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Irradiation-induced absorption edge shifts in colloidal particles of iron(II) sulfide (pyrite)

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10 ps. It is concluded that orientational effects give negligible contributions to the signal transients of Figures 2 and 3 for 10–100 ps.

The measured population lifetimes T_1 of the CH vibrations are summarized in Table II. The values for cyclohexane (solution in CCl_4) and polyethylene (solid) are also included. The polymer results in the range of 10^{-11}–10^{-10} s are very similar to those of cyclohexane and other alkanes, e.g., octane with $T_1 = 12$ ps.[16] This comparison immediately shows that the relaxation rates are not connected to the size and the total level density in the vibrational spectrum. The latter point would suggest notably shorter time constants for the polyalkenes than for the alkanes in contrast to the experimental findings. Obviously energy decay of a molecular vibration is a localized property of a small number of molecular subgroups which are coupled together, e.g., the side chains of polyalkenes.

The rising lifetime values in Table II with increasing length of the side chains are of particular interest; a similar behavior is found for alkanes with growing chain size. It was discussed recently in the literature that vibrational energy decay of several alkanes and alkenes takes place primarily through the methyl groups in these molecules.[17] The results presented here give experimental support to such an explanation for polyalkenes. The larger contribution of a CH_3 group compared to CH_2 groups may be explained considering the anharmonic coupling of the stretching vibrations to the overtones of the corresponding bending modes which also leads to the well-known effect of Fermi resonance in the vibrational spectrum. It was shown in the literature for a number of molecules containing methylene[18] or methyl[1,19] group(s) that this mechanism plays an important role to explain measured population lifetimes. Population decay via the CH_3 bending modes was experimentally verified for a few cases.[12,20,21] According to the phenomenological theory of Fendt et al., the following expression holds in the limit of weak coupling:[19]

$$T_1 \simeq NR^{-1}[\exp(\omega/\Omega)]^{2/3}T_2 \qquad (2)$$

R represents the anharmonic coupling between vibrational levels with energy mismatch $\hbar\omega$. For smaller molecules, R and ω may be deduced from spectroscopic observations. N denotes the number of initially populated levels between a quasiequilibrium is established. The parameters T_2 and Ω serve to estimate the elastic collision rate of neighboring molecules; a typical value of $\Omega \simeq 100$ cm^{-1} was estimated. T_2 is the dephasing time of the final state to which energy is transferred by the anharmonic coupling. Now, the higher frequencies of CH_3 bending modes with corresponding smaller values of the mismatch ω (see eq 2) favor population decay via the methyl groups. Since the number of levels of N involved in the vibrational bottleneck around 2900 cm^{-1} increases with the length of the side chains, larger values of T_1 are correspondingly expected in qualitative agreement with experimental findings.

In conclusion it is pointed out that fast vibrational energy redistribution and population decay is observed for polyalkenes using picosecond spectroscopy with independently tunable IR excitation and probing pulses. Comparison of the polymer data with alkanes demonstrates that the higher level density of the macromolecules in the vibrational spectrum around 2900 cm^{-1} does not accelerate the measured relaxation rates. The larger population lifetimes for increasing lengths of the polymer side chains is explained by the dominant role of methyl groups for the total decay rate in accordance with findings on other methyl and methylene compounds.

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Irradiation-Induced Absorption Edge Shifts in Colloidal Particles of FeS_2 (Pyrite)

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Colloidal ("quantum") particles (ca. 2–40 nm) of FeS_2 (pyrite) were prepared from bulk material. The absorption edges for these particles were at ca. 420 nm or 1.9 eV greater than the band-gap of the bulk material. Irradiation of these particles in MeOH causes a blue shift of about 6 nm, ascribed to generation of excess electrons in the particles, caused by population of the conduction band. A reversible 4-nm blue shift was observed in aqueous solutions under continuous irradiation.

