bination as opposed to improving the minority carrier capture kinetics. This is an active area of investigation and presents a challenge for scientists involved in the chemistry of interfaces.

I have been fortunate to work with a series of talented and enthusiastic co-workers and colleagues over the past nine years and gratefully acknowledge their efforts for initiating and carrying through the work described in this Account. The National Science Foundation, Department of Energy, and Office of Naval Research have provided generous support for these projects, and crucial unrestricted funding was provided by IBM Corp., the Dreyfus Foundation, the A. P. Sloan Foundation, and the Presidential Young Investigator Program.

Semiconductor Crystallites: A Class of Large Molecules

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Introduction

Silicon, gallium arsenide, and cadmium selenide, are examples of semiconductors, a class of materials indispensable to modern solid-state electronics. Their properties can be understood in molecular terms. The Si–Si bond in bulk silicon is localized, tetrahedrally directed, and strong and, in fact, is no different than that in organosilicon molecular compounds. The relationship between bulk silicon and the silicon atom is similar to the relationship between organic polymers and their constituent monomers. A piece of bulk silicon is simply a normal, albeit extremely large, inorganic molecule.

Semiconductor electronic properties are a consequence of the molecular orbitals of the solid. Consider a small silicon crystallite growning from Si atoms, as schematically outlined in Figure 1.[1-4] The atom has four sp hybrid orbitals. Orbitals on neighboring atoms combine pairwise to form doubly occupied bonding orbitals and empty antibonding orbitals. Each new atom adds one orbital to the bonding set and to the antibonding set, for each bond formed. A spread of orbital energies develops within each orbital set, and the HUMO–LUMO separation in the molecule becomes the band gap of the solid.

Semiconductor electronic properties depend strongly on the extent and dimensionality of polymerization, that is, on the size and shape of the oligomer. Only one dimension need become macroscopic for the bands to become continuous. Very thin sheets (termed "quantum wells" in the physics literature) show bulk solid-state properties in the two planar dimensions, but molecular, size-dependent properties in the thin dimension.[5] The interplay of solid-state and molecular properties in such structurally perfect, layered materials has led to remarkable discoveries: the fractional quantum Hall effect, ballistic electron transport, and large nonlinear optical effects.

In 1983 we began studying the *three-dimensional* evolution of molecular to bulk properties in large semiconductor clusters (alternative terms: quantum crystallites or quantum dots).[6] These large structures have the internal geometry of the bulk solid, but electronic properties similar to those of molecules. We attempt to invent methods to synthesize, characterize, and understand *macroscopic amounts* of large (100–5000 heavy atom), chemically passivated clusters. We study large clusters because we find that bulk electronic properties develop slowly with size. The study of these clusters is a new branch of the chemistry of large molecules.

Preparation and Characterization of Large Semiconductor Clusters

Molecular Synthesis of Large Clusters. An ideal synthesis would prepare *pure* isolated clusters, monodisperse at the atomic level, with the surface independently derivatized. Cluster size would be continuously variable, and a wide class of surface ligands would be possible, to impart desired surface properties. The enormity of this project is obvious, yet an encouraging start has been made.

Most progress has occurred with II–VI binary compounds. These semiconductors have small solubility products, ease of internal crystallization, and simple phase diagrams. Crystallinity is essential in the current schemes for internal structural characterization. Simple phase diagrams help ensure that only one type of cluster is formed.

The precipitation of sulfides and selenides occurs in textbook qualitative analysis schemes. The process can be stopped kinetically at a size near the smallest homogeneous nucleation seed by working at very high dilution and/or low temperature.[7,8] The resulting

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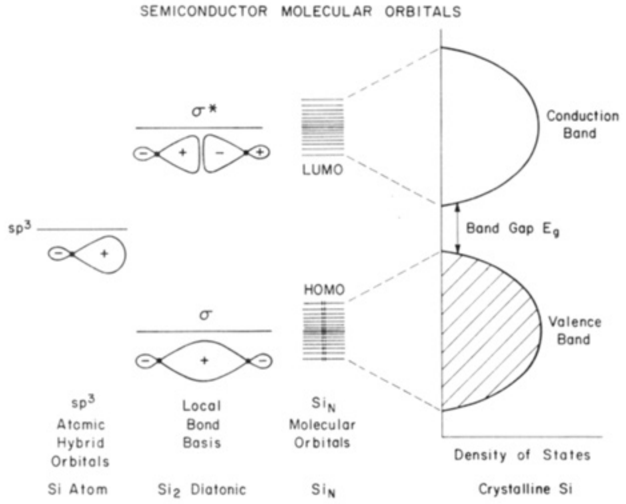


