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 blue-shifted.[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).

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

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.

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

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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

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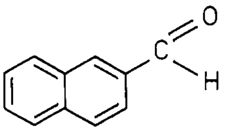

Figure 1. Structural formula of 2-naphthaldehyde.

practice are small. This and the small probability for IR transitions make it nearly impossible to obtain their IR spectra. When the wavenumber σ_0 of the incoming light in Raman scattering lies within the frequency range of an electronic absorption band (resonance) the cross section for Raman scattering may be enhanced several orders of magnitude compared to the case where σ_0 is far away from any electronic absorption band. By selecting σ_0 to be a frequency within a transient electronic absorption it becomes feasible to obtain Raman spectra of transient species.

By preparing a population of triplet states through excitation with a laser pulse of 308 nm, the resonance Raman spectra of acridine and anthracene in their state $T_0(\pi\pi^*)$ have been determined.[1] Thirty Raman lines in the region between 200 and 2000 cm^{-1} were obtained for acridine in the state T_0. Nineteen Raman lines between 500 and 2000 cm^{-1} are found for anthracene in the state T_0. These results are interesting from a spectroscopic point of view. Chemically more interesting results have now been obtained in the case of the laser induced triplet population of 2-naphthaldehyde (Figure 1). The compound is known to have two triplet states separated by an energy gap of 5000 cm^{-1} below the first electronically excited singlet state S_1.[2] The state S_1 is considered to be an $n\pi^*$ state, and the lowest triplet state T_0 is thought to be a $\pi\pi^*$ state.[2] The compound 2-naphthaldehyde may undergo photochemical cycloaddition reactions (Paterno–Buechi reaction) with olefins.[3] Such reactions are usually considered to occur upon encounter of an olefin and a ketone or aldehyde in an $n\pi^*$ triplet state.[3] However, in the case of 2-naphthaldehyde it has been suggested that the reaction involves the excited singlet state molecule.[4]

The present paper is intended to clarify the nature of the lowest triplet states of 2-naphthaldehyde and to provide a basis for the discussion of the mechanism of the triplet state reactions of 2-naphthaldehyde. Both triplet–triplet optical absorptions and triplet state resonance Raman scattering will be discussed.

Experimental Section

Commercially available 2-naphthaldehyde (Aldrich) has been purified by vacuum sublimation. Spectrograde solvents have been used in all experiments. The solutions used in the studies of time-resolved resonance Raman scattering and transient optical absorptions had an optical density of 1.0 at 308 nm. The concentration of 2-naphthaldehyde in cyclohexane and in acetonitrile is then 1.25×10^{-3} and 0.67×10^{-3} M, respectively. The triplet state quencher 3,3,4,4-tetramethyldiazetine dioxide (TMDD) has been prepared according to the procedure given by Ullman and Singh.[5]

Transient optical electronic absorptions are measured with a kinetic spectrometer described previously,[6] in which an excimer laser pulse of 308 nm, width of 7 ns, and integrated energy I_1 of typically 10 mJ generates the short-lived species, which are subsequently probed by monochromatic light emerging from a pulsed (flat pulse top of 200 μs) Xenon lamp, whose emission is transmitted through a monochromator. After passage of the probing light through the sample and a second monochromator, eliminating fluorescence and scattered laser light, the time profile of its intensity is measured with a photomultiplier, which is interfaced with a 500-MHz transient digitizer.

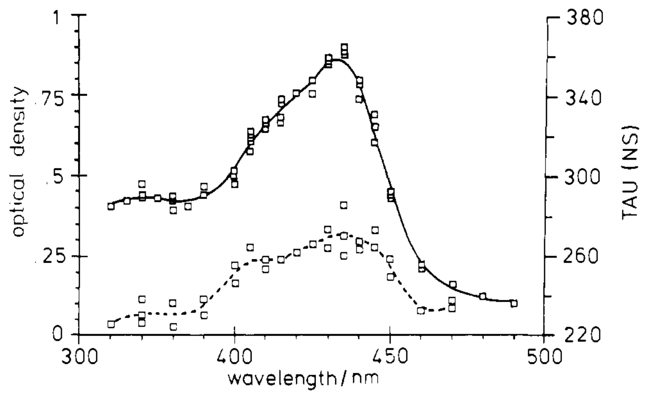

Figure 2. Laser-induced transient optical absorptions of 2-naphthaldehyde in acetonitrile. The vertical scale on the left and on the right refer respectively to the absorption spectrum (—) and to the variation of the lifetime with wavelength (---).

