

Near-field manipulation of spectroscopic selection rules on the nanoscale

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Edited by George C. Schatz, Northwestern University, Evanston, IL, and approved March 28, 2012 (received for review January 1, 2012)

In conventional spectroscopy, transitions between electronic levels are governed by the electric dipole selection rule because electric quadrupole, magnetic dipole, and coupled electric dipole-magnetic dipole transitions are forbidden in a far field. We demonstrated that by using nanostructured electromagnetic fields, the selection rules of absorption spectroscopy could be fundamentally manipulated. We also show that forbidden transitions between discrete quantum levels in a semiconductor nanorod structure are allowed within the near-field of a noble metal nanoparticle. Atomistic simulations analyzed by an effective mass model reveal the breakdown of the dipolar selection rules where quadrupole and octupole transitions are allowed. Our demonstration could be generalized to the use of nanostructured near-fields for enhancing light-matter interactions that are typically weak or forbidden.

absorption spectra | plasmonics | quantum dot | exciton

Light-matter interactions that govern most forms of spectroscopy, light harvesting, optical imaging, photodetection, optical communications, and data storage are conceptually founded on the laws of far-field optics (1, 2). Electronic and vibrational transitions excited by the electromagnetic (EM) field of light involve the motion of electrons and atoms on the length scale of 1 Å, the typical size of a molecule. Because the size (r) of a molecule is 10^3 times smaller than the wavelength (λ) of the light, it is common to approximate that a molecule subjected to light experiences a uniform electric field (1, 2). Spatial variations of this field across the molecule are neglected in the far-field limit. In this limit, the electric field can excite only those transitions that involve the induction of an electric dipole moment across the molecule, which is assumed to be a point (3). The latter is commonly postulated in the form of the electric dipole selection rule (4); however, a range of transitions that are important for spectroscopies such as circular dichroism, Raman scattering, Raman optical activity, singlet-triplet transitions, and magneto-optical phenomena are forbidden in an electric far-field. Common examples include electric quadrupole (q), magnetic dipole (m), and coupled electric dipole-magnetic dipole excitations (μm) (2, 5).

By the use of nanostructures (6–9), photonic crystals (10), or complex laser interference excitation schemes (11, 12), it is possible to engineer electromagnetic fields of light with spatial variations on the nanoscale approaching molecular length scales and to achieve optical phenomena beyond those allowed by conventional far-fields (13, 14). Jain et al. showed that magneto-optical Faraday rotation of a magnetic nanocrystal could be resonantly enhanced by placing it within the near-field of a plasmonic nanoshell, possibly via enhancement of the quadrupolar and μm transitions in the strongly graded electric field near the nanostructure (9). Tang and Cohen (11, 12) recently showed that at the nodes of a standing wave of circularly polarized light, circular dichroism cross-sections are amplified an order of magnitude compared to those in the far-field originating from a superhelical twist of the electromagnetic field at these nodes.

We focused on the most fundamental form of light-matter interaction, electronic absorption spectroscopy, and theoretically

demonstrated the possibility of manipulating the fundamental selection rules of electronic absorption by using nanostructured electromagnetic fields (15). Unlike the allowed electric dipole transition, the strength of which relies only on the intensity of the electric field, an electric quadrupole transition requires an electric field gradient across the extent of the molecule (3). Such gradients approach zero in a far-field. Consequently, the strength of a quadrupole transition is smaller than that of a dipole-allowed transition by a factor of $(r/\lambda)^{-2}$ or $(k \cdot r)^{-2} \sim 10^6$, where k is the wave vector of the excitation. Transitions of higher multipolar order ($l = 3, 4, \dots$) have even lower strengths $\sim (k \cdot r)^{-2(l-1)}$ relative to the dipole-allowed transition. It may be possible, however, to enhance such forbidden transitions by taking advantage of the high wave vector k of nanostructured fields, especially through localized surface plasmon resonances (16–18).

We show how forbidden transitions can become allowed in a semiconductor nanorod (e.g., CdSe or CdS). This model system offers discrete quantized narrow excitonic levels with a range of wave vectors. Our choice of a near-field source is a metal nanosphere tip (19) (see Fig. 1); however, one may use an alternative source such as the tip of a near-field scanning optical microscope (NFSOM) (20). The resonant near-field of the metal nanoparticle produced under light excitation polarized along the nanorod long-axis assumed in the z direction penetrates into the nanorod on one side then rapidly decays from the metal nanoparticle surface providing a strong field gradient in the direction of the long axis (21).

Results and Discussion

When the system composed of a nanorod and a metal tip is exposed to a homogeneous external field $E(t) = E_0 e^{i\omega t} + c$ oscillating at frequency ω , the nanorod is subject to an electric potential $\phi(r, \omega)$, and it will undergo optical transitions with a rate of absorption given by the following equation:

$$\Gamma(\omega) = \frac{2\pi e^2}{\hbar} \sum_{aj} |\langle \psi_a | \hat{\phi}(\omega) | \psi_j \rangle|^2 \delta(\varepsilon_a - \varepsilon_j - \hbar\omega), \quad [1]$$

where ε_a and ε_j are the electron and hole eigenenergies and $\psi_a(r)$, $\psi_j(r)$ are the corresponding orbitals, respectively. The above expression reduces to the well-known dipolar absorption spectrum when $\phi(r, \omega) = -E_0 z$ for a uniform electric far-field (4). The conventional selection rules $\langle \psi_a | \hat{z} | \psi_j \rangle \neq 0$ are replaced

Author contributions: P.K.J., D.G., R.B., E.R., and A.P.A. designed research; P.K.J., D.G., R.B., E.R., and A.P.A. performed research; P.K.J., D.G., R.B., E.R., and A.P.A. analyzed data; and P.K.J., D.G., R.B., and E.R. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1121319109/-DCSupplemental.

higher-order modes on binding of Ag nanoparticles would be manifested as an increase in the ensemble absorbance of the excitonic peak and a blue shift due to greater enhancement of the higher k modes. For resolving individual transitions and their enhancement in a near-field, one would require low temperature measurements on single nanorods that are currently challenging for probing absorbance spectra.