Figure 1. Schematic diagram of the molecular orbital model for band structure, adapted from ref 3.

colloid is metastable, eventually flocculating irreversibly as a chemically bonded network of particles. Nevertheless, the first demonstration of a size-dependent band gap in a semiconductor crystallite occurred via this comparatively crude method.[6]

Structured reaction media improve size control and stability in such "arrested precipitation" reactions. Zeolites, ionomers, porous glass, vesicle and/or micelle media, and gels have been utilized.[9-15] Useful size control is possible, although mechanisms are not well understood. Herron, Wang, and co-workers report the elegant use of small zeolite cavities as hosts for $(CdS)_4$ clusters.[14] Unfortunately there is no known template for significantly larger crystallites. In these syntheses, it was not possible to recover the clusters and then redisperse them. However, Henglein, Weller, and coworkers used polymeric sodium hexametaphosphate to protect the surface of the otherwise bare particles.[15] The coated particles were recovered from solution as a dry powder and, importantly, were then soluble in water.

Fendler and colleagues discovered that CdS particles in the nanometer-sized water pools of inverse micelle media are unusually stable against flocculation.[9] In an equivalent CdSe system, we discovered that the surface surfactant ligand is labile and can be transiently displaced by sequential additions of Se^{2-} and Cd^{2+}, which grow on the seed to make a larger crystallite.[16] The CdSe crystallites are *living polymers*, in that growth stops when the feedstock monomers are depleted, yet continues if the feedstock is replenished. We exploited this surface reactivity to allow the isolation of semiconductor crystallites which are molecular.

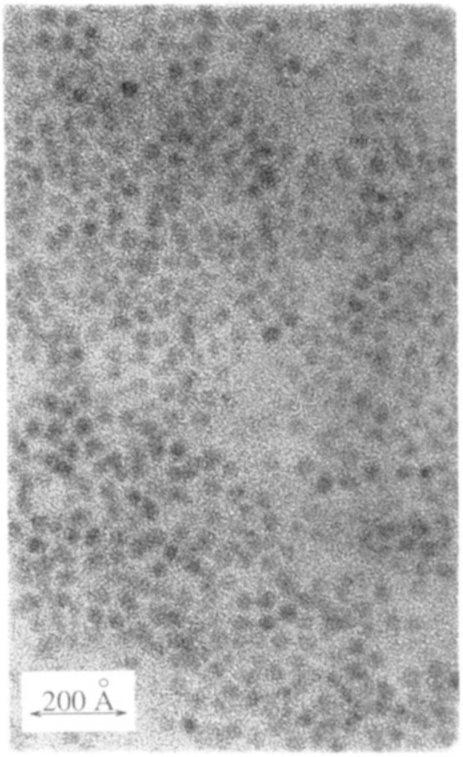
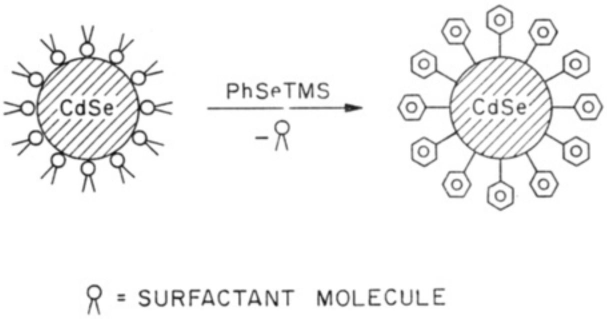


Figure 2. Transmission electron micrograph of wurtzite CdSe quantum crystallites described in ref 19.

