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change in structure O/W \rightarrow bicontinuous \rightarrow W/O has been noted for a few cases. However, the present system is of a novel and interesting type in that the changeover takes place at a constant temperature requiring only a minor modification in the surfactant composition. In Figure 2 should be noted the lack of symmetry in the D_O and D_W curves vs solvent composition, D_W being lower than D_O at high volume fraction of the solvent component and higher at low volume fraction. Such a behavior is strongly indicating a stronger solvation of the surfactant by water than by oil.

We have above only considered that a minor change in surfactant properties can give microemulsions at a very broad range of solvent compositions, but we have not analyzed microstructure in terms of surfactant properties. However, this is the key issue for the understanding of organized surfactant solutions and for the development of efficient surfactants. In Figure 3 we have, therefore, replotted the relative self-diffusion coefficients of water and oil as a function of composition of the surfactant mixture. The surfactant is balanced at ca. 29 wt % of the nonionic component. Decreasing this figure by only ca. 1% unit makes the

surfactant hydrophilic, and the microstructure is one of oil droplets in water; a small increase in the nonionic component conversely makes the surfactant lipophilic, and there are water droplets in oil. While in the present system the surfactant properties are determined by the ratio of nonionic-to-ionic components, the temperature is the critical factor for the oligo(ethylene oxide) alkyl ethers. The similarity is striking between Figure 3 and Figure 4, where we have plotted the self-diffusion data of ref 16 for the main microemulsion region of the system water/ $C_{12}H_{25}-(OCH_2CH_2)_5OH$ /tetradecane as a function of temperature; for the same change in HLB a change by 30 °C in the nonionic system corresponds to a change in the mole fraction of the present system by 0.02. The change of this nonionic surfactant from hydrophilic at lower temperature to lipophilic at higher temperature has recently been discussed in terms of a temperature-dependent conformation of the EO chains.^{41,42}

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Photochemistry of Colloidal Semiconductors. 26. Photoelectron Emission from CdS Particles and Related Chemical Effects

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Laser illumination of small CdS particles in aqueous solution leads to the formation of hydrated electrons, which are detected by their strong absorption. The yield increases with decreasing particle size. The maximum quantum yield observed is 0.07 electrons emitted per photon absorbed. At the highest laser intensities applied, five electrons are emitted from one colloidal particle. The absorption of the remaining holes is also observed. The emitted electrons react with colloidal particles in solution. During the laser flash a strong bleaching signal, attributed to the electrons generated in the particles, is recorded shortly below the onset of absorption. With knowledge of the specific absorbance, the stationary concentration of electrons on the particles during the laser flash is calculated. These effects are studied at various laser intensities. The following conclusions are drawn: (1) the specific rate of recombination of charge carriers increases at high intensities; (2) positive holes cannot be accumulated on the colloidal particles; (3) photoelectron emission is a process in which two photons are involved. They create two excited states (electron-hole pairs), the subsequent interaction between which results in electron emission.

Introduction

When colloidal solutions of cadmium sulfide are exposed to the light of a laser flash or of a xenon lamp, chemical changes occur that can be detected by recording the accompanying optical absorptions. The first observations were made in one of the first papers of this series, where it was found that electrons could be emitted into the aqueous solvent.^{1,2} This process is described here in more detail after more refined detection techniques and improved methods of colloidal preparation became available.³ The colloidal particles in the present work were rather small, i.e., they had a diameter comparable to or even substantially smaller than

the 5-nm diameter of an exciton in macrocrystalline CdS. During the laser flash, several photons are absorbed in one colloidal particle. It is shown here that more than one excitonic state cannot be contained in such small CdS particles as the states react with each other. Photoelectron emission is a consequence of the generation of more than one excitonic state in a particle. Other effects of the excitonic states in small CdS particles, which are often called "size quantization effects", have been described during the past few years.⁴

In the second flash photolysis study on CdS, which was reported by Albery and co-workers, it was observed that the absorption of CdS close to the absorption edge was slightly decreased after

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(3) Reference 1 contains two errors. The mean particle size was 10 times smaller, i.e., 3.7 nm. The laser dose was 3 times greater, which means that the hydrated electron yield was smaller by a factor of 3.

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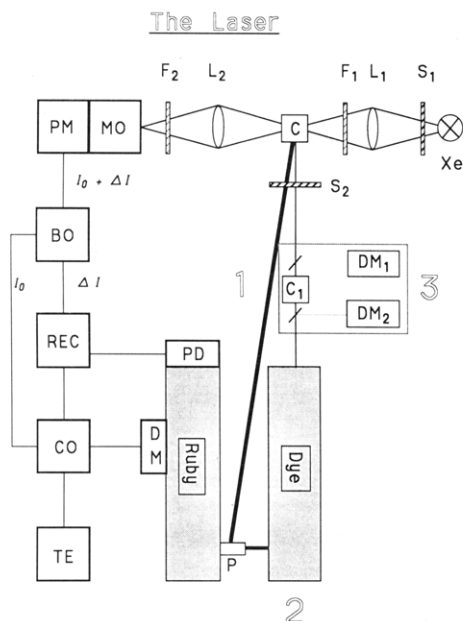


Figure 1. Laser illumination setup.

the flash, and this effect was attributed to the presence of long-lived excess electrons on the colloidal particles.⁵ A pulse radiolysis study yielded more quantitative information about the effect of excess electrons.⁶ In these experiments, hydrated electrons were generated, and their reaction with CdS particles was observed. The maximum bleaching, caused by just one excess electron, occurred with a negative absorption coefficient of $5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which indicated that the excess electron influenced an optical transition where the wave function of the excited state extended over the whole particle. Bleaching and photoelectron emission are related as is shown in the present paper.

