

Optical Transitions in Artificial Few-Electron Atoms Strongly Confined inside ZnO Nanocrystals

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We have studied the optical transitions in artificial atoms consisting of one to ten electrons occupying the conduction levels in ZnO nanocrystals. We analyzed near IR absorption spectra of assemblies of weakly coupled ZnO nanocrystals for a gradually increasing electron number and found four allowed dipole transitions with oscillator strengths in quantitative agreement with tight-binding theory. Furthermore, this spectroscopy provides the single-particle energy separation between the conduction levels of the ZnO quantum dots.

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Colloidal insulating nanocrystals should form ideal hosts for strongly confined artificial atoms, i.e., configurations of one to a few electrons occupying the conduction energy levels of the nanocrystal. Such nanocrystals can be obtained in molar quantities by wet chemical synthesis with increasing control of the size, shape, and surface electronic properties [1]. The dimensions below 10 nm ensure strong quantum confinement of the electrons corresponding to confinement energies in the 0.1 to 1 eV range. For comparison, artificial atoms defined by lithography in bulk semiconductor crystals have dimensions of a few tens to hundreds of nanometers and, accordingly, show much weaker confinement effects in the 1 meV range [2]. The interest in studying artificial atoms in the strong confinement regime is that quantum confinement and Coulomb and exchange interactions all depend in a different way on the dimensions of the nanocrystal host [3]. Thus, in strongly confined systems, as yet unobserved electrical and optical properties should emerge.

A major problem in studying strongly confined artificial atoms is the fabrication of devices in which the *electron number* N , i.e., number of electrons per quantum dot, can be controlled. For example, a transistor consisting of a single CdSe quantum dot, mounted between two electrodes, with a gate to control the electron or hole number has been reported [4]. The technological sophistication required for the fabrication of such a device, however, prevents experimental studies by a wide research community. We have fabricated *assemblies* consisting of ZnO nanocrystals of diameter between 3 and 6 nm in which the electron number can be controlled by the electrochemical potential [5]. In a previous study [6] we have shown that the electrons occupy the atomlike S

and P orbitals of the ZnO nanocrystals which decides the characteristics of long-range electron transport. In this Letter, we report a study of the optical properties of artificial atoms created in such an assembly. We detect the electric dipole transitions in artificial atoms consisting of one to ten electrons by absorption spectroscopy in the near infrared.

The importance of this work for the physics of strongly confined systems is twofold. First, we demonstrate that, by gradually increasing the electron number in the ZnO nanocrystals, the contribution of each individual dipole transition to the absorption spectrum can be identified, despite the size dispersion in the assembly. In this way, we have obtained the relative oscillator strengths of four allowed transitions and found excellent agreement with the predictions of tight-binding theory [7]. In essence, our results indicate that the optical transitions in strongly confined artificial atoms are strictly governed by the symmetry of the *envelope* wave functions. Second, the present method of spectroscopy directly provides the *single-particle energy separations* between the electron levels. This is due to the fact that electrons are transferred from one conduction level to another (keeping the electron number constant), the repulsion energy between two electrons being nearly independent of the orbitals that they occupy [8]. This is in firm contrast to conventional absorption and luminescence spectroscopies that probe transitions between valence and conduction levels. In the latter case the dielectric polarization and the Coulomb interparticle energies of the electron and hole play an important role in the energy of the transition [8] making the extraction of single-particle energies more complex and subject to uncertainties. We obtained the single-particle energy of the S , P , D , and F levels as a

function of the diameter of the ZnO nanocrystals and found a reasonable agreement with the predictions of tight-binding theory. The optical results presented here provide independent confirmation of the truly atomlike character of the electron levels in colloidal nanocrystal-line ZnO quantum dots.

Figure 1 (blue lines) shows the increase in the IR light absorption by an *assembly* of ZnO quantum dots due to charging of the nanocrystals. The spectra shown here were obtained with a Fourier-transform infrared spectrometer at room temperature. The shape of the spectrum, the energy at which the maximum is found, and the integrated intensity depend sensitively on the average electron occupation number per quantum dot $\langle N \rangle$, controlled by the electrochemical potential of the assembly. A detailed explanation follows below. The inset shows the rise of the IR absorption as soon as a *colloidal dispersion* of ZnO nanocrystals in ethanol is excited with near-UV light. Here, few-electron configurations in ZnO nanocrystals are created photochemically: electrons and holes are generated by light absorption; the valence hole is removed by rapid electron transfer from an ethanol molecule to the dot. When the excitation is stopped, the IR absorption slowly decays. This enables us to determine the changes in infrared absorption when a ZnO quantum dot is charged with one or several electrons. These differential absorption spectra, for two different intensities of the near-UV excitation light, are presented as black lines. The spectra are multiplied with a constant factor in order