Scheme I



By treating a micelle-encapsulated CdSe particle, having a Cd^{2+}-rich surface, with Ph–Se^-, we covalently linked an organic coating to the surface as shown in Scheme I. This allowed isolation of molecular particles, designated (CdSe)-Ph (said to be "capped"), as powders which were subsequently redispersible in organic solvents.[16] The organic group has little effect on the HOMO–LUMO absorption and can be varied to give clear differences in chemical properties (particularly solubility). The solubility of the passivated molecular particles allows their purification and subsequent study. It is also possible to nucleate and grow CdSe particles on seeds of ZnS, and vice versa, in inverse micelle media.[17]

An independent synthesis pathway uses controlled thermolysis of molecular precursor compounds and leads to soluble clusters of several II–VI compounds[18a]

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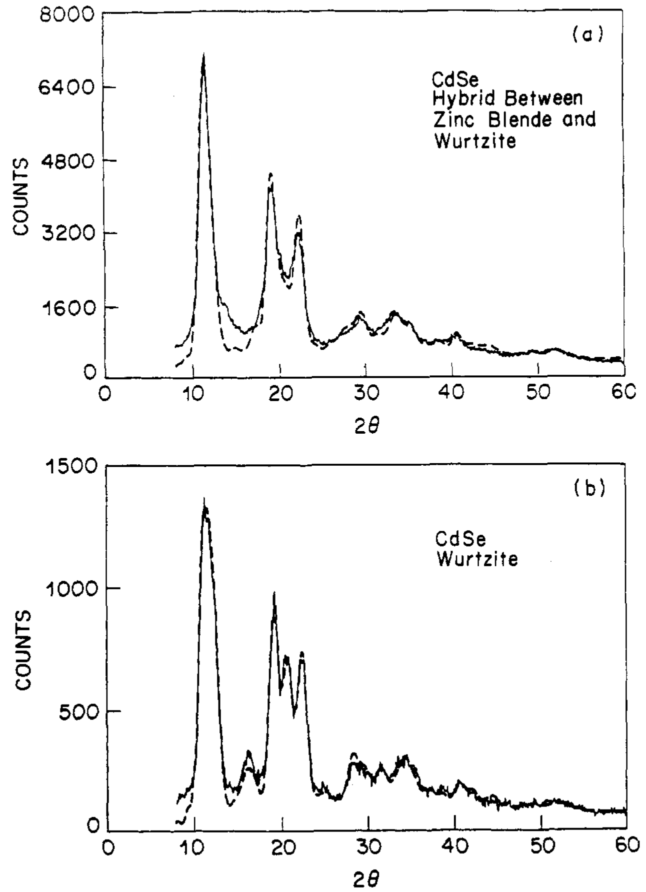

Figure 3. X-ray powder patterns of CdSe crystallites from ref 19.

as well as the III–V compound InP.[18b] This process allows high-temperature reactions, an important feature for III–V materials which do not crystallize well at room temperature. Large clusters can also be grown from small clusters by heating in coordinating solvents, such as pyridines and phosphines.[19] This high-temperature method improves the internal crystallinity of the clusters.

These large clusters have the molecular weights of smaller proteins, yet typically are far more dense, rigid, and electronically polarizable. Proteins are structurally best characterized by X-ray analysis following crystallization. While remarkable small CdS-type capped species prepared by Dance[20] have been crystallized, crystals of large clusters such as ours have not been reported. (The presence of isomers and a distribution in sizes hinder crystallization.) In the absence of crystallization, transmission electron microscopy is the most valuable characterization technique. The size and shape of the inorganic core, as well as the symmetry of the internal lattice, can be directly imaged crystallite by crystallite, as shown in Figure 2.

Bragg powder patterns are sensitive to certain aspects of structure.[19] Figure 3 shows X-ray powder patterns from two different syntheses of approximately 35 Å diameter capped CdSe crystallites. Bulk CdSe exhibits two crystalline structures, zinc blende and wurtzite, each having tetrahedral coordination about each atom. One pattern is that of wurtzite crystallites. The line widths are due to the finite size of the crystallite. The second pattern is neither zinc blende nor wurtzite. It corresponds to polytype crystallites in which the atomic packing alternates randomly between the two ideal structures.

