systematic manner without changing their n_H or n_E values. Examples include $La_{1.85-x}Nd_xSr_{0.15}CuO_4^{36}$ and $Tl_2Ba_{2-x}Sr_xCaCu_2O_8^{37}$ in the p-type cuprates and $Nd_{1.85-x}La_xCe_{0.15}CuO_4^{17a}$ in the n-type cuprates. Substitution of the 8- or 9-coordinate-site cations with isovalent cations of different size changes the in-plane r_{Cu-O} value, which modifies the magnitudes of the t, V, and B parameters, thereby changing the T_c.

Concluding Remarks

In understanding the superconductivity of the cuprates, it is important to distinguish between steric and electronic factors. The T_c versus in-plane r_{Cu-O} and T_c versus in-plane BVS plots of the p-type cuprates are grouped into classes and subclasses due to steric factors. Electronic factors acting on each class or subclass are remarkably similar: the T_c is an inverted parabolic function of n_H. This correlation suggests that the coupling constant for Cooper pair formation is also an inverted parabolic function of n_H. Our study shows that, as the magnitudes of the t, V, and B parameters decrease, the $T_{c,max}$ value of the p-type cuprates should increase whereas that of the n-type cuprates should decrease. These findings must be reproduced by any model Hamiltonian appropriate for the cuprate superconductors.

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Nonlinear Optical Properties of Nanometer-Sized Semiconductor Clusters

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The field of nonlinear optics was launched almost 30 years ago by the observation of second harmonic generation in a quartz crystal.[1] Through intensive research in the following decades, the basic physics behind various nonlinear optical phenomena is now mostly understood.[2] With the maturity of the field, the focus has shifted to the study of nonlinear optical properties of materials, a subject receiving growing interest in recent years.[3-5] The primary objective is to find materials with exceptional nonlinear optical response for possible applications as optical switching and frequency conversion elements in the telecommunication and information processing industries. With this new emphasis and the exciting prospects of replacing electrons with photons in future photonic devices, a growing number of chemists and materials scientists have been attracted to the field. The study of optically nonlinear materials has evolved into a truly multidisciplinary area.

Materials under investigation are traditionally divided into three categories: organics,[3] inorganics,[4] and semiconductors.[5] Each of these classes of materials has its own merits and limitations and is suited for different types of applications. In this Account, I focus on a new class of materials, namely, nanometer-sized semiconductor clusters (sometimes called nanocrystallites, quantum dots, Q-particles, ..., etc.). These clusters possess structures that are essentially the same as bulk semiconductors, yet with properties dramatically dif-

ferent from those of the bulk; often they are better viewed as very large molecules.[6-8] The electronic properties of these clusters depend on the cluster size, a phenomenon commonly referred to as the quantum size or quantum confinement effect.[6-12] The effect is manifested as a blue shift in the exciton (an electron-hole pair bounded by Coulomb interaction) energy and enhancement in the volume-normalized oscillator strength as the cluster size decreases. Several review papers[6-8] summarize the current status of the material synthesis and our understanding of their size-dependent electronic and photochemical properties.

Our studies of the nonlinear optical properties of these clusters were triggered by a paper[13] describing the nonlinear optical properties of commercial color filters (sold by both Corning and Schott). These color filters contain nominally CdS_xSe_{1-x} particles of ~100-1000-Å diameter,[13] a size regime where their optical properties still resemble those of the bulk. The reported large

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nonlinearity induced much interest, and soon the study was extended to CdS clusters in the quantum-confined size regime (that is, below ~60 Å for CdS).[14,15] It was immediately clear that composites containing small clusters can become an important class of nonlinear optical materials since, in principle, a large number of them, with different combinations of semiconductor guests (such as CdS, PbS, GaAs, ..., etc.) and dielectric hosts (such as polymers, glasses, ..., etc.), can be synthesized with good optical quality. However, before any rational design and synthesis of materials can begin, several important questions have to be addressed. For example, what is the origin of their nonlinearity? Is it different from that of the bulk? What are the intrinsic advantages and limitations of semiconductor clusters? How can one improve the nonlinearity through material synthesis? This Account discusses answers to these questions.