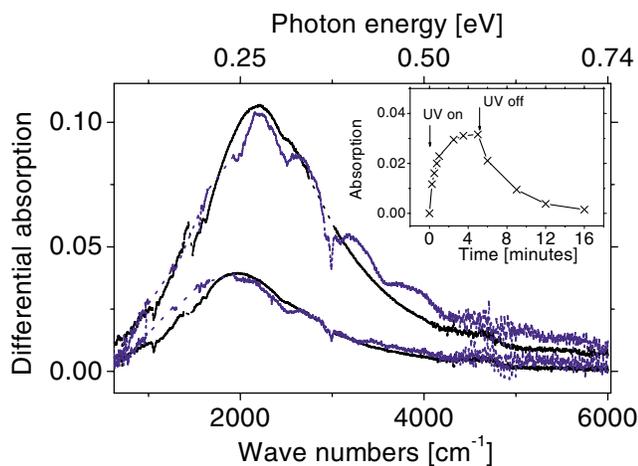


FIG. 1 (color). The increase in the absorption (blue lines) due to charging of a quantum dot assembly (average diameter is 4.2 nm) with on average 0.8 (the lower spectrum) and 3.7 excess electrons per quantum dot. The black lines show the increase in absorption of a colloidal solution of the same ZnO quantum dots, due to excitation with UV light ($\lambda = 300$ nm). The latter spectra are isomorphic to those obtained with ZnO quantum dot assemblies. The spikes in the spectra at 2500 and 3000 cm^{-1} are due to photoinduced absorption by the solvent molecules. Inset: time-dependence of the IR absorption peak of a ZnO quantum dot dispersion upon switching the UV illumination on and off.

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to account for the different number of quantum dots in the IR-optical path in the case of an assembly and a dispersion. It is clear that the absorption spectra obtained with a dispersion containing *uncoupled* ZnO nanocrystals have the same shape as those obtained with an assembly. We have obtained similar results with quantum dots of different diameter in the 3–6 nm range. The similarity between the IR absorption spectra obtained with an assembly and a colloidal dispersion shows that the electronic coupling between the quantum dots in the assembly is weak. The IR absorption spectra obtained with an assembly can, thus, be interpreted in terms of optical transitions between the electron orbitals confined within a single quantum dot (i.e., extended molecular-type orbitals are not important). The picture of weak orbital coupling in such assemblies of ZnO quantum dots is supported by an extensive study of long-range electron transport [6]. The fact that the absorption curves obtained with dispersions

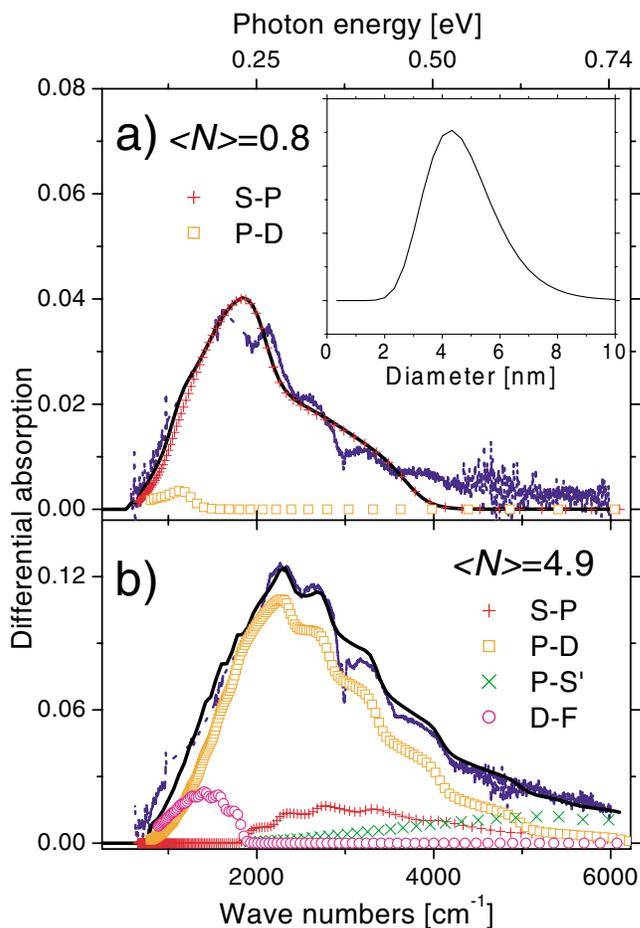


FIG. 2 (color). Absorption spectra (blue) and corresponding fits (black) for a ZnO quantum dot assembly (average diameter is 4.2 nm) at low and higher electron occupation $\langle N \rangle$. The spectrum for $\langle N \rangle = 0.8$ can be fitted with the *S-P* (+) and *P-D* (□) transition. The spectrum for $\langle N \rangle = 4.9$ can be fitted with the *S-P* (+), *P-D* (□), *P-S'* (×), and *D-F* (○) transition. Inset: size distribution of quantum dots with an average diameter of 4.2 nm.

