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Imaging Excited Orbitals of Quantum Dots: Experiment and Electronic Structure Theory

Lea Nienhaus,[†,‡,⊥] Joshua J. Goings,[¶,⊥] Duc Nguyen,[†,‡] Sarah Wieghold,[§] Joseph W. Lyding,[†,*] Xiaosong Li,[¶,*] and Martin Gruebele[†,‡,∧,*]

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Supporting Information

Abstract Electronically excited orbitals play a fundamental role in chemical reactivity and spectroscopy. In nanostructures, orbital shape is diagnostic of defects that control blinking, surface carrier dynamics and other important optoelectronic properties. We capture such nanometer resolution images of electronically excited PbS quantum dots by single molecule absorption scanning tunneling microscopy (SMA-STM). Dots with a bandgap of ~1 eV are deposited on a transparent gold surface and optically excited with red or green light to produce hot carriers. The STM tip-enhanced laser light produces a large excited state population, and the Stark effect allows transitions to be tuned into resonance by changing the sample voltage. Scanning the quantum dots under laser excitation, we were able to image electronic excitation to different angular momentum states depending on sample bias. The shapes differ from idealized S- or P-like orbitals due to imperfections of the quantum dots. Excitation of adjacent quantum dot pairs reveals orbital alignment, evidence for electronic coupling between dots. Electronic structure modeling of a small PbS quantum dot, when scaled for size, reveals Stark tuning and variation in the transition moment of different parity states, supporting the simple one-electron experimental interpretation in the hot carrier limit. The calculations highlight the sensitivity of orbital density to applied field, laser wavelength, and structural fluctuations of the quantum dot.

although the experimental asymmetry cannot be reproduced unless the PbS lattice is displaced in the calculations (see Figure 7 which shows an asymmetric simulated signal).

The 180° phase shift of the absorption signal (black to white), observed when going from positive to negative bias, is easily explained by the tunneling direction. When a positive bias is applied to the sample, the electrons tunnel from the tip to surface. Hence we are imaging unfilled states (UMOs). Laser excitation populates the UMOs and results in a decreased tunneling current due to the lowered tunneling probability from tip to surface *via* the filled ground state UMOs (black signal in Figure 2b). Reversing the bias to negative values results in tunneling from the surface to the tip. Here we are imaging the electrons tunneling from the occupied molecular orbitals. Absorption facilitates tunneling from OMOs and results in an increased tunneling current (white signal in Figure 2b).

The integrated signal strength observed at positive bias is generally higher than the signal strength at negative bias. Such asymmetry can be caused by net rectification of the optical field. Rectification effects have been observed in the case of surface plasmons and also for electron transfer between the HOMO and LUMO of a donor and acceptor.[61-62] In our case, rectification could be caused by tip-surface asymmetry, not necessarily by the quantum dot itself, and our laser accesses highly excited states, not the HOMO/LUMO bandgap region at ≈ 1200 nm.