In another pulse radiolysis study it was found that trapped positive holes in CdS produced a broad absorption in the visible region.⁷ This absorption can also be seen in flash photolysis. Bleaching and absorption effects have also been observed in the flash photolysis of CdS and CdSe in acetonitrile⁸ and of Cd_3P_2 in aqueous solution.⁹

Experimental Section

The Laser System. For the present studies two laser systems were used: a frequency-doubled ruby-dye laser and an excimer laser. The ruby-dye system, shown in Figure 1, could be used in three variations:

Variation 1. The 20-ns light pulse of 347 nm and energy of up to 250 mJ from a frequency-doubled ruby laser (oscillator-amplifier system from JK-Lasers, System 2000) was adjusted by prism P directly into the flow cell C, which was rinsed by fresh solution. The laser illuminated a cell volume of about 500 μL . The path length of the cell was 1 cm in the direction of the probe light. The probe light consisted of a 450-W high-pressure xenon lamp, a shutter S_1 , quartz lenses L_1 and L_2 , optical filters F_1 and F_2 , and a monochromator MO with a photomultiplier PM (R 928, Hamamatsu). Optionally the xenon lamp could be pulsed for 3 ms to a light intensity 100 times higher than in the constant burning operation. At 100 μs before the laser pulse the current of the PM was measured and compensated by a backoff circuit BO.¹⁰ The value of I_0 was sent to the computer CO (Digital

Micro PDP) and used for the calculation of the optical densities. The compensated signal ΔI was analyzed by transient recorders REC (Tektronics 7612 7D 20, or 7912 AD), which were triggered either by delay generators or by a photodiode PD attached to the ruby laser. Each shot of the laser dose was measured by a dose monitor DM (fast integrating photodiode). Data processing and trigger control were done by the computer CO via the terminal TE. Signal averaging was applied for each measurement. By closing shutters S_1 or S_2 before every second pulse and subtracting this signal from the former one, we corrected the averaged decay curves for base-line drift of the xenon lamp or for the fluorescence of the sample, respectively.

Actinometry was carried out at low laser doses with an argon-flushed solution of $3 \times 10^{-3} \text{ M}$ benzophenone, $1 \times 10^{-3} \text{ M}$ methylviologen (MV^{2+}) in 2-propanol-water (1:3) by measuring the methylviologen radical absorption at 605 nm and taking a quantum yield of 2 and $\epsilon(605 \text{ nm}) = 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$.

Variation 2. By removal of prism P, the 347-nm laser pulse was no longer focused into the cell C but was used to pump a dye laser (JK-Lasers, System 2000). Pulse energies of about 30 mJ were obtained in the wavelength region from 380 to 520 nm. The dye laser pulse was focused to the same cell position C as in setup 1. In this case dose monitoring occurred at the dye laser (not shown in Figure 1). The rest of the setup was the same as described under variation 1.

Variation 3. For measurement of an absorption spectrum of the sample under high intense light conditions, arrangement 3 was adjusted into the dye laser beam. It presents, in principle, a single-beam spectrophotometer. The dose monitor DM_2 in combination with a beam splitter (quartz plate) measured the intensity of the incident laser beam before the probe cell C_1 ; DM_1 measured the intensity behind the cell. The dose monitors were calibrated relative to each other by filling C_1 with water and measuring various laser intensities by each instrument. After this procedure the optical densities of the investigated samples could be calculated easily.

The excimer laser system was analogous to the ruby laser system described under variation 1. An EMG 201 MSC laser from Lambda Physics was used as the excitation light source (308 nm, pulse energy 400 mJ, pulse duration 30 ns). High light intensities were obtained by focusing the laser beam with a 500-mm quartz lens to a cell volume of about 200 μL (optical path length 1 cm in the probe light direction), and lower intensities by setting optical filters into the laser beam.

Decay curves obtained with laser photon concentrations below $5 \times 10^{-5} \text{ M}$ were measured by using a flow cell with a 10-cm path length in the probe light direction and a cylindrical quartz lens positioned in the laser beam. The latter gave a homogeneously illuminated area of $1.5 \times 10 \text{ cm}^2$ at the side face of the cell.

Actinometry was carried out at low laser doses with solutions of $(1-5) \times 10^{-4} \text{ M}$ anthracene in argon-flushed cyclohexane by measuring the triplet signal (quantum yield 0.72, $\epsilon(420 \text{ nm}) = 64\,700 \text{ M}^{-1} \text{ cm}^{-1}$).

Absorption Spectra. Absorption spectra were recorded with a Shimadzu UV 260 double-beam spectrophotometer, with water in the reference cell.

Preparation of the Colloidal Solutions. Two solutions of colloidal CdS were used. Sol A contained relatively big particles of 3–5-nm diameter. This solution was yellow-green and did not contain excess Cd^{2+} ions. Its absorption started between 490 and 510 nm, depending on the batch. Sol B contained Q particles, i.e., particles showing size quantization effects, the diameter being 1.5–2.0 nm. This solution was colorless. It contained excess Cd^{2+} ions.