Introduction

We extend our previous work on the effect of excess charge on the absorption spectra of small semiconductor particles[1] by studying very small (quantum or Q) particles of FeS_2 (pyrite). The blue shift observed upon irradiation of FeS_2 particles is explained in terms of an excess-charge-induced degeneracy of the semiconductor. As discussed previously,[1] and first described by Burstein[2] and others,[3-6] when a semiconductor becomes degenerate because the electron concentration has been made high enough to raise the Fermi level into its conduction band, the optical absorption edge shows a shift to higher energy. The energy necessary to excite electrons optically from the valence band to the lowest unfilled level in the conduction band will be larger than the minimum separation between the bands (the width of the forbidden energy gap, E_g, for nondegenerate semiconductors) as shown in Figure 1b. The energy of this transition, $E_{g,opt}$, is given by

$$E_{g,opt} = \hbar^2\vec{k}^2/2m_h + E_g + \hbar^2\vec{k}^2/2m_e \qquad (1)$$

where $\vec{k}$ is the wave vector, $\hbar = h/2\pi$, h is Planck's constant, and

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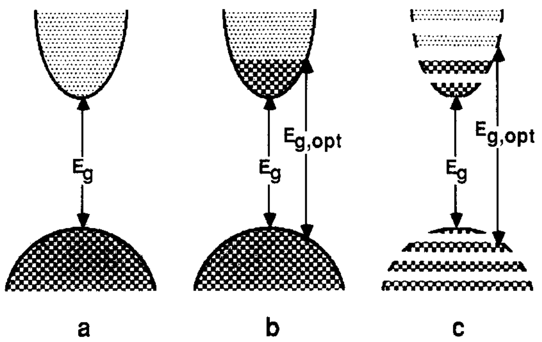

Figure 1. Schematic band energy diagrams of intrinsic (a), degenerate (b), and quantized-degenerate (c) semiconductors.

m_e and m_h are the effective masses of the electron, e^-, and hole, h^+, respectively. This equation can be written[1]

$$E_{g,opt} = E_g + (1 + m_e/m_h)(E_f - E_c - 4kT_e) \qquad (2)$$

and

$$E_f - E_c = h^2/2m_e(3n/8\pi)^{2/3} \qquad (3)$$

where k is the Boltzmann constant, T_e is the electron temperature, n is the excess electron concentration, and E_f and E_c are the energies of the Fermi level and conduction band edge, respectively. This can lead to an absorption edge shift toward shorter wavelengths, when excess electrons are generated in a particle.

Experimental Section

A colloidal dispersion of FeS_2 was prepared as follows. After 100 mg of FeS_2 powder (AESAR, 99.9% Seabrook, NH) was introduced into a test tube containing 20 mL of water, the mixture was intensively stirred for more than 6 h. The mixture was allowed to settle for about 12 h, during which time large black FeS_2 particles formed a layer on the bottom of the tube. The supernatant solution, which was colorless and transparent, contained the FeS_2 colloid used in the absorption spectrum measurements.

Colloidal FeS_2 in methanol was prepared in a similar manner. Nitrogen was bubbled through the solution held in a sealed quartz cell for about 1 h to remove oxygen before the measurement of the absorption spectrum. To observe the photoinduced charge effect for MeOH solutions, the solution was illuminated with a 1000-W xenon/mercury lamp (operated at 700 W) for about 5 min. A water bath with a length of 11 cm was placed between the lamp and the solution to remove infrared heat. The absorbance before and after this irradiation was measured with an HP Model 8451 diode array spectrophotometer.

The absorption measurements of FeS_2 in water were carried out with an HP Model 8450 UV/vis spectrophotometer (Hewlett-Packard, Palo Alto, CA); a 1000-W quartz tungsten–halogen lamp was used as an additional light source for simultaneous irradiation in this experiment. Detailed procedures were described previously.[1]

Dilution of the solution containing FeS_2 particles showed that the absorbance was linearly proportional to the concentration, which is consistent with the Beer–Lambert law. Because we do not know the molar absorptivity of these particles, we could not determine the concentration. Thus, we only describe a qualitative correlation between irradiation and blue shift.

The X-ray diffraction spectrum showed that the FeS_2 powder used was in the pyrite form. The particle size distribution extended from radii of about 2 to 40 nm as determined by transmission electron microscopy (TEM). Energy dispersive X-ray spectroscopy (EDS) of these particles showed an approximately 1:2 ratio of Fe to sulfur in atomic concentrations. The samples for TEM were prepared by dropping a drop of methanol solution containing FeS_2 particles through the holey carbon-supported copper grids, which were placed over tissue paper.