Before I start the discussion of the nonlinearity of clusters (in sections III and IV), a brief introduction to third-order optical nonlinearity and the nonlinear mechanisms for molecules and bulk semiconductors are given in sections I and II, respectively. These provide the necessary background information before I can proceed to the main topic of this Account. In the final section I summarize the results and suggest possible future directions.

I. What Is Third-Order Optical Nonlinearity?

There exists a simple way to describe third-order optical nonlinearity when only one laser frequency is involved in the optical process. A material is said to possess third-order optical nonlinearity if its refractive index (n) depends, reversibly, on the intensity of incident light (I), that is,

$$n = n_0 + n_2 I \tag{1}$$

where n_0 is the refractive index at the low-intensity limit, and n_2 is called the nonlinear refraction coefficient. Under such conditions, it can be shown[17] that the induced polarization of the material contains a term that has cubic dependence on the electric field of the incident light, hence the term third-order nonlinear optical effect.

Such a change in the refractive index can be induced by either a resonant or a nonresonant process. For a resonant process, the frequency of the incident light overlaps with an electronic absorption band, by either a one-photon or a multiphoton process. The energy is absorbed by the sample, and an excited-state population is generated. This induces a transient change in the absorption spectrum of the material due to the bleaching of the ground-state absorption and/or the appearance of the excited-state absorption. This change in the absorption coefficient, α, gives rise to a change in the refractive index, since they are interdependent according to the Kramers–Kronig relations.[16] A nonlinear absorption coefficient α_2 can be defined similarly to eq 1: $\alpha = \alpha_0 + \alpha_2 I$ where α_0 is the absorption coefficient at the low-intensity limit. The best way to

monitor this transient absorption change is the pump–probe technique (flash photolysis), where a short pulse laser is used to excite the material and a second pulse (or lamp) is used to probe the change in the absorption spectrum. This technique has been used for decades in the field of photochemistry but without being generally recognized as a third-order nonlinear optical process.

For a nonresonant process, light is not absorbed by the sample. The optical nonlinearity basically originates from the anharmonicity of the electronic system. Traditionally, the nonresonant optical nonlinearity of a material is described via the perturbational approach. In this approach, the polarization, P_d, induced in a medium by an external electromagnetic field, E, can be written as

$$P_d = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + ... \tag{2}$$

where $\chi^{(n)}$ is the nth-order optical susceptibility. The third-order susceptibility, $\chi^{(3)}$, describes third harmonic generation, four-wave mixing, and the optical Kerr effect.[2] Optical switching[17] and image processing[18] are some of the important technological applications of $\chi^{(3)}$ processes. Where there is only one frequency involved, the real part of $\chi^{(3)}$ is linearly proportional to n_2, that is, n_2 (in cm/kW) = $(4\pi/9n_0)^2\chi^{(3)}$ (in esu).[17]

Different parameters are required to characterize the resonant and the nonresonant optical nonlinearity. This has often been a source of confusion in the literature. For nonresonant processes, the speed of the nonlinearity is determined by the laser pulse width and the magnitude of the nonlinearity can be measured by either $\chi^{(3)}$ or n_2. However, for resonant processes, $\chi^{(3)}$, α_2, or n_2 alone cannot measure the magnitude of the nonlinearity. A complete characterization of the nonlinearity requires the additional knowledge of the ground-state absorption coefficient, the laser pulse width, and the excited-state relaxation time. In section III, I will show that once all these factors are properly taken into account, the best parameter for measuring the resonant nonlinearity is simply the ground-state absorption cross section (i.e., extinction coefficient) of the material.

Other than the resonant and nonresonant nonlinear processes mentioned above, there exist the near-resonant and hybrid-resonant processes. In the near-resonant case, the laser frequency is very close to, but not overlapping with, a sharp exciton absorption band. Under such conditions the exciton absorption band can be changed due to the optical Stark effect, which gives rise to nonlinearity.[19] In the hybrid-resonant case, both electric field and light field are applied to the sample. The nonlinearity originates from the sensitivity of the exciton absorption band to the external applied field (dc Stark effect).[20] These two types of nonlinear processes require material with a very sharp exciton band. They have not been demonstrated with semiconductor clusters and therefore will not be covered here.

In this account, I focus the discussion on the resonant and nonresonant third-order optical nonlinearity.