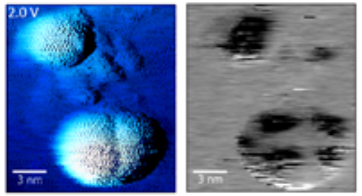
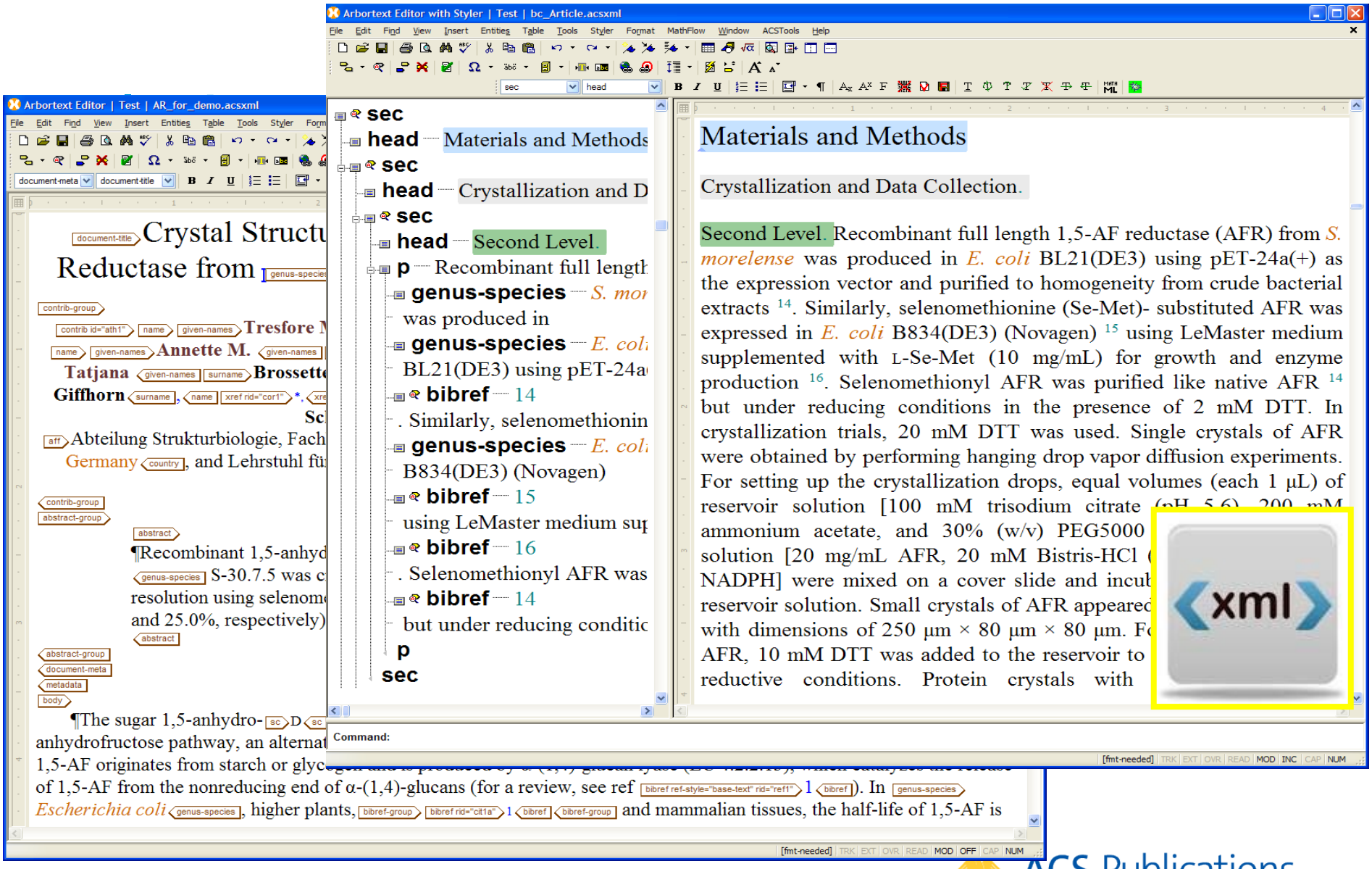


Figure 3: SMA-STM image of PbS quantum dots deposited by aerosol deposition onto a Pt-Au surface. For enhanced contrast of the adjacent quantum dots, the topograph (left) was overlaid with the topographic derivative. The phase lock-in image (right) shows a different absorption signal for a single quantum dot as in ref. 37. The quantum dot (same as ref. 37, Figure 7) shows S-type behavior, while the two dots at the bottom show P-like angular momentum excitations. Scanning conditions: 5 pA, 2 V. Color scale for lock-in image (right): -0

To verify that the absorption signal remains aligned with the surf
geometry, but not with the tip scan direction, we also scanned the tip in
the same quantum dot (SI Figure S6). The SMA-STM image showed n
the scan direction, and is a fixed feature of the laser polarization and



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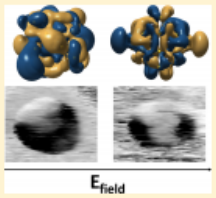
ABSTRACT: Electronically excited orbitals play a fundamental role in chemical reactivity and spectroscopy. In nanostructures, orbital shape is diagnostic of defects that control blinking, surface carrier dynamics, and other important optoelectronic properties. We capture nanometer resolution images of electronically excited PbS quantum dots (QDs) by single molecule absorption scanning tunneling microscopy (SMA-STM). Dots with a bandgap of ∼1 eV are deposited on a transparent gold surface and optically excited with red or green light to produce hot carriers. The STM tip-enhanced laser light produces a large excited-state population, and the Stark effect allows transitions to be tuned into resonance by changing the sample voltage. Scanning the QDs under laser excitation, we were able to image electronic excitation to different angular momentum states depending on sample bias. The shapes differ from idealized S- or P-like orbitals due to imperfections of the QDs. Excitation of adjacent QD pairs reveals orbital alignment, evidence for electronic coupling between dots. Electronic structure modeling of a small PbS QD, when scaled for size, reveals Stark tuning and variation in the transition moment of different parity states, supporting the simple one-electron experimental interpretation in the hot carrier limit. The calculations highlight the sensitivity of orbital density to applied field, laser wavelength, and structural fluctuations of the QD.