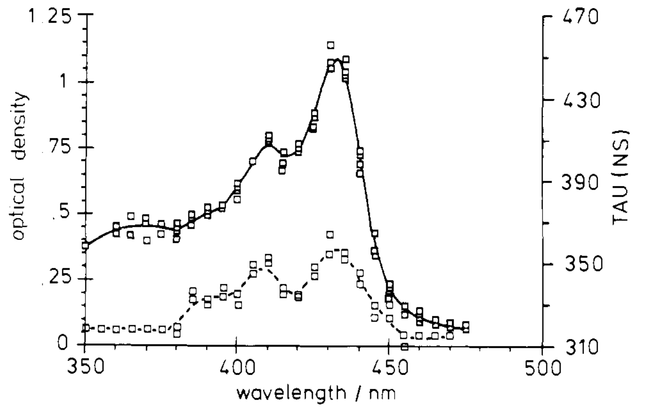

Figure 3. Laser-induced transient optical absorptions of 2-naphthaldehyde in cyclohexane. The vertical scale on the left and on the right refer respectively to the absorption spectrum (—) and to the variation of the lifetime with wavelength (---).

The spectrometer for recording transient resonance Raman spectra has also been described previously.[1] It consists of a pulsed excimer laser used to generate the transient species, a pulsed dye laser, delayed with respect to the former, for probing the Raman scattering, and a 1-m spectrograph, which is interfaced with a digitizing vidicon detector, provided with a two-stage image intensifier. The frequency scale of the spectrometer is calibrated by using the positions of the Raman lines of indene, which is distilled just before use. The error in frequency is estimated to be less than 5 cm^{-1}. In order to compare the intensity of a selected transient Raman line of 2-naphthaldehyde in cyclohexane and in acetonitrile, a small amount of benzene is added to the solutions (2.5% (v/v)). The 992-cm^{-1} line of benzene is then used as an internal standard to determine the intensity ratio of the 1310-cm^{-1} transient Raman lines of 2-naphthaldehyde in the two solvents. In the determination of the excitation profiles of resonance Raman lines, suitable Raman lines of the solvent, e.g., the 1375-cm^{-1} line of acetonitrile and 1266-cm^{-1} line of cyclohexane, are used. The intensities of the (off-resonance) solvent's Raman lines are assumed to be constant when the wavelength of the dye laser is varied between 375 and 485 nm. The intensity of a solvent's Raman line is used as an internal standard in correcting intensities of lines from the solute for variations in dye laser output intensity and detector sensitivity with wavelength. The decay of the intensity $I(t)$ of a number of the transient Raman lines has been studied, by measuring $I(t)$ at different delay times Δt between excimer laser and dye laser. The intensities $I(t)$ have been corrected for partial absorption by the transient species of both the light from the dye laser and the scattered light. This has been achieved by using the intensity of a selected Raman line of the solvent as an internal standard. In practice the intensity of the standard solvent line does not vary more than 20% in the range of variations of Δt.