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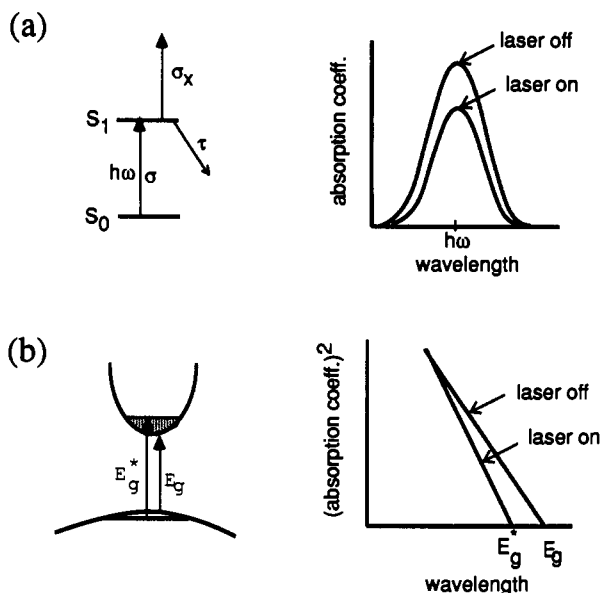(20) Miller, D. A. B. *Opt. Eng.* **1987**, *26*, 72.

Figure 1. (a) The saturation of a molecular electronic transition. The left-hand side shows a three-level molecular system. σ, σ_x, and τ represent the ground-state absorption cross section, the excited-state absorption cross section, and the excited-state relaxation time, respectively. The right-hand side shows the optical bleaching behavior of the S_0-S_1 transition. The bleaching is manifested by a reduction in the absorption coefficient, without a shift in the absorption peak, when irradiated by a laser. (b) The band-filling model for a bulk semiconductor. The left-hand side shows a schematic of the band structure. E_g and E_g^* represent the band gaps before and after optical excitation, respectively. The right-hand side shows the optical bleaching behavior near the direct band gap. Note that the y axis is now the square of the absorption coefficient. The bleaching is manifested by a shift in the absorption edge when irradiated by a laser.

II. Resonant Nonlinearity of Molecules and Bulk Semiconductors

As stated before, the resonant nonlinearity originates from a transient change in the absorption spectrum (and refractive index) of the material. For molecules, the simplest mechanism by which this can happen is the bleaching of the ground-state electronic absorption. Once a molecule absorbs a photon from the ground state, S_0, to an excited state, S_1, the transition can no longer be excited until the excited state relaxes back to the ground state (Figure 1a). During this period, if one measured the absorption spectrum of the molecule, one would observe a reduction in absorption at the S_0-S_1 transition energy (transient bleaching), as shown schematically in Figure 1a. If the excited state has transitions to higher states in the wavelength region probed, then additional induced absorption (σ_x in Figure 1a) can be observed. This change in the absorption coefficient and refractive index is proportional to the laser intensity, eq 1, before the saturation regime is reached and therefore can be described as a third-order nonlinear optical process.[2,17] As I will show in section III, the magnitude of the nonlinearity is basically determined by $(\sigma - \sigma_x)$.

For bulk semiconductors at room temperature, when the exciton contribution is small, the mechanism for the resonant nonlinearity can be described by the band-filling model.[16,21] This is shown schematically in Figure

1b for a direct gap semiconductor such as CdS. Absorption of photons across the band gap, E_g, generates electrons and holes which fill up the conduction and valence bands, respectively, due to the Pauli exclusion principle. If one took a snapshot of the absorption spectrum before the electrons and holes can relax, one would find that the effective band gap, E_g^*, has increased (Figure 1b), since transitions to the filled states are forbidden. The magnitude of the nonlinearity in this case is determined by the absorption coefficient of the semiconductor as well as the electron and hole effective masses. The effective mass is determined by the transfer (or resonance) integral between atoms or molecules in the framework of the Huckel model.[8] Stronger interatomic interaction gives a larger transfer integral, a smaller effective mass, and a steeper curvature in the energy band.[8] For CdS, the dominant contribution comes from the conduction band because the electron effective mass is much smaller than the hole effective mass.