INTRODUCTION

Quantum dots (QDs) are semiconducting nanocrystals and a prototype of artificial atoms.[1−3] If the crystals are sufficiently small, their electronic properties differ strongly from the bulk material, showcasing discrete states and simple orbital shapes analogous to atoms.[4−7] The electronic structure of QDs is very important for their application as photovoltaics,[8−11] LEDs,[12−15] and FRET donors or acceptors.[16−20] In particular, high-energy excited states also are important for multicarrier properties, with applications in high efficiency light harvesting or light amplification.[21−23] Great efforts have been made to investigate the underlying electronic substructure in the broad visible absorption bands of semiconducting QDs using transient spectroscopic techniques. For example, excitons with 1 eV of excess energy can become surface trapped,[24] and at even higher energies[16] they can resemble free bulk carriers because of small scattering length.[25] Theoretical approaches including the effective mass approach[2,3,4,26,27] and atomistic approaches such as density functional theory (DFT)[28] have been tested, with the atomistic picture generally agreeing better with experimentally determined orbital symmetries.[28,27,29,30] Additionally, defects and surface reconstructions will require atomistic approaches such as DFT calculation.[24]

Due to their size (10^2−10^4 atoms), QDs are prone to structural or electronic defects that break the perfect symmetry present in atoms. These defects may be tailored on purpose to achieve specific optoelectronic properties, or they may be present naturally, causing problems such as fluorescence blinking when electronic excitation is trapped in surface states.[31,10] If the electronic density of excited QDs could be directly imaged, we would have a sensitive visual diagnostic of orbital symmetry and hence of presence or absence of defects. Scanning tunneling microscopy (STM) can image ground-state electron density, such as the dangling bonds on Si(100) surfaces,[32] but cannot image specific excited states. Transient or steady-state absorption spectroscopy can access specific excited states, but without the spatially resolved information on STM.

Here we combine single molecule absorption and STM (SMA-STM)[33−36] to image optical excitation of individual and paired PbS QDs. Dots deposited on a transparent conductive substrate[37] are excited by laser light. The dots are subject to a tunable electric field from the STM tip.[36] The well-studied quadratic Stark effect of QDs[38−42] allows different electronic

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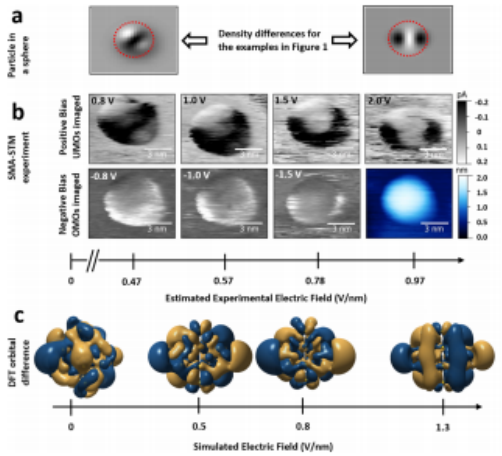

Figure 2. (a) Electron density differences for the examples in Figure 1, reproduced for direct comparison with (b). (b) SMA-STM images of a single PbS QD under 532 nm illumination. The dot was deposited by DCT on the atomically flat gold surface. Top row: phase-optimized absorption signal as a function of electric field at a positive tunneling bias. Bottom row: same dot at negative tunneling bias; a topography image collected at −1 V is shown in the blue inset. The *x*-axis shows the estimated absolute experimental electric field value based on the tip−sample distance of ca. 1.9 nm. Tunneling current: 10 pA. (c) DFT orbital density difference at constant excitation energy and increasing field, taken as the point-wise difference of the LUMO versus OMO. A scaled excitation energy of about 2.35 eV was used for comparison with experiment. The applied field is perpendicular to the plane of the page, like the major field component in the experiment. As in the experiment, a trend from more uniform to more left−right polarized density difference is observed in the calculations, although the experimental asymmetry cannot be reproduced unless the PbS lattice is displaced in the calculations (see Figure 7 which shows an asymmetric simulated signal).

the surface. Thus, the tip field, which has a ca. 10−20% lateral component depending on tip position near the QD, is relatively uniform when the tip is in proximity of the QD.

