Photochemistry of Semiconductor Colloids. 22. Electron Injection from Illuminated CdS into Attached TiO_2 and ZnO Particles

Lubomir Spanhel, Horst Weller, and Arnim Henglein*

Contribution from the Hahn-Meitner-Institut Berlin, Bereich Strahlenchemie, 1000 Berlin 39, Federal Republic of Germany. *Received May 11, 1987*

Abstract: Colloidal solutions of CdS containing colloidal TiO_2 or ZnO were illuminated with visible light. The fluorescence of CdS (decay time ~50 ns) was quenched by TiO_2, several TiO_2 particles being required per CdS particle. The rate of photoanodic corrosion in aerated solution was drastically increased in the presence of TiO_2. In deaerated CdS solutions containing methanol and Cd^{2+} ions, cadmium metal was formed when TiO_2 was present. Methyl viologen was reduced with a quantum yield of close to one, while it reacted about ten times more slowly in the absence of TiO_2. These effects are explained in terms of improved charge separation by rapid electron injection from illuminated CdS into the conduction band of attached TiO_2 particles. Electron injection into ZnO was less efficient and occurred only in the case of Q-CdS particles (very small particles having a greater band gap). The injected electrons caused a blue shift of the absorption threshold of ZnO.

The photocatalytic action of colloidal or suspended semiconductor particles is based on the generation of electrons and positive holes which rapidly move to the surface of the particles and initiate redox processes. The efficiency of charge separation is often increased by contacting the semiconductor particle with a metal or another semiconductor. Typical examples are platinized titanium dioxide[1] and cadmium sulfide[2] as well as RuO_2-covered TiO_2.[3] Serpone et al. reported a few years ago that H_2 was formed from H_2S on CdS powder illuminated with visible light in aqueous solution and that the yield was slightly increased in the presence of TiO_2 powder.[4] The effect was explained by an improved charge separation due to electron transfer from the illuminated CdS particles into the conduction band of the TiO_2 particles. The increase in yield was only 20%, i.e., little above the increase which could be explained by more efficient light absorption of CdS due to the increased internal light scattering by the TiO_2 additive.

In the present paper, experiments with transparent colloidal solutions of CdS containing colloidal TiO_2 or ZnO as additives are described. Efficient electron injection from the excited CdS part of the "sandwich" colloids to the TiO_2 or ZnO part was observed with three methods of observation: (1) With use of a CdS colloid that fluoresces with a high quantum yield, the quenching of the fluorescence by added TiO_2 or ZnO was studied. (2) Redox processes, such as the reduction of excess Cd^{2+} ions and of methyl viologen and the photoanodic dissolution of CdS, were initiated by visible light illumination and the influence of added TiO_2 investigated. (3) In the case of ZnO as additive, the electron injection was accompanied by the typical changes in the absorption spectrum of ZnO which have recently been observed in other experiments on the deposition of excess electrons on small semiconductor particles.[5,6]

Experimental Section

The details of the preparation of colloidal CdS,[7] Q-CdS[8] (very small particles which show size quantization effects), TiO_2,[9] and ZnO[5] have previously been described. Typical absorption spectra are shown in Figure 1.

CdS. A solution of 2×10^{-4} M $Cd(ClO_4)_2$ and 2×10^{-4} M $(NaPO_3)_6$ (Riedel de Haen) was deaerated and 2×10^{-4} M H_2S added. The starting pH of the solution was adjusted with NaOH. The band gap of the CdS produced could be changed slightly by varying the starting pH. At pH_{start} = 7.5–8, particles with a mean diameter of 6 nm and a band gap energy of 2.5 eV were obtained. At pH_{start} = 10.2, particles of 4 nm were formed (band gap energy = 2.6 eV). These CdS solutions had a weak red fluorescence. Activation of the green or blue strong, near band gap fluorescence was achieved by bringing the pH up to 10.5 and adding 6×10^{-4} M $Cd(ClO_4)_2$. The mean agglomeration number of the CdS particles was between 1000 and 2000 depending on their mean size.

Q-CdS. A solution (500 mL) containing 2×10^{-4} M $Cd(ClO_4)_2$ and 3×10^{-4} M $(NaPO_3)_6$ and having a pH of 9.8 was bubbled with argon for 20 min. The stoichiometric amount of H_2S was injected under vigorous shaking. A Q-CdS sol was obtained, which had a structured absorption spectrum with several maxima.[8] This sol could not be used in the electron injection experiments with ZnO unless the pH was adjusted to 11.5 and 2×10^{-4} M $Cd(ClO_4)_2$ added. The structure in the absorption spectrum disappeared upon this addition and a long wavelength tail developed as can be seen from Figure 1.