Laser-induced transient dielectric loss at microwave frequencies has been measured as described previously.[7,8]

Results and Discussion

Optical Absorptions of Transient Species. Figures 2 and 3 show the transient absorption spectrum of 2-naphthaldehyde in ace-

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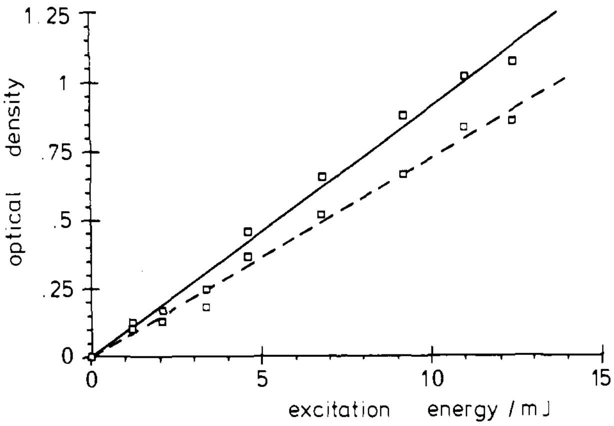

Figure 4. Laser-induced transient optical density at 435 nm and at Δt = 10 ns as a function of the integrated laser pulse energy I_l for the solution of 2-naphthaldehyde in cyclohexane (—) and in acetonitrile (---).

tonitrile and cyclohexane, respectively, at 10 ns after excitation with the 308-nm pulse from the excimer laser. A transient absorption spectrum of 2-naphthaldehyde in cyclohexane, with a structure similar to that in Figure 3, has been reported.[9] The spectrum has been assigned to absorptions from the lowest electronic triplet state of 2-naphthaldehyde.

A single exponential function provides a good fit of the decay of the transient absorption at 435 nm. The fitted function yields a lifetime τ^a of the transient absorption in the solutions in acetonitrile and in cyclohexane of 260 and 355 ns, respectively. Inspection of the lifetime τ^a of the transient absorption at several wavelengths λ in the spectrum reveals small but significant and reproducible variations of τ^a with λ as shown by the dotted curve in Figures 2 and 3. For both solvents the lifetime has a maximum value at 435 nm, drops toward the edges of the spectrum, and reaches a value common to both edges at 370 and 470 nm. The solution in acetonitrile has τ_1^a = 260 ns and τ_2^a = 230 ns, and the solution in cyclohexane has τ_1^a = 355 ns and τ_2^a = 305 ns.

The lifetimes τ_1^a and τ_2^a have been studied as a function of laser energy I_l. Variation of I_l between 10 and 0.2 mJ does not cause any change in either τ_1^a or τ_2^a. Therefore bimolecular reactions between two transient species as well as between transient species and ground-state 2-naphthaldehyde are absent. The way in which the lifetime τ^a varies with wavelength is not affected by variations of the concentration of 2-naphthaldehyde. This means that excited states of multimers (e.g., dimers) are not involved in the transient absorption. Pseudo-first-order reactions between transient species and the solvent cannot be excluded on this basis. A conceivable photochemical reaction between solute and solvent is hydrogen abstraction from the solvent. However, this type of reaction may be ruled out, since the transient absorption spectrum of the solution in benzene shows also a variation of lifetime with wavelength similar to what is observed for the solutions in cyclohexane and acetonitrile.

Figure 4 shows that the transient optical density varies linearly with I_l and that the plotted lines pass through the origin. This means that the transient species are formed monophotonically and that the linearity does not arise from quasi-linear behavior on a section of a curve. The transient absorption of the solution in acetonitrile may be quenched by TMDD and oxygen. The transient absorption of the solution in cyclohexane may be quenched by oxygen, but not by TMDD. The solubility of TMDD in cyclohexane is too low to get quenching of triplet states with lifetimes less than 1 μs. Figure 5 shows a Stern–Volmer plot of the quenching of the absorption at 430 nm by TMDD. In that particular case the rate constant k_q for quenching amounts to (4.4 ± 0.3) × 10^9 $\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$, which is about the value for a diffusion-limited rate constant. A diffusion-limited rate constant k_q is obtained for all wavelengths in the transient absorption spectrum, independent of the solvent.