III. Resonant Nonlinearity of Semiconductor Clusters

For large semiconductor particles (e.g., larger than several hundred angstroms for CdS), the origin of the optical nonlinearity should be similar to that of the bulk semiconductors, and the band-filling model is in principle applicable,[22] if defects in the sample can be minimized. However, once the cluster size is smaller than the exciton size (~ 60 Å for CdS[6-8]), the band-filling model becomes fundamentally invalid.[23] In this size regime, there are discrete states rather than a continuous energy band, and bound electron–hole pairs (bound excitons) rather than free electrons and holes. For extremely small clusters ($< \sim 10$ Å), when both the valence and conduction bands are fully quantized, the clusters are essentially molecules; and the nonlinear mechanism for molecules applies. It is in the intermediate size regime that a new mechanism has been discovered, which will be discussed here.

The immediate result after the excitation of a semiconductor cluster by a short laser pulse[23-32] is the generation of an electron–hole pair, bounded by the cluster surfaces (a bound exciton). Because of the large surface area in small clusters, this bound exciton is rapidly trapped by surface defects within subpicoseconds, forming a trapped electron–hole pair.[24,31-34] It is

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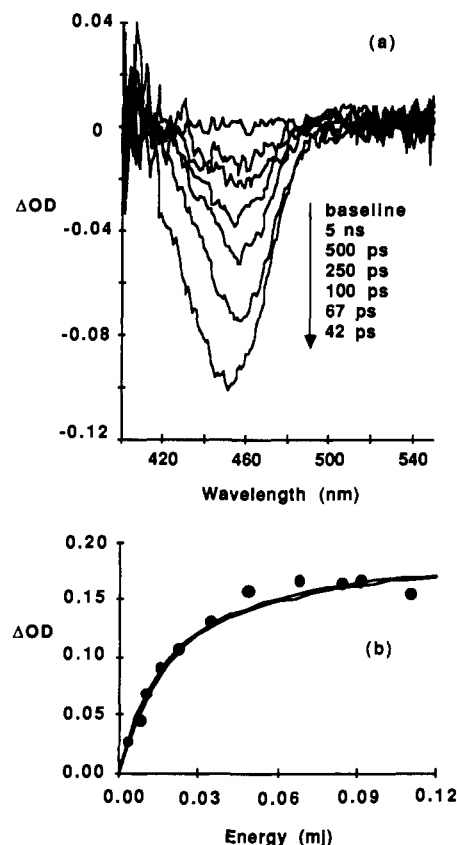
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Figure 2. (a) A series of difference absorption spectra recorded at selected times after excitation of ~40-Å CdS clusters in Nafion with a 355-nm, 30-ps, 87-μJ laser pulse. (b) A plot of the maximum negative absorbance change at 450 nm induced in the ~40-Å CdS clusters in a Nafion sample as a function of 355-nm, 30-ps pump pulse energy. The bleaching saturates when there is about one trapped electron–hole pair per cluster. Reprinted with permission from ref 32. Copyright 1990 American Institute of Physics.

the presence of these trapped electron–hole pairs that affects the cluster absorption spectrum and gives rise to the optical nonlinearity, at least for experiments performed with laser pulse duration comparable to or longer than picoseconds. In the very early time domain there are some discussions on the possible formation of a biexciton (two excitons bounded together) and its effect on the absorption spectrum of the clusters.[35,36] There is not yet definitive experimental evidence to support this hypothesis.[24,32]

Figure 2a shows the time-resolved absorption spectral change of ~40-Å CdS clusters obtained with the pico-second pump–probe technique.[31,32] The main result in Figure 2a shows that the exciton absorption is bleached during the lifetime of the trapped electron–hole pair and recovers as the trapped electron–hole pair decays away. Furthermore, from the intensity dependence of the bleaching efficiency (Figure 2b) one can calculate that bleaching saturates when there is about one trapped electron–hole pair per cluster[31,32] a conclusion independently obtained from a combined flash photolysis and pulse radiolysis study of CdS colloids.[29,30]

This important result indicates that one trapped electron–hole pair is sufficient to bleach the exciton

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absorption of the whole cluster. A cluster, which contains several thousand atoms, therefore behaves like a single molecule. This can happen only if there exists a strong interaction between the trapped electron–hole (e–h) pair and the exciton to cause the loss of the exciton oscillator strength. Otherwise another e–h pair could be excited (with the same transition strength) in the same cluster after the first pair is trapped.