TiO_2. Distilled $TiCl_4$ (5.8 mL) was added dropwise and under stirring to 500 mL of water at about 0 °C. The colloidal TiO_2 solution then was dialyzed until the pH lay between 2 and 3. The solvent was removed by rotary evaporation. Then 0.8 g of the TiO_2 powder obtained was dissolved in 100 mL of water. The colloidal stock solution had a concentration of TiO_2 of about 0.1 M. The pH was 2. The TiO_2 particles had a mean agglomeration number of about 800.

ZnO. A solution (20 mL) containing 0.1 M $Zn(ClO_4)_2$ in methanol was added dropwise and under stirring to 100 mL of 0.1 M NaOH in methanol. The solution was then diluted by a factor of 10 with methanol. The growth of the colloidal ZnO particles was then accelerated by adding 1 vol % water to the solution. The stock solution so obtained was ready for use after standing for 5 h. It contained 2×10^{-3} M colloidal ZnO and about 10^{-2} M excess OH^- ions.

CdS–TiO_2. NaOH was added to the CdS colloid until a pH slightly above 11 was reached. The desired amount of the TiO_2 stock solution, which generally amounted to less than 2 vol %, was injected under rapid stirring.

CdS–ZnO. The 2×10^{-4} M CdS solution was mixed with the 2×10^{-3} M ZnO stock solution in the ratio 2:1.

The concentration of Cd metal deposited on the colloidal particles was measured spectrophotometrically. An absorption coefficient of cadmium metal of 6×10^3 M^{-1} cm^{-1} at 360 nm was used. This coefficient was determined by the MV^{2+} method described previously.[10]

Fluorescence intensities were measured with a Shimadzu RF540 fluorimeter. Fluorescence lifetimes were measured with a single photon counting apparatus (199 fluorescence spectrometer from Edinburgh In-

---

[1] Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5985–5992.

[2] Darwent, J. R.; Porter, G. *J. Chem. Soc., Chem. Commun.* **1981**, 145–146.

[3] Kalyanasundaram, K.; Grätzel, M. *Angew. Chem.* **1979**, *91*, 759–760.

[4] Serpone, N.; Borgarello, E.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1983**, 342–344.

[5] Koch, U.; Fojtik, A.; Weller, H.; Henglein, A. *Chem. Phys. Lett.* **1985**, *122*, 507–510.

[6] Henglein, A.; Kumar, A.; Janata, E.; Weller, H. *Chem. Phys. Lett.* **1986**, *132*, 133–136.

[7] Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.*, in press.

[8] Fojtik, A.; Weller, H.; Koch, U.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 969–977.

[9] Moser, J.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6547–6555.

[10] Gutiérrez, M.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 474–478.

0002-7863/87/1509-6632$01.50/0

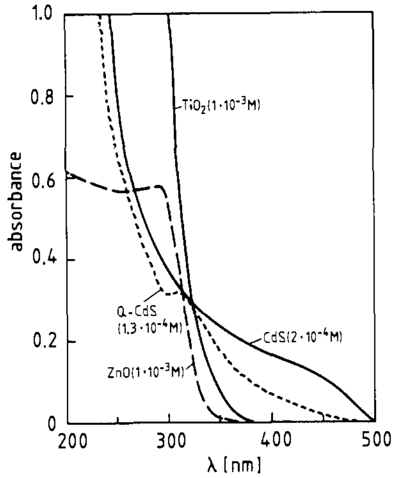

Figure 1. Absorption spectra of the colloids used.

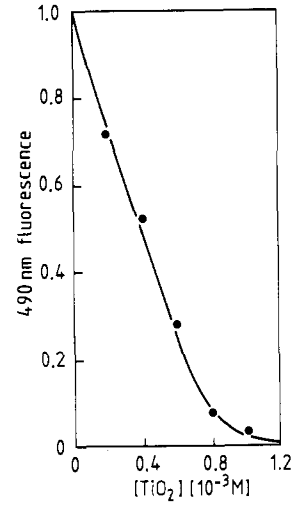

Figure 2. Intensity of the 490-nm fluorescence of the green fluorescing activated CdS colloid as a function of the TiO_2 concentration. pH 11. [CdS] = 2×10^{-4} M, $[(NaPO_3)_6]$ = 2×10^{-4} M. Excess Cd^{2+} = 6×10^{-4} M. Excitation of the fluorescence at 360 nm.

struments, Ltd.). As the fluorescence of CdS is not influenced by oxygen, all measurements were carried out with solutions under air.