Preparation of Sol A. The sol was prepared in a 2-L three-neck flask fitted with a septum, pH electrode, and gas inlet. After the aqueous solution of $5 \times 10^{-5} \text{ M}$ sodium polyphosphate ($\text{Na}_{17}\text{P}_{15}\text{O}_{46}$, MW = 1592, from Sigma) and $5 \times 10^{-4} \text{ M}$ Cd(ClO_4)₂ had been bubbled free from dissolved CO_2 and O_2 with pure argon, the pH was adjusted to 9.5 with 1 M NaOH (stable

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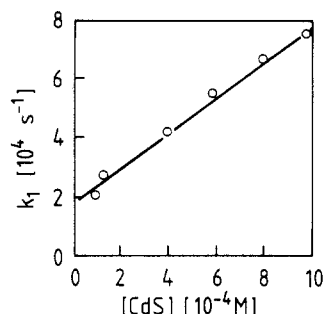


Figure 2. Pseudo-first-order rate constant of the decay of the 700-nm e_{aq}^- absorption as a function of CdS concentration. The solutions were made by diluting a stock solution of 1×10^{-3} M CdS with polyphosphate solution of pH 9.5.

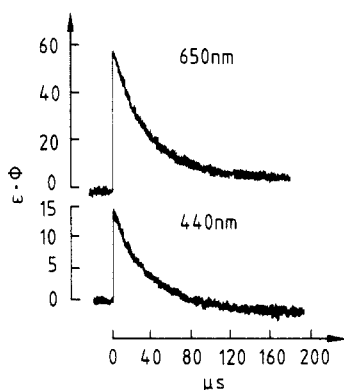


Figure 3. Decay of the e_{aq}^- absorption at two wavelengths (ϵ = absorption coefficient, ϕ = quantum yield).

colloids with higher CdS concentration can be prepared by using 1×10^{-3} M $\text{Cd}(\text{ClO}_4)_2$ and 1.5×10^{-4} M polyphosphate). Under a weak negative pressure, a stoichiometric quantity of H_2S was injected through the septum into the free volume above the stirred solution. As soon as the pH fell below 7.5, NaOH was added until the pH again attained 9.5. The solution was then stirred until a constant pH was obtained. Finally, the pH was adjusted to the required value, and Ar passed through the colloidal solution for 20 min to remove last traces of oxygen. The solution was aged overnight before use.

Preparation of Sol B. A solution containing 4×10^{-4} M $\text{Cd}(\text{ClO}_4)_2$ and 3×10^{-4} M sodium hexametaphosphate and having pH 9.0 was bubbled under the above conditions with argon. (The commercial sodium hexametaphosphate (Riedel de Haen) consists of polyphosphates of different chain lengths up to 450. The molarity refers to the formula $(\text{NaPO}_3)_6$.) H_2S (2×10^{-4} M) was injected into the gas phase above the solution, and the flask shaken vigorously. As soon as the pH fell below 6.0, 0.1 M NaOH was added until the pH was 10. The solution was bubbled again with argon for 20 min. The CdS particles were always negatively charged as was shown by experiments on their migration in an electric field.

Results

Photoelectron Emission. As in the previous studies,¹ it was observed that the absorption of the hydrated electron was present immediately after the laser flash. The absorption decayed in the 10- μs range, the half-life depending on the CdS concentration. Figure 2 shows the pseudo-first-order rate constant k_1 as a function of the CdS concentration. In the absence of the colloid, the half-life of the hydrated electron was 36 μs or $k_1 = 1.9 \times 10^4 \text{ s}^{-1}$ as measured by pulse radiolysis. In the presence of CdS, larger values of k_1 were observed, which indicates that the emitted electrons reacted with the CdS particles. Typical curves of the decay of the absorption of the emitted electrons are shown in Figure 3. Note that the absorption signal often did not return to zero at longer times. At wavelengths where CdS itself absorbs, one could find a negative signal at longer times, i.e., bleaching

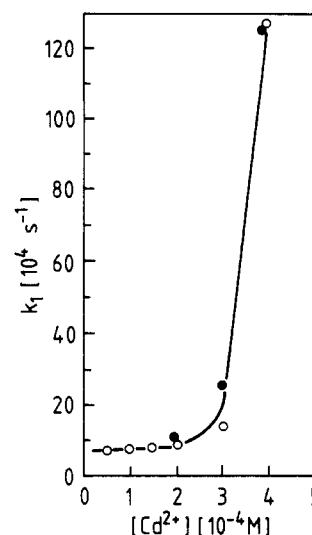


Figure 4. Pseudo-first-order rate constant of the disappearance of e_{aq}^- (O) and appearance of Cd^+ (●) in solutions of different Cd^{2+} concentrations; sol A, pH 9.5.