Conclusions

We described an approach to control and manipulate the optical selection rules in nanometer scale systems by virtue of near-fields generated from a nearby source, i.e., metal nanoparticles or NFSOM tip. Atomistic calculations on a specific metal-tipped semiconductor nanorod system revealed how the near-field would induce an enhancement in the oscillator strength of the dipole-forbidden transitions relative to the dipole-allowed ones. The near-field effect on excitonic transitions is physically rationalized using a simple effective mass model and awaits experimental verification.

Materials and Methods

Absorption Spectrum. The calculation of the absorption spectrum is based on linear response. To lowest order in the amplitude of the incoming field, E_0 , one can show that the absorption rate is given by the following equation (see *SI Materials and Methods* for a full derivation):

$$\Gamma(\omega) = \frac{2\pi e^2}{\hbar} \sum_{aj} |\langle \psi_a | \hat{\phi}(\omega) | \psi_j \rangle|^2 \delta(\varepsilon_a - \varepsilon_j - \hbar\omega), \quad [3]$$

where ε_a and ε_j are the electron and hole eigenvalues, respectively, and $\psi_a(r)$ and $\psi_j(r)$ are the corresponding single particle wave functions that are the solutions of the real-space pseudopotential model. The Eq. 3 expression reduces to the well-known dipolar absorption spectrum when $\phi(r, \omega) = E_0 z$:

$$\Gamma(\omega) = \frac{2\pi e^2}{\hbar} \sum_{aj} |\langle \psi_a | E_0 z | \psi_j \rangle|^2 \delta(\varepsilon_a - \varepsilon_j - \hbar\omega). \quad [4]$$

Electronic Structure. The electronic structure of the nanorods was described within the real-space screened pseudopotential method (23). The local screened pseudopotentials used in the results shown here were fitted to reproduce the experimental bulk band-gap and effective masses neglecting spin-orbit coupling. The form of the pseudopotential is given in ref. 23 along

with the parameterization for CdSe. For CdS, we performed a parameterization similar to the one describe in ref. 23. Ligand potentials were used to represent the passivation layer.

We studied a series of nanorods with varying aspect ratios (ξ), i.e., Cd₂₅₆Se(S)₂₅₅ ($\xi = 1$), Cd₅₄₈Se(S)₅₄₇ ($\xi = 2$), Cd₈₄₀Se(S)₈₃₉ ($\xi = 3$), Cd₁₁₃₂Se(S)₁₁₃₁ ($\xi = 4$), Cd₁₄₂₄Se(S)₁₄₂₃ ($\xi = 5$), Cd₁₇₁₆Se(S)₁₇₁₅ ($\xi = 6$), Cd₂₀₀₈Se(S)₂₀₀₇ ($\xi = 7$), Cd₂₁₅₄Se(S)₂₁₅₃ ($\xi = 7^{1/2}$), and Cd₂₃₀₀Se(S)₂₂₉₉ ($\xi = 8$). Grid size ranged from $64 \times 64 \times 64$ for the smallest nanorod to $64 \times 64 \times 512$ for the largest nanorod depending on its aspect ratio. The diameter of the nanorods was smaller than the experimental value to reduce the computational cost. For CdSe and CdS, the diameter was $D = 2.8$ and 2.6 nm, respectively. To obtain the lowest transitions and calculate the absorption cross-section, we used the filter-diagonalization approach (23, 24) to filter states near the conduction and valance band edge. Filtering about 300 states was sufficient to obtain converged results for the first peak in the absorption spectrum (*SI Materials and Methods*).

Near-Field. To obtain the near-field generated by the metal tip, we followed standard procedures based on solving the relevant Maxwell equations (*SI Materials and Methods*). For a sphere of radius and dielectric constant $\varepsilon_1(\omega)$ embedded in an infinite medium of dielectric constant $\varepsilon_m(\omega)$ and an external field $E_0(\omega)$ in the z direction, this equation has a simple solution outside the sphere:

$$\phi_+(r, \omega) = -E_0(\omega)z \left[1 - s(\omega) \left(\frac{a}{r} \right)^3 \right] \quad [5]$$

and inside the sphere:

$$\phi_-(r, \omega) = -E_0(\omega)z[1 - s(\omega)], \quad [6]$$

with

$$s(\omega) = \frac{\varepsilon_1(\omega) - \varepsilon_m(\omega)}{\varepsilon_1(\omega) + 2\varepsilon_m(\omega)}. \quad [7]$$

ACKNOWLEDGMENTS. P.K.J. was supported by a Miller Fellowship from the Miller Institute at University of California, Berkeley. D.G. was supported by a National Science Foundation American Competitiveness in Chemistry Postdoctoral Fellowship. E.R. was supported by a visiting Miller Professorship from the Miller Institute at University of California, Berkeley. This work was supported by the Physical Chemistry of Semiconductor Nanocrystals Program, KC3105 of the Director, Office of Science, Office of Basic Energy Sciences, of the United States Department of Energy under contract DE-AC02-05CH11231 (to A.P.A.), by the United States-Israel Binational Science Foundation (R.B.), and by FP7 Marie Curie International Outgoing Fellowships project Hierarchical Junction Solar Cells (E.R. and A.P.A.).

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