The size of the colloidal particles was determined with an electron microscope as previously described.[7]

Results

CdS–TiO_2 Solutions. The activated CdS colloid emitted a strong green or blue fluorescence depending on particle size. The mean life of this fluorescence was 50 ns. In the presence of 1×10^{-3} M TiO_2, it was 3.5 ns. Figure 2 shows how the fluorescence intensity decreased. It can readily be calculated that many more particles of TiO_2 have to be present than CdS particles to achieve efficient quenching. For example, the TiO_2/CdS particle concentration ratio was 6:1 at 90% quenching. The fluorescence partially recovered when additional 5×10^{-3} M excess Cd^{2+} ions were introduced into the CdS–TiO_2 solution (already containing 6×10^{-3} M excess Cd^{2+}).

The nonactivated CdS colloid dissolved upon illumination in the presence of air:

$$CdS + 2O_2 \xrightarrow{h\nu} Cd^{2+} + SO_4^{2-} \quad (1)$$

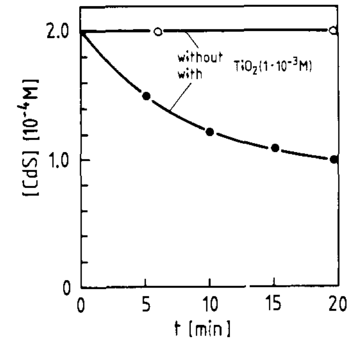

Figure 3. Illumination with polychromatic light (λ > 400 nm) of the activated CdS sol in the absence and presence of TiO_2. CdS concentration as a function of time.

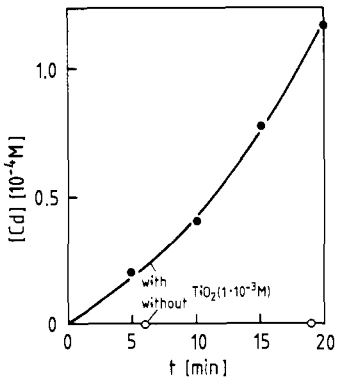

Figure 4. Cadmium metal formation as a function of time. Deaerated solution of 2×10^{-4} M CdS, 2×10^{-4} M $(NaPO_3)_6$, 6×10^{-3} excess Cd^{2+}. Solvent: 70% water and 30% methanol. Illumination with polychromatic light (λ > 400 nm).

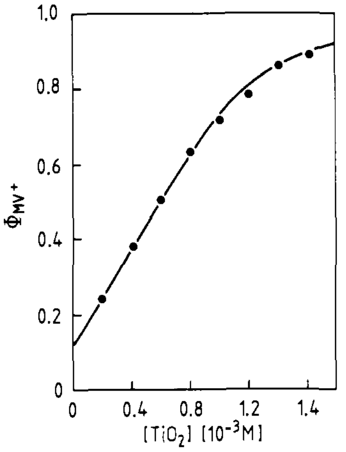

Figure 5. Monochromatic illumination at 436 nm of a solution containing 2×10^{-4} M activated CdS, 2×10^{-4} $(NaPO_3)_6$, TiO_2, and 30 vol % methanol. Quantum yield of MV^+ formation as a function of TiO_2 concentration.

This process of photoanodic corrosion has often been studied previously.[7,11] The activated CdS colloid was very stable toward photoanodic dissolution. In Figure 3, the concentration of activated CdS is plotted as a function of the illumination time. In the absence of TiO_2, no changes in the CdS concentration were found after illumination for 1 day. In a previous experiment of this kind, a slight decrease in CdS concentration had been found after 3 days of illumination.[7] However, in the presence of TiO_2, a rapid decrease in CdS concentration was observed (Figure 3). From the initial rate of this decrease one can estimate that the added TiO_2 increased the rate of photoanodic dissolution of activated CdS by a factor of more than 4000.

Illumination of the activated CdS colloid in the absence of air did not lead to any noticible chemical changes. In the presence of 30 vol % methanol in the solution, also no changes were observed. However, when 1×10^{-3} M TiO_2 was present in such a solution, it darkened rapidly under illumination as cadmium metal was deposited on the colloidal particles. Figure 4 shows the concentration of cadmium metal as a function of the illumination

---

(11) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 301–305.