FeS_2 films (ca. 1.5 μm thick) were prepared by evaporating FeS_2 powder onto glass substrates in a vacuum chamber (ca. 1.5 $\times 10^{-6}$ Torr).

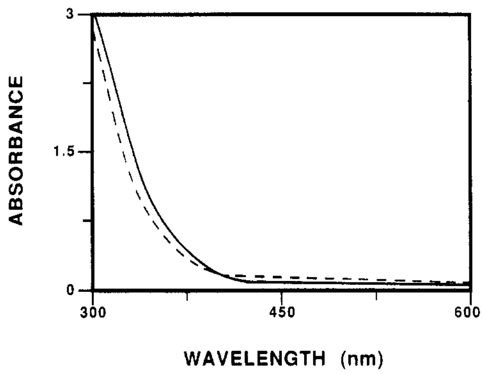

Figure 2. Absorption spectra of FeS_2 (pyrite) particles in methanol (—) before and (---) after irradiation with 1000-W Xe lamp.

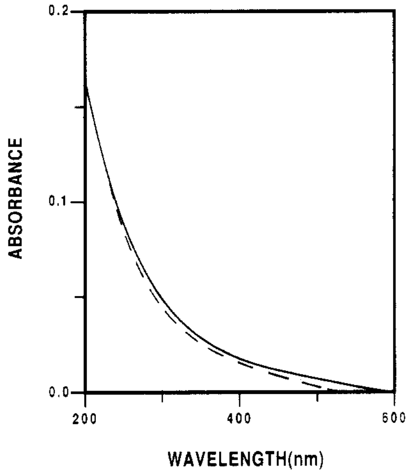

Figure 3. Absorption spectra of FeS_2 (pyrite) particles in water (---) with and (—) without simultaneous irradiation with a tungsten–halogen lamp.

Results and Discussion

FeS_2 (pyrite) crystallizes in the cubic (sodium chloride) structure, where each iron atom is octahedrally coordinated to sulfur with the anion sites occupied by S_2^{2-} ions.[7] The d states of the iron atoms split in the octahedral crystal field of the S_2^{2-} ions to form bonding and antibonding levels corresponding to the valence and conduction bands, respectively.[8-11] Present knowledge of the semiconducting properties of FeS_2 (pyrite) is limited. The reported value for the energy gap of bulk FeS_2 is about 1 ± 0.2 eV.[11-20]

The absorption edges of our FeS_2 films were at ca. 1140 nm corresponding to an energy gap of ca. 1.1 eV. Compared to bulk FeS_2, a blue shift of about 1.9 eV was observed for the absorption edge of the small semiconductor particles suspended in both methanol and water, as shown in Figures 2 and 3. There are at

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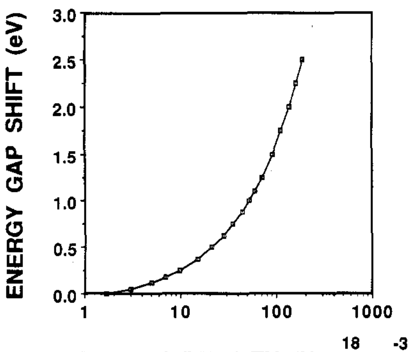

Figure 4. Dependence of the optical energy gap shift on excess charge-carrier density in FeS_2 (pyrite) particles.