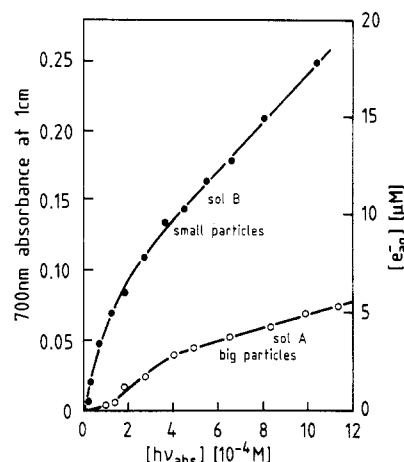


Figure 5. 700-nm absorption and e_{aq}^- concentration as functions of the absorbed laser dose.

of CdS, and at longer wavelengths a positive rest absorption was found. In the presence of substances such as acetone, nitrate, and Cd^{2+} ions, which are known to react rapidly with hydrated electrons, the absorption of e_{aq}^- decayed much faster after the flash. The bimolecular rate constants derived from these decays were in agreement with the authentic ones.¹¹ In the case of Cd^{2+} , the absorption of Cd^+ ($\lambda_{\text{max}} = 300 \text{ nm}$) built up concomitantly with the decay of e_{aq}^- . Figure 4 shows the pseudo-first-order rate constant as a function of the Cd^{2+} concentration. It can be seen that no reaction of e_{aq}^- with Cd^{2+} took place in the concentration range up to about 3×10^{-4} M, the reason lying in the fact that the Cd^{2+} ions are strongly bound to the polyphosphate stabilizer and, in this state, show little reactivity toward e_{aq}^- . Above about 3×10^{-4} M almost all the binding sites on the polyphosphate chains are occupied, so that additional Cd^{2+} can react with e_{aq}^- in homogeneous solution.

In Figure 5, the 700-nm absorption immediately after the laser flash is plotted versus the laser dose, the latter being expressed as concentration of absorbed photons. On the right-hand side one finds the concentration of hydrated electrons formed. This concentration was calculated from the observed 700-nm absorption corrected for the absorption by the hole (the latter obtained after the decay of e_{aq}^- was completed or by using a solution containing 10^{-7} M acetone as e_{aq}^- scavenger) and by use of the well-known absorption coefficient of $1.5 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ of e_{aq}^- . The yields

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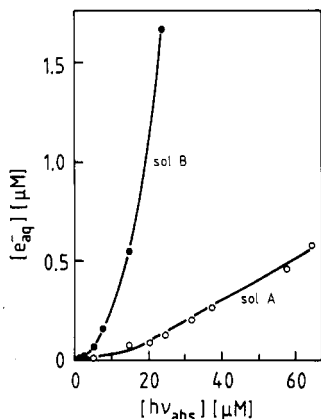


Figure 6. Concentration of emitted electrons at low laser doses.

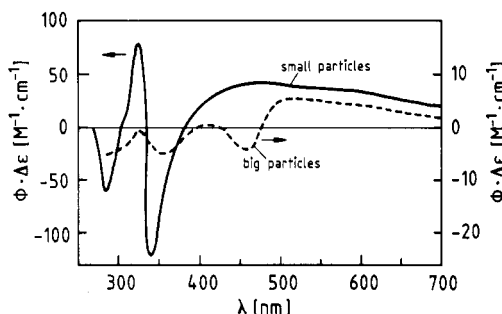


Figure 7. Difference spectra of sols A and B at 100 μ s after the laser flash.

are substantially higher for sol B, which contained smaller particles than did sol A. At the highest doses used, each colloidal particle absorbed many hundred photons during the flash. Figure 6 shows the curves at low doses on an enlarged scale. It is recognized that the e_{aq}^- concentration initially did not increase proportionally to the laser dose but increased faster. This indicates that the photoelectron emission from CdS particles is not a single-photon event but requires more than one photon. At the higher doses, up to about 2×10^{-4} M absorbed photons in the case of sol B and about 4×10^{-4} M in the case of sol A, the e_{aq}^- concentration increased linearly with dose. In this range, the quantum yield for sol B was 0.07 electrons emitted per photon absorbed, and it was about 10 times lower for sol A. At still higher doses the curves bent over into a second linear range. This complex relation between concentration of emitted electrons and dose of absorbed photons indicates that the mechanism of photoelectron emission changes with dose, competing processes taking place more successfully at higher doses. This aspect will be discussed further after we described the accompanying bleaching effects.

The yield of hydrated electrons in sol A was also determined at much longer wavelengths of the dye laser (operational mode 2 in Figure 1). The absorbed photon concentrations were close to 3×10^{-5} M, i.e., in the range where the e_{aq}^- yield increased linearly with dose in Figure 8. At 420 nm, the quantum yield was the same as at 347 nm, while it was half as great at 480 nm. The yield at 480 nm is only apparently lower. It was calculated by using the 480-nm absorbance of the solution as measured in a conventional spectrophotometer. However, as shown below, the absorbance at this wavelength decreases upon laser illumination (nonlinear optical effect, Figure 10), i.e., less light was absorbed than assumed in the calculation.

As in the previous studies,¹ it was observed that excess NaSH in sol A increased the yield of hydrated electrons by 30%. Above 3×10^{-3} M NaSH no further increase took place.