The basic physics of this effect is easy to understand. This reduction of the exciton oscillator strength is due to the reduced overlap of the electron and hole wave functions in the presence of a trapped e–h pair,[8] illustrated schematically as follows:
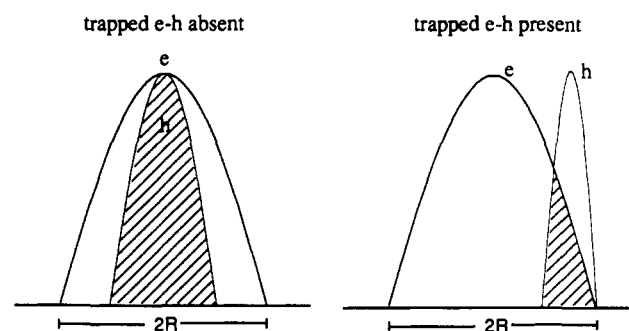
In the absence of a trapped e–h pair (left side of the illustration), the electron and hole wave functions (sine functions) have a good overlap with maximum at the center of the cluster (shaded region). When a trapped e–h pair is introduced to the cluster surface, the hole wave function becomes localized at the surface by the trapped electron, while the electron wave function is still delocalized because of the small electron effective mass. This reduces the spatial overlap (shaded region) of the electron and hole wave function and thus the oscillator strength of the exciton. On a more quantitative scale, we have performed a variational calculation which shows that, in the presence of a surface-trapped e–h pair, the exciton energy is lowered by only ~50 meV but its oscillator strength is reduced by 90% for a 50-Å CdS cluster.[32]

One interesting prediction from this model is that *a trapped electron is more efficient than a trapped hole in bleaching the exciton absorption* in the case of CdS. This is because a trapped hole is not capable of localizing an electron with small effective mass and therefore is inefficient in reducing the electron–hole overlap. This was proven by a pulse radiolysis experiment[30] where the electron and hole can be separately injected into the cluster and their effects probed separately. One can also use sensitized photoinduced electron transfer to inject either an electron or a hole into the clusters and study their effects separately. Such experiments should be very informative.

With the basic mechanism understood, the resonant nonlinearity of semiconductor clusters can now be quantitatively analyzed. The resonant nonlinearity originates from the change in the relative absorption coefficient, $\Delta\alpha/\alpha_0$, induced by the absorption of a photon. The magnitude of the nonlinearity is therefore determined by how efficiently an incident photon can induce a change of $\Delta\alpha/\alpha_0$ in a material, which in turn depends on the laser pulse width and the excited-state relaxation time.

By solving the relevant rate equations describing optical excitation and relaxation of the excited state

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(Figure 1a),[32] the bleaching efficiency per photon absorbed can be derived as

$$\frac{\Delta\alpha}{\alpha_0(I/\hbar\omega)} = (\sigma - \sigma_x)\tau(1 - e^{-\tau_p/\tau}) \qquad (3)$$

where τ_p is the laser pulse width (assumed to be a δ function), τ is the excited-state lifetime, $\hbar\omega$ is the photon energy, I is the incident laser intensity (J/(s·cm²)), σ is the absorption cross section (1/cm²) of the molecule or the cluster, and σ_x is the excited-state (or induced) absorption cross section (Figure 1a). Equation 3 is an important equation describing the resonant nonlinearity of molecules as well as quantum-confined semiconductor clusters. For a given τ_p and τ, it is simply the $(\sigma - \sigma_x)$ term that determines the resonant optical nonlinearity. A similar equation can also be derived for bulk semiconductors using the band-filling model. In this case it is the absorption coefficient of the semiconductor, plus the electron and hole effective masses, that determines the optical nonlinearity.