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of illuminated quantum dots are the same as those for assemblies, also in the case that $\langle N \rangle > 1$, demonstrates that more than one electron per ZnO nanocrystal can be injected with the photochemical method. This is in agreement with measurements of the strong increases of the electrochemical potential under illumination and with previous work by another research group [9].

Figure 2 presents the IR absorption spectra for a quantum dot assembly (diameter of ZnO nanocrystals is 4.2 nm) for $\langle N \rangle$ equal to 0.8 and 4.9. With increasing $\langle N \rangle$, the maximum of the absorption spectrum shifts to higher energy, and the integrated intensity of IR absorption increases markedly. The latter observation indicates that the number of optical transitions increases when, besides the S , the P orbitals also become occupied with electrons. We have fitted [10] the absorption curves, with the energy separations between the S , P , D , S' , and F electron orbitals and the relative oscillator strengths for the allowed transitions as adjustable parameters. We took into account the size distribution of the quantum dots [11] [see Fig. 2(a) inset] and the electron occupation of the S, P, \dots orbitals at room temperature. Figure 2(a) shows the results for a low average occupation number; $\langle N \rangle = 0.8$. The absorption curve can be accounted for by the allowed S - P dipole transition ($\Delta l = +1$). For $\langle N \rangle = 0.8$, the sample consists of nanocrystals with zero, one, and two electrons. The contribution of the nanocrystals with one electron corresponds to the right shoulder in the fit. (Note that the dip at 3000 cm^{-1} is due to absorption by the electrolyte.) The contribution of the nanocrystals with two electrons provides the left part. The energy separation between the S and P electron levels is obtained from the position of the absorption peak. There is a very small contribution from a P - D transition. This is due to the fact that a small fraction of the (largest) quantum dots in the assembly have an electron in a P orbital. The width of the S - P transition is about 200 meV. This width is due solely to the size distribution of the quantum dots. This is supported by measurements at 10 K, which provide absorption spectra that are nearly identical to those at room temperature. A similar width has been observed for the S - P transition in a sample of CdSe quantum dots [12].

For $\langle N \rangle = 4.9$, the zero-Kelvin occupation is S^2P^3 ; thus transitions from the P orbitals to higher lying orbitals are expected. Figure 2(b) shows the contributions of the distinct transitions to the overall absorption spectrum. The main contribution comes from the P - D optical transition ($\Delta l = +1$). The steps on the high energy side are due to the contributions of subensembles of nanocrystals, each with a distinct number of P electrons. Each subensemble has a different average diameter and gives thus a contribution at slightly different energy due to the effect of quantum confinement. The energy separation between the P and D levels is obtained from the position of the peak in the absorption spectrum. The oscillator strength of the P - D transition (relative to the S - P transition) is

obtained from the intensity of the absorption curve. The remaining S - P contribution is merely due to the subset of the smallest quantum dots in the sample. Note that the maximum of the S - P contribution is therefore at higher energy than that of the S - P contribution for $\langle N \rangle = 0.8$. Moreover, despite the fact that there are two electrons in the S orbitals, the total S - P intensity has decreased markedly compared to that for $\langle N \rangle = 0.8$. At $\langle N \rangle = 4.9$ most particles have already three electrons in a P level, which strongly reduces the S - P intensity. The subset of largest particles has occupied D orbitals. This leads to a D - F contribution ($\Delta l = +1$) at the low energy side of the spectrum. The tail at the high energy side of the spectrum is merely accounted for by the allowed P - S' ($\Delta l = -1$) transitions. We have thus shown that, by fitting the IR absorption spectra for a gradually increasing occupation of the ZnO quantum dots, we obtain the relative oscillator strengths for the allowed transitions and the energy separations between the S , P , D , and F levels. The contribution from P - S' is too broad and too weak to obtain reliable data for the P - S' energy separation.