Bleaching and Absorption Effects after the Flash. Figure 7 shows the difference spectra of the two CdS solutions at 100 μ s after the 347-nm laser flash. The solutions contained 10^{-2} M acetone to scavenge the emitted electrons within less than 10^{-7} s. The observed changes in absorption are due to changes in the colloidal particles, as the product of the reaction of e_{aq}^- with

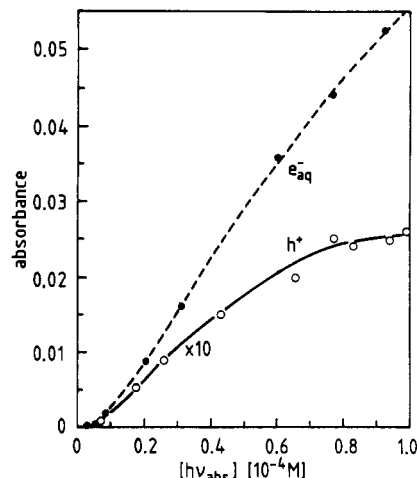


Figure 8. 700-nm absorption of e_{aq}^- (determined immediately after the flash in the absence of acetone) and 700-nm absorption of h^+ (determined at 100 μ s after the flash in the presence of 10^{-2} M acetone) as functions of the laser dose.

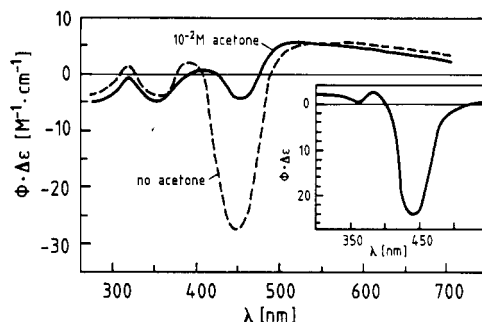


Figure 9. Spectra of sol A at 100 μ s after the flash in the absence and presence of 10^{-2} M acetone. Inset: Difference of the spectra in the main part of figure.

acetone has negligible absorption. Note that the difference spectrum of sol A, which contained the bigger particles, is shown on a 5 times more expanded ordinate scale. One recognizes in both spectra a broad absorption band at longer wavelengths. This band extends in the case of sol B, which contained small particles, to shorter wavelengths. The absorptions were present immediately after the flash and did not decay in the observed time range of 500 μ s. A comparison with Figure 1 in ref 7 tells that the absorptions are the same as those produced in the reaction of OH radicals with CdS particles. This reaction leads to surface-trapped positive holes.⁷ One should expect that the number of positive holes generated is equal to the number of electrons emitted. Figure 8 shows how the hole absorption depended on the laser dose. The figure also contains the absorption of hydrated electrons as measured in the absence of acetone in the solution. While the hole absorption reaches a limiting value at relatively small doses, that of the electron continues to increase. In the presence of 4×10^{-4} M NaSH in sol A the hole absorption was increased by 40%, which corresponds to the increased yield in e_{aq}^- mentioned above.

The oscillatory behavior at shorter wavelengths in the spectra in Figure 7 was also observed in the previous studies on hole injection by OH radicals.⁷ The effect is more pronounced for the small particles. As pointed out in the previous work, oscillations in the difference spectrum occur when the transient product of reaction has a spectrum that is slightly blue-shifted with respect to the spectrum of the particles before reaction. Similarly, the bleaching around 460 nm in sol A in Figure 7 was also observed in the case of hole injection by radicals.⁷ Sol A was also flashed in the absence of acetone, the spectrum measured at 100 μ s after the flash when the hydrated electron absorption had completely decayed. Figure 9 shows this spectrum. For comparison, the spectrum in the presence of acetone is also shown. The spectrum in the absence of acetone possesses a much stronger bleaching

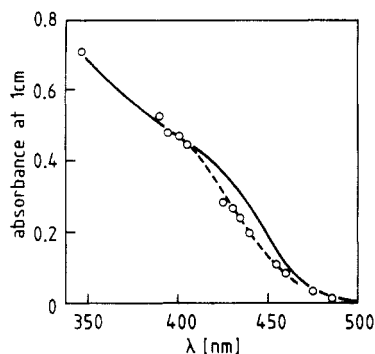


Figure 10. Observation of nonlinear optical absorptions in sol A: solid line, spectrum under normal spectrophotometric conditions; points and dashed lines, spectrum under laser illumination as measured in the operational mode 3 of Figure 1.

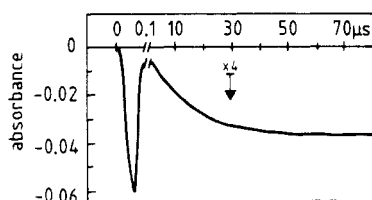


Figure 11. 460-nm bleaching signal as a function of time during and after the laser flash; sol A without addition of acetone.

band, while the other features of the spectrum are not remarkably different. The inset shows the spectral difference of the two spectra in the main part of the figure. In the absence of acetone, the emitted electrons react with CdS particles (see Figure 2), and the spectral difference has therefore to be attributed to the product of this reaction. In this reaction, the electrons interact with CdS particles that do not carry an excess hole, since the number of emitted electrons (and therefore of particles carrying an excess hole) is small as compared to the number of colloidal particles. A comparison with Figure 1 in ref 6 shows that the bleaching band in the inset of Figure 9 is practically identical with the one observed in the reaction of radiolytically generated hydrated electrons with CdS.

Bleaching within the Laser Flash. Figure 10 shows the results of a typical experiment in which nonlinear optical absorption effects were observed. The solid curve is the spectrum of sol A as measured under normal spectrophotometric conditions. The points and dashed curve were obtained under laser illumination by determining the transmission of the solution at various wavelengths of the dye laser, i.e., in the operational mode 3 of the setup in Figure 1. It is recognized that bleaching occurred during the laser flash in the same way as in the experiments of Figure 9.