Powder patterns reveal *average* long-range structure, but are blind to local deviations (either random or systematic) about the average, such as those that would occur because of surface reconstruction.[19] Therefore measurements such as NMR and EXAFS, which probe *local* structure and chemical shift, are valuable. ^{77}Se NMR spectra of CdSe crystallites as a function of size show two absorptions: a line at the bulk resonance position, assigned to internal Se atoms in clusters, and a broader line shifted upfield.[21] This line is assigned to near-surface Se; the upfield shift is thought to reflect a decreased Ramsey paramagnetic shift for near-surface atoms and for smaller crystallites. Selenium EXAFS measurements yield the net Cd coordination seen by Se in the cluster: it is lower than 4 because of the surface structure.[22]

Biosynthesis of Large Clusters. In 1989 it was discovered that certain yeasts, when exposed to Cd^{2+} ion in the growth medium, begin to synthesize both short peptides rich in cysteine and sulfide ion.[23] The peptides complex intracellular Cd^{2+} and incorporate sulfide to grow CdS particles with Cd^{2+}-rich surfaces complexed by the peptides. These particles were isolated and characterized. The inorganic diameter is about 20 Å, corresponding ideally to the cluster (CdS)$_{85}$-cap.

The cluster biological function in these yeasts appears to be detoxification by sequestering of Cd^{2+}. Nevertheless, there may be organisms that use such larger semiconductor clusters for redox[24] and/or photosynthetic purposes. (In nanometer-sized clusters, an extra electron becomes a stronger reducing agent as size decreases.[6]) Many microscopic organisms on earth are not yet biochemically characterized.

Elementary Molecular Orbital Theory[1-4]

In Si$_n$ (Figure 1) there are two doubly occupied bonding MOs and two empty antibonding MOs per atom. New orbitals are created near the (diatomic) σ and σ^* energies and move toward the band edges as size increases.[3] The HOMO asymptotically approaches the valence-band upper edge from below, and the LUMO approaches the conduction-band lower edge from above. This increase in the "band gap" with decreasing size led to the discovery of the cluster quantum size electronic effect in 45 Å diameter CdS crystallites in 1983.[6]

In a Hückel or "tight-binding" MO structure formed from repeating units, the shift of discrete MOs from the limiting band edge varies quadratically with dimension and linearly with resonance integral. The eigenvalues are mathematically equivalent to those of a "particle in a box" calculation, *if* the electron is assigned an "effective mass" that is inversely proportional to the resonance integral. In a semiconductor, there are a "hole effective mass" that applies to the top few levels

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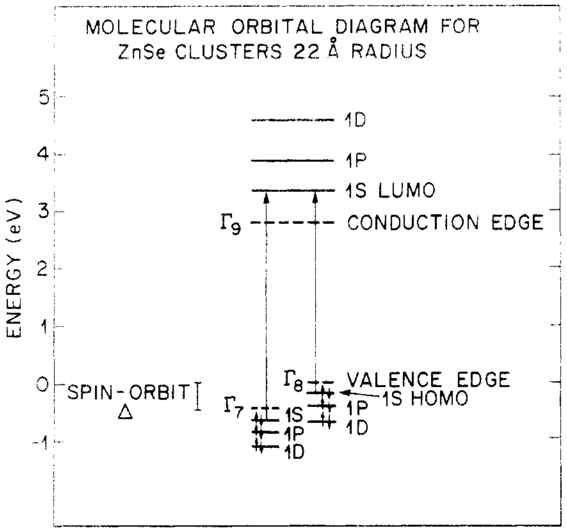

Figure 4. Molecular orbital diagram for ZnSe crystallite from ref 26.

of the valence band and an "electron effective mass" that applies to the bottom few levels of the conduction band. These effective masses are well characterized as they also govern dynamics in bulk crystals. $\hat{H}$ is a model Hamiltonian in which the orbital effects look like kinetic energies:[25]

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\epsilon|r_e - r_h|} \qquad (1)$$

The third term is the (shielded) Coulombic attraction between the electron and hole; it introduces (relatively weak) electron–hole correlation for intermediate-sized crystallites.

$\hat{H}$ describes mobile electrons and holes and yields Bloch (band) eigenfunctions in infinite crystals. It also correctly predicts the hybrid molecular–solid-state electronic structures of "quantum well" thin films. In small crystallites, an entirely discrete MO structure is predicted.[25] For example, the MO structure of a 45 Å diameter ZnSe spherical crystallite is shown in Figure 4.[26] There are radial and angular quantum numbers N and L, and allowed optical transitions obey $\Delta N = 0$ and $\Delta L = 0$. These rules conserve the number of nodes and are equivalent to the $\Delta k = 0$ rule for allowed transitions in bulk crystals.

