopy

Wei Xiong¹, Daniel D. Hickstein¹, Kyle J. Schnitzenbaumer², Jennifer L. Ellis¹, Brett B. Palm³, Chengyuan Ding¹, Molly B. Beernink², Gordana Dukovic², Jose L. Jimenez³, Margaret M. Murnane¹, Henry C. Kapteyn¹

¹Department of Physics and JILA, University of Colorado and NIST, Boulder, CO 80309, USA

²Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA

³Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, CO 80309, USA

Wei.Xiong@jila.colorado.edu

Abstract: Using time-resolved photoelectron spectroscopy in a gas phase environment, we observed the evanescent electron wavefunction of quantum dot excited states, and the effect of solvent on QD charge transfer.

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Quantum dots (QDs) represent one of the fundamental building blocks for complex nanoscale devices. To design effective nano-systems, a thorough understanding of the ultrafast electronic structure and dynamics of QDs is required. However, to date, this information has been obtained only for samples prepared as films or in solution phase, introducing an interaction of the QD with its environment. These interactions are not thoroughly understood, and therefore can obscure the interpretation of any electronic structure or dynamics measurement. In this work, we report the first photoelectron spectroscopy of QDs suspended in the gas phase, allowing us to measure QDs decoupled from any solvent or substrate interactions. We report two major findings. First, this new apparatus shows that the total photoelectron yield from the QDs is proportional to the fraction of the photoexcited electron wavefunction that extends outside the QD, thereby making the first direct measurement of the evanescent electron density of the QD excitons [1]. Second, we present a general method to study solvent effects on QD charge transfer reaction, and show that hexane does not influence the charge transfer rate.

We prepare a collimated aerosol beam of CdSe QDs using an aerodynamic lens (Aerodyne) that is injected into the interaction region of a velocity map imaging (VMI) spectrometer (Fig. 1a). We use ultrafast two-photon photoelectron spectroscopy (2PPE) to first create excitons using a 400nm pulse and subsequently liberate an electron using a 267nm photon (Fig. 1c). By adjusting the time-delay between the two pulses, we can collect angle, energy, and time-resolved photoelectron spectra of the QD excitons.

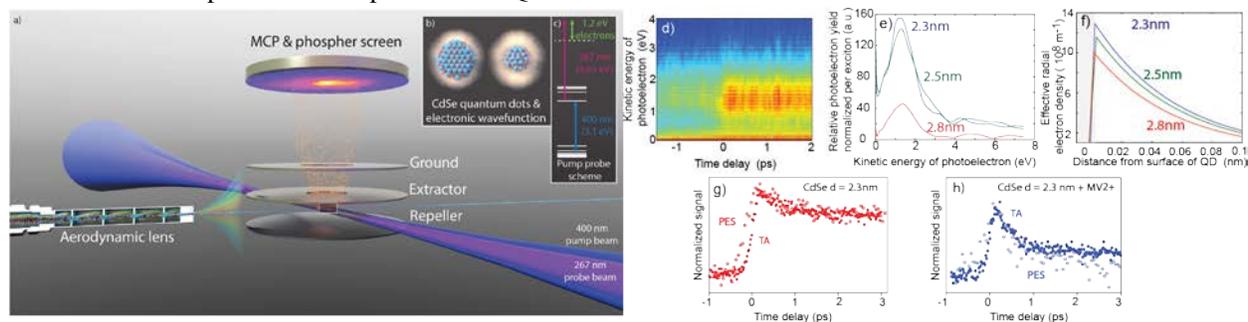


Figure 1. a) The experimental apparatus. b) Smaller QDs impose stronger quantum confinement, which results in a larger evanescent electron wavefunction. b) 2PPE pulse sequence and energy diagram. d) Time-resolved PES signal. e) PES signal normalized to give signal amplitude per electron and f) calculated electron density for various diameter QDs. Comparison data from transient absorption and photoelectron spectroscopy measurements of charge dynamics in g) bare CdSe QDs and in h) CdSe+Methyl viologen complex

The time-resolved 2PPE spectrum from the 2.3 nm CdSe QDs (Fig. 1d) shows a broad peak near 1.2 eV that exists for positive time delays. This peak does not decay appreciably on the ~100 ps timescale explored in this study. The 2PPE spectra of 2.5 and 2.8 nm QDs show a very similar behavior. For each size QD, the 2PPE spectrum (Fig. 1e) peak at 1.2 ± 0.1 eV, corresponds to an exciton state 3.45 eV below the vacuum level (Fig. 1c), given our probe photon energy of 4.65 eV. Effective mass calculations show that the 1S electron should be bound by -3.4 eV. Therefore, we assign the peak at 1.2 eV to the 1S electron, an assignment that is further substantiated by the long lifetime (>100 ps) of this peak.