The bleaching signal practically followed the flash profile as can be seen from Figure 11. Note the broken time scale in this figure. After the signal had almost disappeared at the end of the flash, it recovered within a few tens of microseconds, although its final value was 7.0 times smaller than in the maximum of the flash. In a solution containing added acetone this recovery, which is due to the reaction of emitted electrons with colloidal particles, did not occur. The slow buildup of the negative signal after the flash (Figure 11) is an indication of the fact that the emitted electrons escaped their original particles and reacted with others in the solution. The escape is favored by the overall negative charge of the colloidal particles, which produces a repulsive force on the emitted electrons. In fact, it was found previously that the hydrated electron reacts with CdS particles more slowly than expected for a diffusion-controlled reaction.⁶

Experiments on the bleaching below the absorption edge were also carried out with sol B. Figure 12 shows the spectrum of the bleaching band as measured in the maximum of the laser flash (full line). The band of sol A is also included (dashed line). It is recognized that the bleaching band is shifted to shorter wavelengths with decreasing particle size, which is a typical size

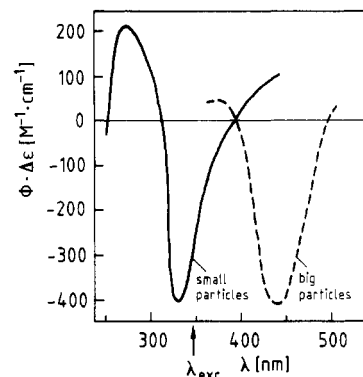


Figure 12. Spectrum of bleaching during the laser flash for sols A and B.

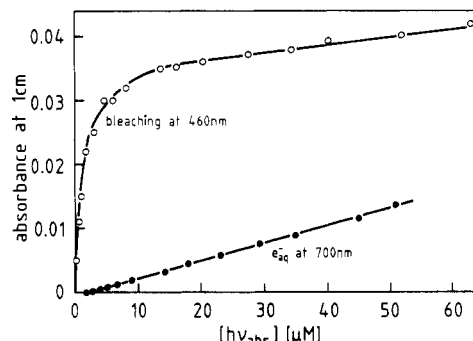


Figure 13. Bleaching at 460 nm during the laser flash and e_{aq}^- absorption immediately after the flash as functions of the absorbed dose.

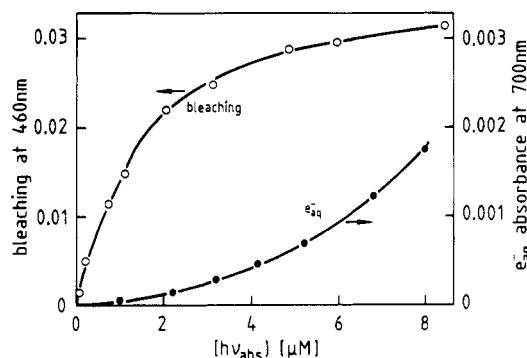


Figure 14. 460-nm bleaching and 700-nm absorption of e_{aq}^- at small laser doses.

quantization effect. In these experiments the signals had to be corrected for the stray light of the laser. The maximum correction was 15% for sol A (big particles) and 70% for sol B (small particles). A comparison of the bleaching band of sol A with the band shown by the inset of Figure 9 shows that they are practically identical.

Bleaching and Electron Emission. Figure 13 shows how the 460-nm bleaching signal of sol A in the maximum of the laser flash depended on the absorbed dose. The absorption signal of the hydrated electron is also included in the figure for comparison. Both signals are shown again in Figure 14 at very small doses.

In the dose range up to about 10^{-5} M photons absorbed, the bleaching signal and the electron signal do not increase linearly with dose. In fact the curve for the electron signal bends in a convex manner with respect to the abscissa as already described in Figure 6, and the bleaching signal is correspondingly bent in a concave manner in this dose range. At high doses the signal increases in a linear fashion, as does the bleaching signal, although in the latter case the slope of the straight part of the curve is rather small.

Bleaching and electron emission are coupled, and this has to be taken into consideration in the following discussion of the mechanism.

Preliminary experiments with a JK System 2000 frequency-tripled active-mode locked Nd:YAG laser (pulse duration 100 ps; absorbed photon concentration 1×10^{-4} M) yielded the following results: (1) The absorption of the hydrated electron appeared within the time resolution of 100 ps. (2) The bleaching signals practically followed the laser profile. (3) The fluorescence followed the laser profile with the exception of a small fraction that decayed after the flash in the 10-ns range, i.e., the range of lifetimes that are encountered in single-photon counting experiments. Details of these investigations will be described elsewhere.

Discussion

As was pointed out previously,¹ electrons cannot be photoemitted from CdS into water via a process in which only one photon is involved as the photon energies of the lasers applied were not high enough. On the other hand, it was observed in the previous work that the number of emitted electrons was proportional to the laser dose, a relationship typical for one-photon processes. In the present work, the emission at lower doses could be investigated, and it was found that a nearly square relationship existed in this range. One therefore concludes that photoelectron emission is a process in which two photons participate and that is complicated at higher doses by a competing process. Photoreactions in which two photons are involved generally follow one of the following routes: (1) The two photons are absorbed consecutively. The first photon creates an excited state, which then absorbs the second photon. (2) The two photons are absorbed simultaneously.