One surprisingly simple, yet not always recognized, conclusion emerging from the above discussion is that the resonant third-order optical nonlinearity of a material is essentially determined by the absorption cross section, σ, of the electronic transition involved. The induced absorption, σ_x, tends to reduce the nonlinearity and changes its frequency dependence. With the knowledge of the absorption cross section (or extinction coefficient) of the material, one already has a very good idea of the magnitude of the nonlinearity, without even doing any sophisticated experiment. Furthermore, inorganic semiconductors are usually stronger absorbers than organics, which is why semiconductors usually have larger resonant nonlinearity than organics. For quantum-confined semiconductor clusters, theoretically the absorption cross section of the first excited state can be very large due to the enhanced spatial overlap of the electron and hole wave functions (see ref 8 for a detailed discussion). In reality it is limited by the cluster size dispersion and the presence of surface defects.[8] To enhance the resonant nonlinearity of semiconductor clusters, one therefore needs monodisperse clusters of strongly absorbing semiconductors.

IV. Nonresonant Nonlinearity of Semiconductor Clusters

When the wavelength of the laser is far off-resonant from any electronic transitions, so that one can safely ignore the effects of excitons and multiple photon absorption, then the situation becomes quite simple. For semiconductor clusters embedded in a dielectric medium, the major factor to be considered is the local field effect.

Inorganic semiconductors usually possess large refractive indices. When they are embedded in media with lower refractive indices such as glasses, polymers, or solvents, a boundary is established by the difference in the refractive indices. When illuminated by light, the local electric field experienced by the clusters can be enhanced compared to the incident field because of the presence of this boundary. The local field effect can also arise from the dipole–dipole interaction between the molecule and the surrounding medium, a subject treated by the classical Lorentz and Onsager reaction field models.[37]
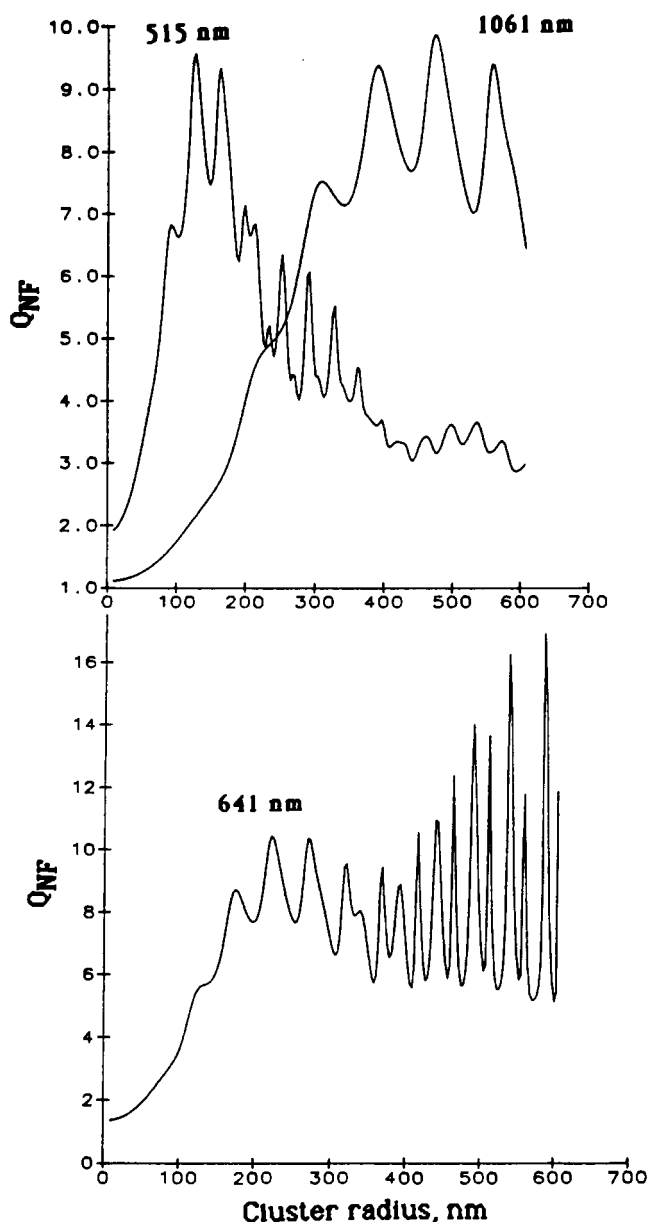

Figure 3. The near-field enhancement factor, Q_{NF}, plotted as a function of CdS particle radius at light wavelengths of 515, 1061, and 614 nm. The refractive index of the surrounding medium is 1.4. Reprinted with permission from ref 40. Copyright 1991 American Chemical Society.