We analyzed the absorption spectra for ZnO quantum dots of three different sizes: 3.7 nm ($0 < \langle N \rangle < 1.7$), 4.2 nm ($0 < \langle N \rangle < 4.9$), and 5.2 nm ($0 < \langle N \rangle < 8.6$). In Fig. 3 the single-particle energy separations that we

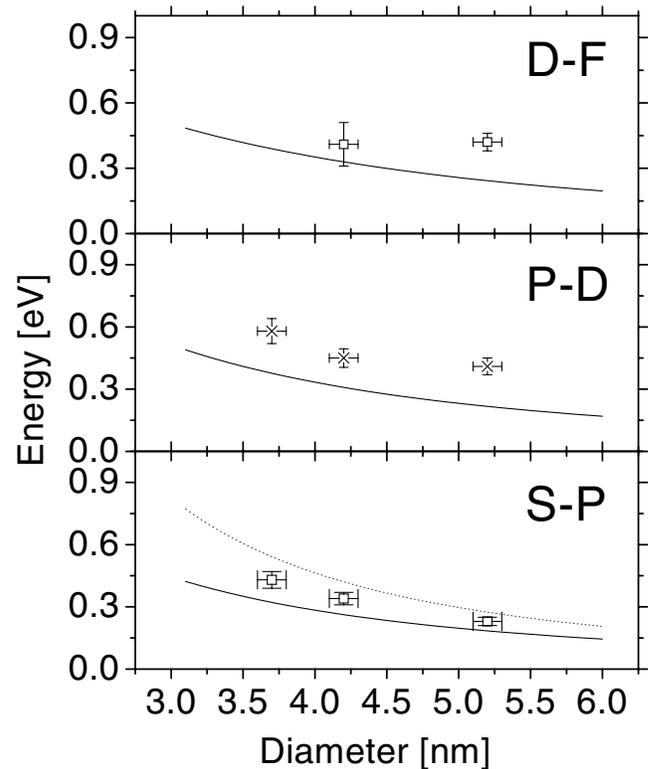


FIG. 3. The separations between the single-electron energy levels obtained from analysis of the IR absorption spectra (symbols) and calculated with tight-binding theory (lines) as a function of the diameter of the ZnO nanocrystals. The dashed line shows the S - P separation calculated with an effective mass approximation.

TABLE I. The dipole oscillator strength for different transitions summed over all degenerate states. Theoretical values are obtained with tight-binding model. The experimental S - P oscillator strength is set equal to the theoretical value. This allows us to compare the oscillator strengths of the P - D , D - F , and P - S' transitions with the theoretical values.

Diameter (nm)		S - P	P - D	D - F	P - S'
3.7		6.1	18 ± 2
	Theory	6.1	18.3	33.8	3.2
4.2		6.4	21 ± 2	36 ± 14	4 ± 2
	Theory	6.4	19.2	36.2	3.4
5.2		6.6	29 ± 4	54 ± 10	4 ± 3
	Theory	6.6	20.7	40.5	3.7

obtain from analysis of the spectra are compared with the tight-binding values. The dependence of S - P and P - D energy separation on the nanocrystal diameter is in line with tight-binding theory. Clearly, the energy separations rise more slowly with decreasing diameter of the nanocrystal than predicted by an effective mass approximation ($\Delta E \approx 1/R^2$). Quantitatively, the experimental S - P , P - D , and D - F separations are somewhat larger than the values calculated with the $spds^*$ tight-binding model used here.

The oscillator strengths that we have obtained from a fit of the IR absorption spectra are compared with the tight-binding values in Table I. For the quantum dots of 3.7 and 4.2 nm, we find a remarkable agreement between observed and calculated values. The oscillator strengths observed for the particles of 5.2 nm are slightly higher than those predicted by tight-binding theory. In addition, our experimental results point to zero oscillator strengths for the S - D and P - F transitions, which are forbidden in ordinary atoms.

Electric dipole transitions in ZnO quantum dots are thus governed by the symmetry of the envelope wave functions. This means that the oscillator strengths of the allowed transitions are very robust for atomic details, i.e., the ZnO crystal lattice and the surface of the ZnO nanocrystals. In contrast, the eigenenergies of the artificial atoms depend sensitively on atomic details and the crystal field. This might explain the slight differences in the measured single-particle energy separations and the tight-binding values.

In summary, we have shown that a gradual and controlled increase of the electron number in ZnO nanocrystals allows us to study the electric dipole transitions between the atomlike electron orbitals of ZnO nanocrystals despite the natural broadening of the spectra due to the size distribution. Control of the electron number in assemblies or supercrystals of quantum dots forms the basis for far-reaching research, for instance, on long-

range transport phenomena [6] and the energetics and dynamics of charged excitonic states [13].

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