The theoretical size dependence of the lowest excited state of four different semiconductors is shown in Figure 5. These curves can be approximated by[25]

$$E(R) = E_g + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\epsilon R} \qquad (2)$$

where m_e and m_h are the effective masses and ϵ is the bulk optical dielectric coefficient. For every material, there is a diameter where the negative Coulombic attraction is balanced by the positive kinetic energy. In CdS this occurs at about a 70-Å diameter, where each term is about 0.1 eV. This expression fails at large diameters, where electron-hole correlation becomes dominant.[27] This model is quite elementary[28] and ignores two important effects in real crystallites: coupling of electronic states to vibrations, and the structure of the crystallite surface.

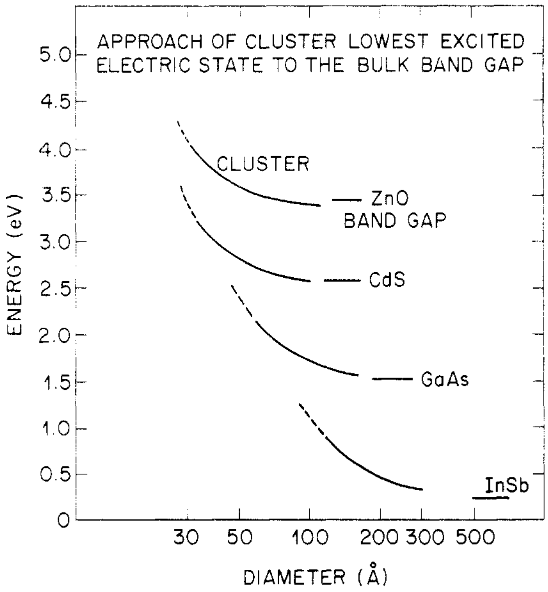

Figure 5. Predicted size dependence of lowest excited state, from ref 25.

Coupling to vibrations is modest in bulk crystals: this is a technologically important fact as weak coupling implies high electron and hole mobility. However, in small clusters, the electron and hole are delocalized over fewer atoms and therefore coupling to vibrations could be stronger.[29] That is, excited electronic state geometries might be different from ground-state geometries.

The chemistry of semiconductors influences surface structure. On a nonpolar surface of a zinc blende semiconductor, the surface distorts ("reconstructs") so that a lone pair on a surface anion forms a dative bond to a surface cation.[30] Substantial anion displacements occur, and the surface-localized optical transition associated with this bond is predicted to lie at high energy, resonant with internal band optical transitions. In small crystallites, this reconstruction should have little effect on the internal MOs (Figure 4), which have nodes on the surface. Surface-localized optical absorptions should be important in clusters, yet they have never been identified. Nevertheless, the surface profoundly influences crystallite photophysics since electrons and holes can localize on (uncharacterized) surface sites after particle excitation (via an internal MO transition[7,31]). Surface photophysics is sensitive to surface derivatization that leaves the absorption spectrum unchanged.

Excited Electronic States of Semiconductor Clusters

The MO theory predicts a discrete, albeit possibly dense, electronic absorption spectrum. Some excited-state transitions are allowed and some forbidden under electron dipole rules. The situation is analogous to the optical spectrum of a large aromatic hydrocarbon. Actual optical spectra show substantial line broadening, as in Figure 6 for ZnSe crystallites.[26] In smaller crys-

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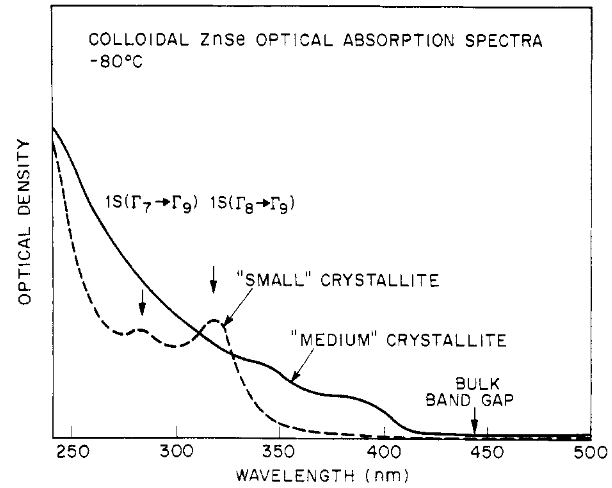

Figure 6. ZnSe crystallite optical spectra from ref 26.