The size- and wavelength-dependent local field enhancement factor can be calculated with the Lorenz–Mie theory[38] in the near-field limit.[39] Figure 3 shows an example of the local field intensity enhancement factor, Q_{NF}, of a CdS sphere as a function of cluster size at several selected wavelengths.[40] Initially Q_{NF} increases gradually with increasing cluster size and then becomes oscillatory in the large particle size regime (Figure 3). These sharp peaks correspond to the conditions when the wavelength of light is in resonance with the geometric modes of the sphere (analogous to

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a laser cavity). For large particles, large intensity enhancement factors up to ~20 can be achieved for CdS. The enhancement factor is relatively small for very small clusters. One should note that the Lorenz–Mie theory does not include the reaction field[37] arising from the dipole–dipole interaction between the clusters and the surrounding medium. The inclusion of the reaction field factor will make the Q_{NF} value slightly higher (about a factor of 1–2 depending on the medium).

For a third-order nonlinear optical process, the effective $\chi^{(3)}$ in eq 2 is enhanced by a factor of $(Q_{NF})^{3/2}$ due to the local field effect, at one particular wavelength. Several trends in the nonresonant $\chi^{(3)}$ of semiconductor clusters can be established based on the effects of local field enhancement: (1) the magnitude of $\chi^{(3)}$ should increase with increasing cluster size; (2) $\chi^{(3)}$ can be enhanced by either lowering the refractive index of the surrounding medium or raising the refractive index of the semiconductors; and (3) quantum confinement, which shifts the band gap to higher energies and lowers the refractive index of the semiconductor clusters, reduces the magnitude of nonresonant $\chi^{(3)}$. This is in direct contrast to the resonant nonlinearity which is enhanced by the quantum confinement effect.

Experimentally, systematic study on the local field effect is rare.[40-43] Recently we performed a third harmonic generation study on the size-dependent $\chi^{(3)}$ of CdS clusters.[43] We found that in the quantum confinement regime, the nonresonant $\chi^{(3)}$ of CdS clusters decreases with decreasing cluster size. Also, the effective $\chi^{(3)}$ increases when the surrounding medium is changed from dimethylformamide ($n = 1.427$) to Nafion ($n = 1.35$). Both observations are consistent with the local field model.[43]

I now draw attention to the quite large local field factors associated with large clusters (Figure 3). Such local field effects should play a role in any spectroscopic and photophysical studies of these clusters. For example, their photoluminescence spectra should be enhanced and show structures corresponding to the structural resonances.[40] As to the question of whether or not one can use these large local field factors to enhance the nonresonant $\chi^{(3)}$ for all-optical switching application, the answer is unfortunately no. This is because the same local field also enhances the extinction (i.e., scattering plus absorption), σ_{ext}, which reduces the figure of merit, $\chi^{(3)}/\sigma_{ext}$, for all-optical switching. Small clusters just outside the quantum confinement regime (~60 Å for CdS) are therefore still preferred.

When it comes to all-optical switching, low optical loss is as important as optical nonlinearity. This is best illustrated by the fact that, at present, the only good material for all-optical switching is still glass, in spite of its very low $\chi^{(3)}$, ~10^{-14} esu. About 100 m of glass is needed for a complete switching.[44] If this length can be reduced to less than 1 m by using a material with $\chi^{(3)} \sim 10^{-12}$ esu, then it becomes practically interesting. There are many semiconductors[45] and a few polymers[3,46]

with nonresonant $\chi^{(3)}$ of that magnitude, but none can be grown into meter (or tens of centimeter) length with optical loss as low as glass. This is precisely where the potential of semiconductor cluster composites lie (especially glass-based composites). It may give the best compromise between the optical nonlinearity and optical loss.