least two effects that can cause an absorption edge shift to the blue in semiconductors. (1) The quantum size effect.[21] This is based on the fact that the very small particles have an orbital structure that is closer to that of the discrete atomic energy levels of individual atoms than to that of the bulk material where the orbitals have merged into bands. A simple "particle-in-a-box" model has been proposed to describe the shift of the optical absorption edge to the blue as the semiconductor particle size decreases,[21] i.e., that the energy band spacing increases as the semiconductor particles become very small. The reported blue shifts can be as large as 2.8 eV,[22] and the size region of Q particles varies from different materials. For example, the diameters of CdS Q particles are less than 50 Å, but the Q particle diameters are hundreds of angstroms for the smaller band-gap material PbS.[23] For the FeS_2 (pyrite) semiconductor particles considered here, the increased band-gap observed can probably be explained, at least partially, by such a particle size effect. (2) The excess charge effect.[1,2] An excess-charge-induced absorption edge shift was observed in FeS_2 particles as shown in Figure 2. In this experiment, FeS_2 particles were suspended in MeOH, which acted as a sacrificial electron donor. After irradiation of the solution for 5 min with the 1000-W Xe lamp, the absorption edge shifted to shorter wavelengths by about 6 nm. We ascribe the shift to the presence of excess photogenerated electrons in the semiconductor particle that build up under irradiation as photogenerated holes react with MeOH. Note that the shifts shown in Figure 2 became only slightly stronger on further illumination, indicating that the rate of scavenging of holes by MeOH becomes smaller than that of e^-/h^+ recombination as excess electrons accumulate in the conduction band. The absorption spectra revert to the original ones after the irradiated sample is exposed to air, suggesting that the excess electrons stored in the semiconductor particles are responsible for the absorption edge shift and can react with oxygen. Note that the excess electrons produced in the particles have a long lifetime, as observed for other colloidal semiconductor systems under irradiation in the presence of sacrificial agents.[24-27] The rate of buildup of this excess charge is primarily governed by the rates of interfacial charge-transfer processes (hole transfer to MeOH, electron transfer to intermediates) and the rate of decay of intermediates.

A similar steady-state shift of irradiated FeS_2 particles was seen in water. In this case, additional steady tungsten–halogen lamp irradiation was employed during the measurement of the absorption spectra. An absorption edge shift of about 4 nm was observed under irradiation, as shown in Figure 3. Note that the two curves differ only in the absorption edge region. The shift was reversible, and the original spectrum was regenerated when the irradiation source was removed, suggesting that formation and removal of excess electrons in the excited states of FeS_2 caused the absorption edge shift. Similar results were also found in other semiconductor particles, such as CdS,[1,24,25,28] CdO,[26] In_2O_3,[26] ZnO,[27,29] and TiO_2.[30] Excess-charge-induced absorption edge shifts have been observed not only on small semiconductor particles but also on bulk materials, such as indium antimonide. Here an absorption edge for an n-type sample containing 5×10^{18} electrons/cm^3 lies at 3.2 μm, compared to that of an intrinsic sample at 7.2 μm.[2-5]

Since comparable shifts can be observed in both small particles and bulk semiconductors, there is no reason to focus just on particle size when a blue shift is discussed. Clearly, the generation of a higher density of excess electrons (or holes) by irradiation is easier, however, as the particle size decreases. The theoretical dependence of optical energy gap shift, ΔE, on charge-carrier density for FeS_2 (pyrite) bulk material is given in Figure 4 (calculated for $m_e = 0.05m_o$, $m_h = 0.52m_o$,[31] where m_o is the free electron mass). A critical electron density n_{crit} of 1.7×10^{18}/cm^3 is obtained. Therefore, $E_{g,opt}$ should be equal to E_g when the electron density is smaller than n_{crit} and approximately equal to that given by eq 2 when the electron density is larger than n_{crit}. For example, a 1.6-eV optical energy gap increase can be obtained for the n-type sample containing 9.9×10^{19} electrons/cm^3. In other words, only three excess electrons are sufficient for a FeS_2 particle with a diameter of 40 Å to produce this shift. One must note, however, that additional effects, e.g., the trapping of charge in surface states, can also be important.

Note also that although the calculations assume excess charge within the band structure of the bulk material, a more exact calculation would take account of the quantum size effect and the formation of discrete energy levels as the particle size decreases. Qualitatively, under these conditions, an even smaller number of excess charges would be able to cause a sizable blue shift, as suggested in Figure 1c. We should also mention an alternative model that predicts a charge-induced band-gap shift,[32] where a trapped electron on the particle surface causes a polarization of the exciton wave function within the particle, as well as a recent paper confirming a band-filling (Burstein-shift) approach.[33]

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