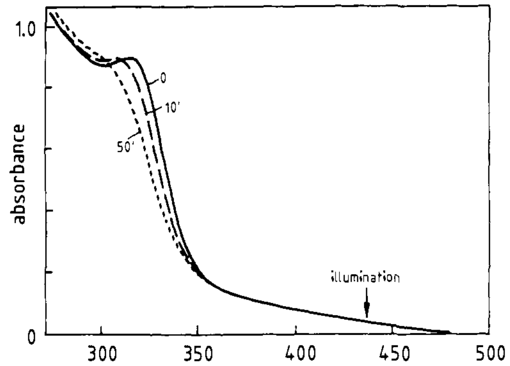

Figure 6. Absorption spectrum of a deaerated solution containing 1.3×10^{-4} M Q-CdS, 1.3×10^{-4} M $(NaPO_3)_6$, 7×10^{-4} M ZnO, and 33 vol % methanol; pH 11.5. Different times of illumination with 436-nm light.

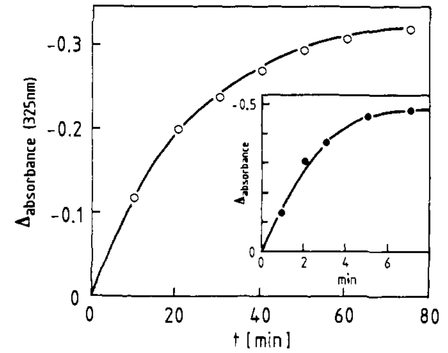

Figure 7. Change in the 325-nm absorption of a Q-CdS/ZnO solution (composition as in Figure 6) as a function of time. Inset: Change in absorption in the γ-irradiation of a 7×10^{-4} M ZnO solution in methanol-water (30:70%). Dose rate = 2×10^4 rad/h.

time. With increasing time, i.e., increasing amount of cadmium deposited, the rate of metal formation became greater. The initial quantum yield of metal formation was about 1%.

Solutions containing 30% methanol were also used in the experiments of Figure 5. Methyl viologen, MV^{2+}, was present at a concentration of 2×10^{-4} M. The quantum yield of formation of half-reduced methyl viologen, MV^+, is plotted as a function of the concentration of added TiO_2. A drastic increase is observed, the quantum yield reaching values close to 1 at the higher TiO_2 concentrations used. These solutions were very sensitive toward sun light. They developed the blue color of MV^+ even while being stirred under air during the exposure to sun light.

CdS-ZnO Solutions. Figure 6 shows the spectrum of a solution containing Q-CdS and ZnO before and after 10 and 50 min of illumination. The spectrum before illumination is a superposition of the spectra of the pure colloids. The illumination with 436-nm light excited only the CdS part of the colloidal solution. However, changes in the absorption of the ZnO part resulted as can be seen from the figure. In fact, the absorbance of the ZnO part was decreased in a wavelength range of about 60 nm below the 350-nm threshold of ZnO. Figure 7 shows how this decrease developed during the illumination. It is recognized that the change in absorption strives toward a limiting value at longer times.

The same decrease in absorption below the absorption edge has been observed in the photolysis of ZnO solutions.[5,12] More recently, we observed this effect also in the γ-radiolysis and pulse radiolysis of ZnO solutions in which reducing CH_2OH radicals were generated. A detailed report on these experiments will be published elsewhere. The inset of Figure 7 shows a typical result of such a γ-radiolysis experiment. Again, the bleaching of the ZnO absorption reached a limiting value, which was higher by about 45% than in the present studies.

Experiments were also carried out with activated CdS samples of different particle size. The green fluorescing sample (mean particle size = 6 nm) and the turquoise fluorescing sample (mean particle size = 5 nm) were not active in promoting the changes in absorption of added ZnO. However, an effect was found for the blue fluorescing samples (mean particle size = 4 nm), although the effect was still three times smaller than that for the above Q-CdS sample in which the mean particle size was much lower (~2.5 nm). It can therefore be said that the effect is the stronger the greater the "band gap" energy in the CdS particles.

Discussion

All the observed effects are understood in terms of electron injection from excited CdS particles into the conduction band of TiO_2 or ZnO particles. Because of the much more positive potentials of the valence bands in TiO_2 and ZnO, the positive hole created by light absorption in the CdS particle remains there or reacts with an acceptor such as methanol. The two partners of the e^--h^+ pair originally generated in a CdS particle thus find themselves in different semiconductor particles shortly afterwards, i.e., an efficient charge separation is achieved.