By determining the QD density in the particle beam for each size QD, we can compare the absolute PES signal level per excited-state QD. As shown in Fig. 1e, the 2PPE intensity decreases as the diameter of the QDs increases from 2.3 to 2.8 nm. This decreasing PES intensity with increasing size can be explained by the weaker quantum confinement in larger QDs, resulting in a decreasing evanescent electron density. The Bohr radius for the CdSe 1S exciton is around 5.6 nm, so intuitively, the exciton orbital extends farther outside with shrinking size of the QD (Fig. 1b). To gain a more quantitative understanding, we performed effective mass model calculations for the three sizes of quantum dots in our experiment. From these calculations, we obtained the electron wavefunctions and electron densities (Fig. 1f) of the 1S excitons, and found the probabilities of finding the electron outside the quantum dots are 7.4%, 6.7% and 5.6% for the 2.3, 2.5 and 2.8 nm QDs, respectively.

Conceptually, the photoemission process can be divided into two parts: electrons liberated from the interior of the QDs, and electrons liberated from the exterior; i.e. the evanescent electron wavefunction. Following the three-step model of surface photoemission, the photoemission cross section of the interior electrons is greatly reduced by the relatively low density of final states and the small acceptance angle for an electron escaping from within. In contrast, the evanescent electrons are easier to liberate since they are already located outside the QD and can be directly ejected into the vacuum. Therefore, the photoelectron signal is dominated by the evanescent electron and should follow Fermi's golden rule. Since the final states are free electron wavefunctions for all three samples, the amount of evanescent electron density in the initial state determines the intensity of the photoelectron yield. Therefore, the increasing evanescent electron densities with smaller QD size (Fig. 1f) can qualitatively explain the trend of different photoelectron yields (Fig. 1e).

In addition to understanding the electronic structure, another unexplored but important area of QD dynamics is the effect of solvents on ultrafast charge transfer reactions. Thus, it is fruitful to compare our PES data from a solvent and substrate free environment with conventional transient absorption measurements in a solvent environment. We use this approach to study the effect of hexane solvent on QD charge transfer to the LUMO of methyl viologen. In optical transient absorption, the transient bleaching results from saturation of the transition (state filling), and relaxes as the excited electron move away from the conduction band of the QD into any available acceptor molecules. In PES, the total photoelectron signal decreases with charge transfer to the LUMO of methyl viologen, since this energy level is too deeply bound to be photoionized by the 267nm probe photon. Therefore, dynamic curves from transient absorption and PES both represent the charge transfer dynamics. Since transient absorption is conducted in solution phase, whereas PES is measured solvent free, the difference in dynamics reveals the solvent contribution.

To demonstrate these two experiments have provide comparable data on electron dynamics, we first compared bare QDs samples in solution and in gas phase, observing the lifetime of the band-edge excited electron. These measurements show similar dynamic curves (Figs. 1d and 1g), indicating that PES indeed does follow charge dynamics comparable to optical transient absorption. We then introduce methyl viologen in both cases; i.e. in solution, and precipitated onto the QD's while the solvent is removed by vacuum in the aerodynamic lens. Surprisingly, the dynamics from both measurements are indistinguishable (Fig. 1h), indicating that hexane has a negligible effect on the charge transfer process. From a simplified Marcus theory picture, since hexane is a non-polar solvent ($\epsilon=2$), its contribution to reorganization energy would be expected to be similar to that from vacuum ($\epsilon=1$); i.e. very small. In future, other solvents (polar, nono-polar and hydrogen bonding) can be studied following the same methods to develop a complete understanding of how solvents influence charge transfer reactions in QDs.

In summary, by combining a nanoparticle aerosol source with a velocity map imaging spectrometer, we implemented two-photon photoelectron spectroscopy of quantum dots suspended in the gas phase. This allows us to study QD electronic structure and dynamics independent of external interactions. First, we found that the photoelectron yield per exciton decreases as the diameter of the quantum dot increases. This trend can be attributed to the different evanescent electron densities that extend outside the QD surface. Second, by a comparison of dynamics obtained in solution and gas phase, we can unambiguously determine the effect of solvent on the donor-acceptor charge transfer reaction. Both observations provide fundamental structural and dynamic information that can facilitate understanding and optimization of charge transfer between QDs and other elements within such a system, therefore facilitating more effective design of quantum dot devices.

References

- [1] W. Xiong, D. D. Hickstein, K.J. Schnitzenbaumer, J.L. Ellis, B.B. Palm, K.E. Keister, C. Ding, L. Miaja-Avila, G. Dukovic, J.L. Jimenez, M. Murnane, H.C. Kapteyn, " Photoelectron spectroscopy of CdSe nanocrystals in the gas phase: a direct measure of the evanescent electron wavefunction of quantum dots", *Nano Lett*, **13**, 2924 (2013).