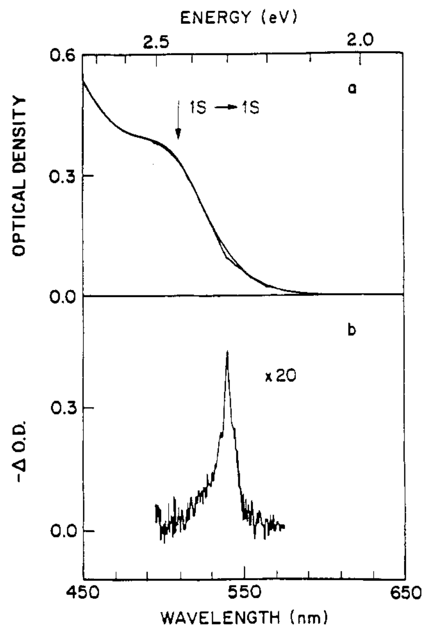

Figure 7. Hole-burning spectra from ref 32.

tallites, two discrete states are partially resolved and assigned to the two lowest allowed states in Figure 6. Higher energy absorption is intense and apparently continuous.

Why do the absorptions remain broad as they shift with size? At low temperature, the discrete transitions narrow modestly and shift further to higher energy, indicating that part of the line width reflects coupling to vibrations. Part of the line width must also come from the distribution of sizes. Assuming that a single ZnSe crystallite does have a narrow 1S–1S transition, a sample with a 15% standard deviation about an average diameter of 40 Å would have the HOMO–LUMO transition spread over an energy range of about 1500 cm^{-1} (according to eq 2).

If different species absorb at different wavelengths, then *individual* spectra can be obtained from a hole-burning experiment. Figure 7 shows the broad HOMO–LUMO transition of capped CdSe 45 Å diameter crystallites at an energy 0.5 eV higher than the bulk band gap. Excitation with a narrow laser primarily excites those crystallites whose (assumed) narrow HOMO–LUMO transition is coincident with the laser wavelength. In the absorption spectrum measured before the excited population returns to the ground state, a narrow hole is superimposed due to the missing population. Since CdSe crystallites luminesce at low temperature with lifetimes of 10^{-9}–10^{-6} s, spectral holes should be detected on this time scale.

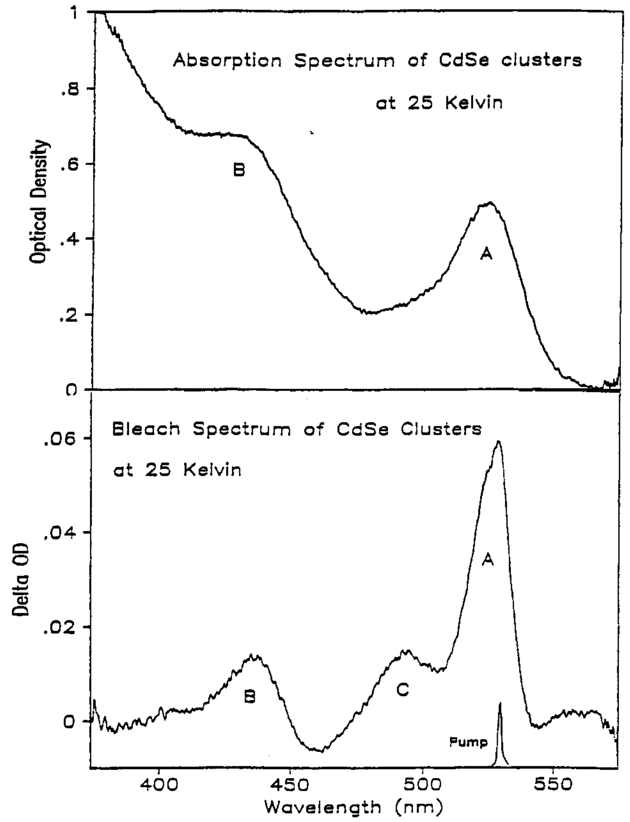

Figure 8. Hole-burning spectra of wurtzite CdSe crystallites from ref 34.