Strong effects were observed when the concentration of TiO_2 particles substantially exceeded that of the CdS particles. Probably an equilibrium exists between pure CdS particles and sandwich structures ($CdSTiO_2$), this equilibrium being shifted to the latter at sufficiently high TiO_2 particle concentrations.

The strong quenching of the fluorescence of activated CdS by TiO_2 (Figure 2) can be understood only if CdS and TiO_2 particles are attached to each other. The lifetime of the near band gap fluorescence of CdS in the absence of TiO_2 is about 50 ns. If the particles were separated, an encounter of an excited CdS particle with a TiO_2 particle would occur after $\tau = 1/k_e[TiO_2]_p$. Taking a rather extreme value of 10^{10} M^{-1} s^{-1} for the specific rate of encounters k_e and a TiO_2 particle concentration $[TiO_2]_p$ of 10^{-5} M, one calculates $\tau = 10^{-5}$ s, i.e., a time very much longer than the fluorescence lifetime. Efficient quenching is not conceivable under these conditions.

The quantum yield of charge injection from CdS and TiO_2 is close to 1 provided that a large number of TiO_2 particles are present per CdS particle. This can be concluded from the fact that practically complete quenching of the fluorescence was possible at overall concentrations of TiO_2 above 2×10^{-3} M (Figure 2) and also from the large yield of reduction of methyl viologen in CdS solutions containing methanol and TiO_2 (Figure 5).

All the solutions contained 6×10^{-4} M excess Cd^{2+} ions. As previously described, such high Cd^{2+} concentrations are necessary to bring about the intense near band gap fluorescence of CdS.[7] It was proposed that the excess Cd^{2+} ions form a layer of HO-Cd-S bonds around the colloidal particles that blocks surface states in which the charge carriers are trapped and recombine in a radiationless manner. The excess Cd^{2+} ions also possibly play an important role in linking together TiO_2 and CdS particles. Cd^{2+} ions are adsorbed on both kinds of particles, and there may exist Ti-O-Cd-S bridges between the particles. One has also to remember that polyphosphate chains, to which CdS particles are bound, were present in the solutions. These chains are also possibly important for holding TiO_2 and CdS particles together although no detailed binding mechanism can be given. A large excess of Cd^{2+} ions leads to a detachment of the colloidal particles from the polyphosphate chains and possibly to the breakage of the above bonding between TiO_2 and CdS particles.

The activated CdS colloid is very stable towards photoanodic dissolution. It was proposed that this is due to the protecting layer of OH-Cd-S bonds, mentioned above, which prevents positive holes created by light absorption to react rapidly with oxygen in the solution.[7] The holes are accumulated and this leads to a faster recombination with the electrons formed upon further illumination. In the presence of TiO_2 the electrons rapidly leave the CdS particles and are picked up by oxygen on the TiO_2 particles. The lifetime of the remaining holes in the CdS particles is increased and enables them to react with O_2 molecules. This mechanism

---

(12) Bahnemann, D.; Kormann, C.; Hoffmann, M. R. *J. Phys. Chem.* **1987**, *91*, 3789.

explains the drastic increase in the rate of photoanodic corrosion of CdS by added TiO_2 (Figure 3).

The increased charge separation in the presence of TiO_2 also explains why cadmium metal is formed in deaerated solutions containing methanol (Figure 4). However, the quantum yield is far below that of methyl viologen reduction (Figure 5). The reduction of Cd^{2+} requires two electrons which have to be stored on the TiO_2 particles. It seems that the probability of back reaction of such stored electrons with positive holes created upon further illumination of the CdS part in the CdS–TiO_2 associate is rather large. The role of methanol consists of scavenging the positive holes. This reaction, however, is relatively slow and cannot compete with the electron-hole recombination. Only under conditions where the electron is rapidly removed, such as by charge injection into attached TiO_2 or by a scavenger adsorbed on CdS, can this reaction occur efficiently. These kinetic relations in microheterogeneous systems containing acceptors simultaneously for the scavenging of electrons and of holes have previously been outlined in detail.[13]

The most convincing evidence for charge injection from CdS into ZnO is the change in the absorption spectrum of ZnO (Figure 6). In our previous studies on the changes in absorption which accompany the transfer of an electron to a small colloidal semiconductor particle or the creation of electrons by light absorption in a particle it was shown that the onset of absorption is blueshifted.[5,6] For example, an electron is deposited on ZnO in the reaction of CH_2OH radicals which are formed by ionizing radiation in methanol solutions of colloidal ZnO (Figure 6, inset).