V. Conclusions

I have discussed both the resonant and nonresonant third-order optical nonlinearity of quantum-confined semiconductor clusters. The mechanism for the resonant nonlinearity is attributed to the reduction of the exciton absorption strength in the presence of an optically generated trapped electron–hole pair. The magnitude of the resonant nonlinearity is mainly determined by the absorption cross section of the cluster and should increase with decreasing cluster size. To improve the resonant nonlinearity, one needs (1) a sharp exciton absorption band (which means smaller and monodisperse clusters) and (2) semiconductor clusters with a larger absorption coefficient, such as GaAs or PbS. For nonresonant nonlinearity, the important factor to be considered is the local field enhancement effect. The magnitude of the nonlinearity increases with increasing cluster size. However, since scattering also increases with the cluster size, smaller clusters still give better figures of merit. To maximize the nonresonant nonlinearity, small clusters of semiconductors with large intrinsic nonlinearity and high refractive index (such as GaAs and Ge) are preferred. They should be embedded, in high concentrations, into a medium with low refractive index. Since long interaction length is required for nonresonant operation, minimizing the optical loss is as important as maximizing the nonlinearity. These requirements point to glasses or solutions as the best media.

From the perspective of nonlinear optics, future material research in the area of semiconductor clusters should concentrate on synthesizing monodisperse clusters with a sharp exciton absorption band, as well as extending the synthesis to III–V clusters such as GaAs and single element clusters such as Ge. Initial successes toward achieving these goals have just appeared in the literature.[47-51] The introduction of magnetic ions into semiconductor clusters adds another dimension to this already interesting problem and opens the doorway for studying the magnetic field effects.[52] It should be noted that although there are competing technologies for making nanometer-sized semiconductor structures, such as the combination of molecular beam epitaxy with lithography or etching,[53] the clusters of interest here are in a size regime not easily accessible

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by these techniques. It is not an exaggeration to say that chemistry indeed holds the key to future progress in this area.

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Stereochemistry of Intramolecular Free-Radical Cyclization Reactions[†]

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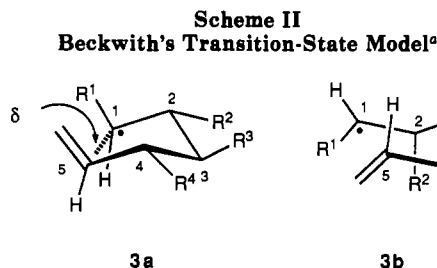
Free-radical reactions are ubiquitous in nature. They have been among the most widely used methods for the manufacture of various vinyl polymers for several decades, yet the applications of these reactions for the synthesis of complex organic molecules are of recent origin. Of all the free-radical reactions that have been used for the construction of carbon–carbon bonds,[1] the hex-5-enyl radical cyclization (Scheme I) is the most well-known. The development of this reaction, which was known in the polymer literature since the early 1960s,[2] has followed a traditional course. Following the pioneering synthetic works of Lamb[3] and Julia,[4] several physical organic studies from the laboratories of Walling, Beckwith, and Ingold[5] helped delineate kinetic and thermodynamic parameters for the individual steps of this radical chain process. By the late 1970s synthetic organic chemists realized the power of this method for rapid assembly of architecturally complicated polyfunctional molecules, and a number of elegant syntheses followed.[6–8]

The rapid growth in free-radical synthetic methodology that followed was highlighted by the large number of publications dealing with new methods of generation of the radicals as well as their compatibility with various functional groups and reaction conditions. Application of these developments further enhanced the utility of the hex-5-enyl cyclization. However, the full potential of this reaction was yet to be realized since stereochemistry remained a problem and only limited structural types were accessible by this reaction. The stereochemistry at the newly created centers was predictable in some of these cases, but the origin of the selectivity was not understood. This limitation was rarely addressed in the context of substituted hex-5-enyl radical cyclizations even though Beckwith, in a classic series of papers,[9,10] had laid the foundation for such a study. We undertook a systematic study of these con-

Scheme I
Hex-5-enyl Radical Cyclization[a]

[a] At 60 °C, $k_{1,5}$ is approximately 10^5–10^6 s^{-1}; $k_{1,5}/k_{1,6}$ = 50.

Scheme II
Beckwith's Transition-State Model[a]

[a] For the transition state, $\delta \sim 2.3$ Å. For cyclohexane C_1–C_5, $\delta \sim 2.5$ Å.

trol elements in highly functionalized and synthetically useful systems, and this Account summarizes the significant progress we made in this area. On the basis of our work, we can propose models for transition states which can be used to rationalize the stereochemistry of hex-5-enyl radical cyclizations, including a number of seemingly anomalous results recently reported in the literature. As a corollary, since we can incorporate these

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