The second case does not seem to apply in our studies for two reasons. First, such two-photon processes are generally observed only when the solution does not absorb at the wavelength of the laser light. Our solutions absorbed, and under these conditions the first route is generally much more likely to be followed. Second, the cross section of a two-photon reaction would be as great as 10^{-40} cm⁴ s, as can readily be calculated from the photon flux and the observed electron yield at low doses. Two-photon processes generally have smaller cross sections, of the order of 10^{-50} cm⁴ s.¹²

Therefore, we are going to discuss our results in terms of consecutive absorption of two photons. In the previous work an electrostatic mechanism was proposed, i.e., buildup of a high negative potential in a colloidal particle (as the positive holes oxidize SH groups on the surface, the charges escaping in the form of H⁺ into solution) which facilitates the escape of an electron.¹ However, this mechanism requires a rather low rate of recombination of the charge carriers produced, i.e., a high stationary concentration of electrons on the particles during the flash. As is shown below, the opposite is true; the stationary electron concentration is found to be low. The electrostatic mechanism is therefore abandoned.

Other authors have treated the recombination of charge carriers generated in particles of semiconductors as in macrosystems. Under these conditions, the stationary concentration of electrons during the laser flash should be

$$[e^-]_{st} = (R/k_r)^{1/2} \quad (1)$$

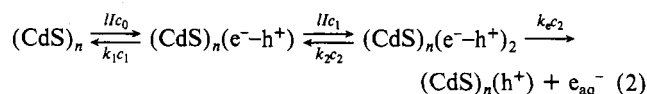
neglecting other reactions of the charge carriers. R is the rate of formation of electron-hole pairs, which is proportional to the light intensity I , and k_r is the bimolecular rate constant. k_r was always assumed to be constant as in the kinetics of a macrosystem. For example, $k_r = 9 \times 10^{-11}$ cm³ s⁻¹ was obtained by Nosoka and Fox in a study on electron transfer from illuminated CdS to methylviologen.¹³ Applying the model of two consecutive photon absorptions, where the second photon is absorbed by an electron present in the stationary state, one would expect the number of emitted electrons to be proportional to the 1.5th power of light intensity, as the rate of reaction should be proportional to $I[e^-]_{st}$. However, the curves in Figures 5 and 6 indicate a more complex relationship.

According to eq 1, the stationary electron concentration on the colloidal particles should be proportional to the square root of the laser dose. The electron concentration may be calculated from the observed bleaching by using a negative absorption coefficient of 5.2×10^4 M⁻¹ cm⁻¹.⁶ At a laser dose of 10^{-5} M absorbed photons in Figure 13, where the initial steep increase in bleaching ended, a negative absorbance of 0.033 was measured. One calculates that $0.033/(5.2 \times 10^4) = 6.3 \times 10^{-7}$ M stationary electrons were present, which is about half the concentration of the colloidal particles. At still higher doses the bleaching, i.e., the stationary concentration, increased very slowly (Figure 13). This can only be understood in terms of k_r not being constant but increasing drastically under conditions where there is one electron-hole pair already present upon the arrival of the next photon.

The stationary-state treatment with constant k_r (eq 1) can therefore be applied only at lower laser doses. Taking a volume of 2.2×10^{-20} cm³ for a particle average size (3.5 nm) in sol A and a stationary concentration of 0.5 electrons per particle at $[h\nu_{abs}] = 10^{-5}$ M, one obtains $[e^-]_{st} = 0.5/(2.2 \times 10^{-20}) = 2.2 \times 10^{19}$ cm⁻³. Ten photons were absorbed in one particle during the flash of 3×10^{-8} s. $R = 10/(3 \times 10^{-8} \times 2.2 \times 10^{19}) = 1.5 \times 10^{28}$ cm⁻³ s⁻¹ is calculated. With these values and eq 1, one obtains a k_r value of 3×10^{-11} cm³ s⁻¹, which is of the same order of magnitude as the value of Nosoka and Fox.¹³

Mechanism 1 is now examined in more detail. According to this mechanism the second photon should be absorbed by the electron of the excitonic state (e^-h^+) produced upon the absorption of the first photon. A substantial yield of emitted electrons can be expected only when the electron strongly absorbs at the exciting laser wavelength. However, neither in the previous studies on electron deposition⁶ nor in the present laser studies was a significant increase in absorption observed. One must conclude that the electron produced by the first absorbed photon does not absorb light more strongly than one CdS molecule. The probability of absorption of the second photon by the electron in the particle can therefore not exceed $1/n$ th of the absorption of a photon by the particle as a whole (n being its agglomeration number). Assuming that electron emission takes place with unit probability after absorption of the second photon by the electron, the quantum yield of emission cannot be greater than $1/n + 1$. The mean agglomeration number of the small particles in sol B being slightly below 100, one would not expect the yield to be much greater than 0.01 electrons emitted per photon absorbed.

The much larger yields, up to 0.07, can only be understood if the second photon is absorbed by the colloidal particle as a whole. This means that a second excitonic state is produced in the particle. The electron emission is attributed to the interaction of the two states. During the laser flash, the following photostationary equilibria are established:



Absorption of the first photon yields a particle carrying one excited state (e^-h^+). This excited particle may either lose its excitation or absorb a second photon to receive a second excitonic state. The doubly excited particle in turn may lose its second excitation or emit an electron into the aqueous phase with the specific rate k_e . The k 's are first-order rate constants, and the c 's are stationary concentrations of particles carrying i excitonic states. I is the light intensity, and I the specific rate for the absorption of a photon by a colloidal particle. As pointed out above, the specific rate of recombination of the charge carriers increases at high light intensities, i.e., $k_2 \gg k_1$ in the scheme of eq 2.