$$(ZnO)_x + CH_2OH \rightarrow (ZnO)_x^- + H^+ + CH_2O \quad (2)$$

The shift in the absorption spectrum of ZnO in the CdS–ZnO solution upon illumination of the CdS part exactly corresponds to the previous observations on electron deposition on ZnO particles. Only a certain number of electrons can be stored as can be seen from the limiting value of the absorption shift at longer illumination times (Figure 7). In the case of the deposition of electrons by CH_2OH radicals more electrons can be stored than in the case of electron injection from CdS. This is probably due to the fact that reaction 2 is not simultaneously accompanied by the creation of positive holes, while in the ZnO–CdS system such holes are generated and have a certain chance to recombine with the transfered electrons. In a forthcoming paper the reaction of eq 2 and other experiments on electron deposition of ZnO particles will be described in detail. It was possible to determine the absorption change per stored electron and in this way to determine the quantum yield of the formation of electrons stored in photoexperiments. From the shifts observed in Figure 6 and the number of absorbed photons, it was calculated that the quantum yield of electron injection from CdS to ZnO was of the order of 0.001, and that only one electron could be injected and stored.

The low efficiency of electron injection from CdS to ZnO particles may have different reasons. It could, for example, be that the association between CdS and ZnO particles is not so good as in the case of TiO_2. Another reason is recognized from the experiments with CdS samples of different band gap energy. The larger the band gap, the more efficient is the electron injection. It has previously been shown that reduction processes on various colloidal semiconductor particles occur more efficiently if the particles are very small.[14] The effect has been attributed to the quantization of the energy levels due to the spatial restriction of the charge carrier created by light absorption in these particles. Our observations on the charge injection from CdS to ZnO represent an additional example for this fact. Electron injection has to compete with recombination with the hole in a CdS particle. In order to make electron injection fast enough a certain driving force has to exist which is given by the difference in the potential energies of an electron in excited CdS and in ZnO. This difference becomes greater with decreasing CdS particle size.

Acknowledgment. The authors express their gratitude for the excellent assistence in the laboratory of M. Weller, for helpful discussions with Mrs. L. Katsikas, and for advice in the electron microscopic investigations by Dr. W. Kunath, Dr. B. Tesche, and K. Weiss in the Fritz-Haber-Institut, Max-Planck-Gesellschaft.

---

(13) Henglein, A.; Gutiérrez, M.; Fischer, Ch.-H. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 170–175. Henglein, A. *Top. Curr. Chem.*, in press.

(14) Nedeljković, J. M.; Nenadović, M. T.; Mićić, O. I.; Nozik, A. J. *J. Phys. Chem.* **1986**, *90*, 12–13.

Two Metastable Triplet States of 2-Naphthaldehyde at 300 K Corresponding to Twisted and Planar Molecular Geometry. Time-Resolved Optical Absorption and Raman Spectroscopy

Alexander M. J. van Eijk, Peter F. A. Verhey, A. Herbert Huizer, and Cyril A. G. O. Varma*

Contribution from the Department of Chemistry, Gorlaeus Laboratories, Leiden University, 2300 RA Leiden, The Netherlands. *Received February 13, 1987*

Abstract: It is shown that excitation of solutions of 2-naphthaldehyde in either cyclohexane or acetonitrile at 300 K with light of 308-nm wavelength leads in both cases to the formation of two triplet states which have slightly different lifetimes τ in the range $250 < \tau < 350$ ns. These triplet states, formed monophotonically by excitation with an excimer laser pulse of 308 nm, have been studied by means of time-resolved optical absorption spectroscopy, time-resolved resonance Raman scattering, and transient dielectric loss measurement. Only one of these triplet states exhibits resonance Raman scattering. It is concluded that this state is a $\pi\pi^*$ triplet state, in which the conjugation between the aldehyde and the naphthyl groups is broken and which does not have the character of a twisted intramolecular charge-transfer state.

Bands in electronic absorption spectra of even relatively small molecules in liquid solutions are usually broad and with little or no vibrational structure. They are not so characteristic for the molecules as their IR and Raman spectra. Therefore IR spectra and Raman spectra may be more helpful than electronic absorption spectra in identifying intermediates in reactions unambiguously. Very often and in particular in the case of photochemical reactions the concentrations of reaction intermediates encountered in

0002-7863/87/1509-6635$01.50/0