For some isolated QDs, the excitation image remains irregularly shaped at all fields we can access (Figure 2). For others the signal, which projects electronic density modulation into the sample plane, has nearly perfect spherical symmetry (Figure 3, top dot and ref 37). At the spatial resolution of our topography scans (rightmost image in the bottom row of Figure 2b), we cannot determine whether the irregular shape of the orbital we image is due to electronic defects (e.g., pinned charges, dopant atoms) or due to an irregularly shaped surface (e.g., missing atom at a terrace edge).

Quantum Dot Pair Excitation and Wavelength Dependence. Another interesting result in Figure 3 is the excited-state−ground-state density difference observed in an anisotropic local environment. The two PbS QDs at the bottom are in direct contact. In contrast to the single dot at the top, they show an electron density difference between the ground and excited states characteristic of higher angular momentum orbitals (e.g., P) at 532 nm excitation. The two excitations are aligned perpendicular to the center-to-center axis of the two QDs. If two nanoparticles are in close proximity, coupling

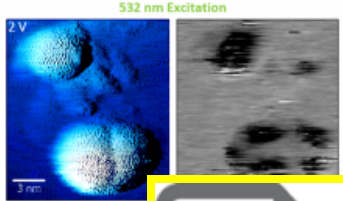

Figure 3. SMA-STM imag
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Abstract

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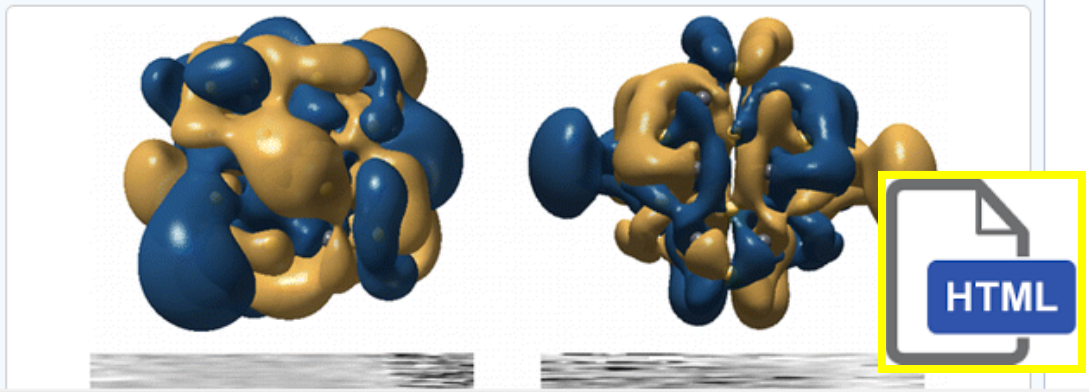

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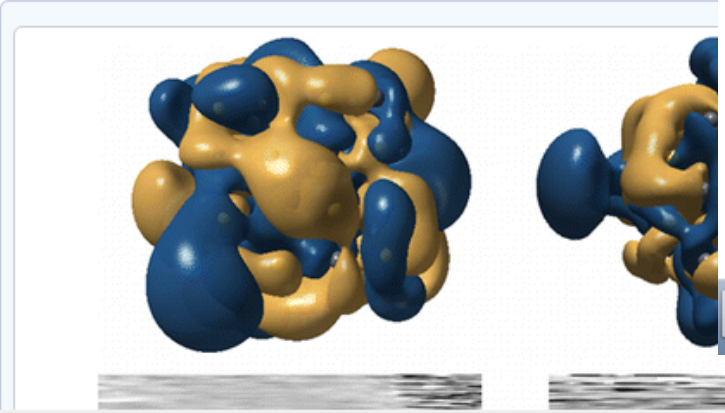

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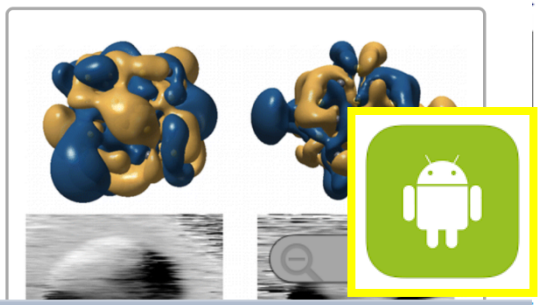

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