A few words have to be said now about the nature of the excited states (e^-h^+). Previous fluorescence measurements by single-photon counting techniques have shown that the lifetimes are in the 10-ns range, and it has been concluded that the recombining charge carriers are trapped. In the present experiments with the 100-ps laser, the greatest part of the fluorescence decayed during the flash. The nature of the traps are not exactly known. The fact that the fluorescence light is blue-shifted with decreasing

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particle size^{4b} indicates that the trapped electron senses the rest of the particle, i.e., it is not completely localized, its wavefunction extending to a certain degree over the whole particle. The fact that the absorption of e_{aq}^- and bleaching occur within less than 100 ps shows that the reaction between the excited states must be very fast. As a consequence, one has to conclude that such states cannot be accumulated to a large extent on a small colloidal particle.

At very low light intensities, where $k_1 c_1 \gg I/c_0$, c_1 and c_2 are much smaller than c_0 . Ordinary stationary-state treatment of the reactions of eq 2 leads to the following rate of electron emission:

$$r(e_{aq}^-) = \frac{k_e I^2 P^2}{k_1(k_2 + k_3)} C \quad (3)$$

where C is the overall concentration of colloidal particles. This explains the shape of the rate versus dose curves at low doses (Figure 6). At medium light intensities, where c_0 is still greater than c_1 and c_2 , one obtains

$$r(e_{aq}^-) = \frac{k_e I^2 P^2}{(k_2 + k_3)(I + k_1)} C \quad (4)$$

i.e., the rate of e_{aq}^- formation is proportional to a power in intensity between 1 and 2. Finally, at high intensities where $c_0 \ll c_1$ and c_2 (or $c_1 \approx C$), the rate is

$$r(e_{aq}^-) = \frac{k_e I}{k_2 + k_3} C \quad (5)$$

i.e., the rate of emission increases linearly with intensity. Equations 4 and 5 enable one to understand the shape of the curves in Figures 5 and 6. At doses above about 10^{-4} M absorbed photons, conditions are reached where more than one electron is emitted from a colloidal particle. The slope of the curves in Figure 5 decreases in this region of absorbed photon concentration. In fact, the mechanism of eq 2 can be expected to change as the second, third, etc., electron emitted during the laser flash stems from a particle carrying one, two, etc., excess holes. Under these circumstances, the recombination rate is further increased, which results in decreased probability of emission of the second, third, etc., electron.

When more than one electron is emitted from a particle, several holes will remain on it. It was observed that the absorption of the remaining holes did not parallel that of the emitted electrons

at higher doses. In fact, it strived toward a limiting value (Figure 8). This indicates that positive holes cannot be accumulated on small CdS particles as has already been pointed out in a recent study on luminescence quenching by excess holes.¹⁴ Chemically, a hole is a S^- radical anion. Annihilation reactions between holes could be $2S^- \rightarrow S_2^{2-}$ (or $S + S^{2-}$).

With decreasing particle size, the yield of photoelectron emission was found to increase. The electron to be emitted must first be promoted into a high-lying state in the particle from which it subsequently tunnels into a level of acceptance in water. Two reasons for the dependence of the yield on particle size can be given: (1) the distance of tunneling gets shorter with decreasing size; (2) the density of states in smaller particles is lower, which makes it more difficult for the promoted electron to lose its energy.

Two kinds of nonlinear optical effects in small particles could be of interest, i.e., conjugate reflection¹⁵ and absorption shifts.⁶ A shift in absorption near the threshold is demonstrated in Figures 9-12. It could be used in optical switch experiments provided that the bleaching band possesses a high negative absorption coefficient and that the signal follows the shape of the exciting light pulse. The latter property is fairly well fulfilled for the CdS particles of sol A, while the change in absorption does not seem sufficiently great. Colloidal zinc oxide, on the other hand, was found to have a much stronger bleaching effect, while the signal unfortunately did not rapidly decay after the laser flash.^{16c} These aspects should be kept in mind in further work on small semiconductor particles.

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Rheological Properties of Viscoelastic Surfactant Systems

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Aqueous solutions of cationic surfactants with strongly binding counterions exhibit gellike properties. In this paper we discuss new results that have been obtained from dynamic rheological measurements. We examine the zero shear viscosity, the shear modulus, and the stress relaxation time as a function of the surfactant and the salt concentrations. At constant surfactant concentration and increasing ionic strength the viscosity shows a complicated curve with a maximum that is followed by a minimum and a second maximum. The shear modulus is constant as a function of the salt concentration, but it increases monotonously with the square of the reduced surfactant concentration, which is in excellent agreement with the theoretical predictions of percolation models. At moderate and high electrolyte concentrations the relaxation behavior of the surfactant solutions can be described by only one single time constant, indicating that the flow behavior in this region is mainly controlled by micellar kinetics.

Introduction

Dilute solutions of ionic and nonionic surfactants usually behave as Newtonian liquids with viscosities only slightly greater than that of water. In contrast to these simple fluids there are viscoelastic surfactant systems that are known to have a more

complicated rheological behavior.¹⁻⁶ Some surfactants that show this interesting flow phenomenon contain charged positive

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