At low temperature, holes can be burned[32] (with a width of approximately 240 cm^{-1}), each having weak shoulders on both sides. The hole is the autocorrelation function of the single crystallite spectrum. The shoulder represents the (1,0) vibronic absorption band of the out-of-phase radial vibration of Se and Cd ions (an LO phonon). This mode also dominates the resonance Raman spectrum.[33] Such Franck–Condon activity implies that, in the HOMO–LUMO excited state, the equilibrium geometry changes. If the excited state is a displaced harmonic oscillator, then the excited state shift is calculated to be $\Delta = 0.7$, in units normalized to the width of the $v = 0$ wave function. The same Franck–Condon shift in bulk CdSe is $\Delta = 2.9$. That is, the excited-state coupling to this LO vibration is *far weaker* in 40 Å diameter crystallites than in the bulk crystal.[33]

This effect was predicted by Schmitt-Rink et al.[29] In the bulk crystal, the light electron orbits around the heavy hole, thereby creating a radial electrical field. However, in the crystallite, both electron and hole are in the same spatial orbital (in the elementary model), and the net electric field averages to 0. The electric field couples the excited state to the LO vibration, since LO vibration creates electric fields that extend coherently over many unit cells ("Frohlich interaction" in

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solid-state language). That fact that the coupling is smaller *but not 0* appears to imply that the hole is not in a pure 1S state.

The hole-burning technique is necessary because the sample is a mixture of different crystallites. Advances in synthesis that narrow the distribution of sizes and isomers and eliminate electron–hole recombination sites (by eliminating random defects in the structure) directly reflect themselves in an improvement in spectra and photophysics. The upper panel of Figure 8 shows the spectrum[34] of the wurtzite CdSe particles whose X-ray powder pattern appears in Figure 5. The HOMO–LUMO transition is sharper than that in Figure 7. In the hole-burning spectrum, the second lowest 1S–1S type transition and a new small peak, C, are also resolved. The HOMO–LUMO transition can be $\simeq 90\%$ bleached in Figure 8, while only $\simeq 10\%$ bleached in Figure 7. Thus the wurtzite particles *all* have nanosecond or longer excited-state lifetimes, while most of the Figure 7 particles have much shorter lifetimes, presumably due to the presence of structural defects.

In the excited state, the 1S-type (i.e., HOMO–LUMO) absorptions bleach, and there is broad transient optical absorption shifted to higher energy. The bleaching of the 1S transitions is expected for an excited state having both the electron and the hole delocalized inside the crystallite and also should occur for surface-trapped carriers.[35] The dynamics of these spectroscopic changes, together with the accompanying luminescence, reflect in some way the localization and reorganization of the wave function after optical excitation. This area of research is under active current investigation.

Conclusion and Outlook

Synthesis, characterization, and theory are now approaching the point where study of large semiconductor clusters is a quantitative branch of chemistry. The fundamental ideas involved are the same as those that underlie all of chemistry. This Account discusses recent progress, as well as present needs, either for further synthetic invention or for further physical understanding. It is especially intriguing that these large molecules combine phenomena that normally are associated with separate disciplines: surface science, solid-state physics, molecular electronic spectroscopy, and molecular synthesis.

We deeply appreciate collaboration with many colleagues whose names appear in the references. The supportive and stimulating environment within AT&T Bell Laboratories made this research possible. We are thankful to A. Lovinger and F. Padden for graciously allowing the use of electron microscope facilities.

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Role of Mass Transport in Laser-Induced Chemistry

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The use of laser light to selectively drive chemical reactions on a micron scale is an extremely rapidly evolving technology. Laser light can be used as a source of local heating on a solid surface in order to accelerate surface reactions, or alternatively it can provide radiation of an appropriate wavelength to drive a photochemical reaction in a localized region, either above or at the gas–solid interface. The ability to focus light beams to diameters on the order of microns allows the high-resolution patterning of materials, which can be useful in the fabrication of high-density microelectronic circuitry. In addition, laser technology has made an impact on many new processes because materials can be deposited or removed at lower temperatures and with higher rates than can be obtained with conventional processes.[1]

A unique aspect of driving chemical reactions in a localized region is size effects that can influence the kinetics of reaction phenomena by influencing gas-phase transport of atomic and molecular species. Mass-transport kinetics are important in photochemical and thermal deposition, etching, and cluster- or particle-formation processes. In conventional chemical vapor deposition (CVD), the overall rate of the deposition

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