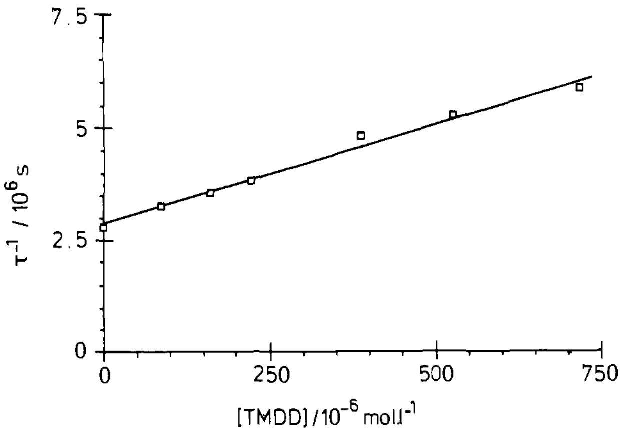

Figure 5. Variation of the decay rate constant $1/\tau_1^a$ of the transient absorption at 430 nm as a function of the concentration of the triplet state quencher TMDD for 2-naphthaldehyde in acetonitrile.

The observations mentioned above lead to the conclusion that each of the transient absorption spectra of 2-naphthaldehyde shown in Figures 2 and 3 arises from two different types of triplet state species. This is in contrast with the conclusion of Boldridge,[9] who assigned the transient spectrum to a single species, namely 2-naphthaldehyde in its lowest electronic triplet state. Apparently the lifetimes of the two species do not differ enough to be separable. Loss of sensitivity in determining the tail of the transient absorption signal makes a distinction between biexponential and monoexponential decay impossible. The variation of the decay of the transient optical density with wavelength excludes the possibility of a fast dynamic equilibrium (i.e., with rate constants larger than 4 × 10^6 $\mathrm{s^{-1}}$) between the two species, since then the decay should have been both monoexponential and wavelength independent.

The absence of structure in the transient spectrum of the solution in acetonitrile may be due to merging of the bands due to solvatochromic shifts or to weak solute–solvent exciplexes. The difference in height of the maximum in the spectra in Figures 2 and 3 does not arise from a difference in the decay rate of the transient absorptions, since the spectra were both recorded at an early stage of the decay. The difference in height is most likely due to a variation of extinction coefficients with solvent, because the invariance of both the total triplet quantum yield ϕ_T[10] and the transient optical absorption at 365 nm indicates negligible differences between the two solutions with respect to concentrations of transient species.

Note that the observation of two triplet states does not mean necessarily that their populations are in thermal equilibrium. Since there is no kinetic evidence of a fast equilibrium between the two states, it is likely that their interconversion requires a thermal activation that is not achievable at 300 K and that they are populated independently via the manifold of excited singlet and triplet states.

Transient Resonance Raman Scattering. The Raman spectrum of 2-naphthaldehyde in its electronic ground state has been obtained by using a 0.5 M solution in acetonitrile and a probe beam of 382.5 nm. Raman lines are observed in the region 400–1750 $\mathrm{cm^{-1}}$, and these are listed in Table I. They appear, within experimental error, at the positions reported earlier.[11] The Raman spectrum of the molecule in its ground state is shown in Figure 6.

Figures 7 and 8 show the transient resonance Raman spectra of 2-naphthaldehyde in acetonitrile and cyclohexane. They have been obtained at 100 ns after the primary excitation and with the dye laser wavelength tuned at 435 nm. The wavenumbers of the

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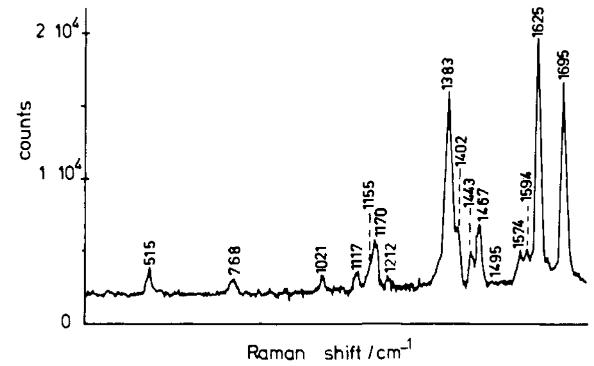

Figure 6. Raman spectrum of ground-state 2-naphthaldehyde in acetonitrile, obtained with excitation at 382.5 nm.

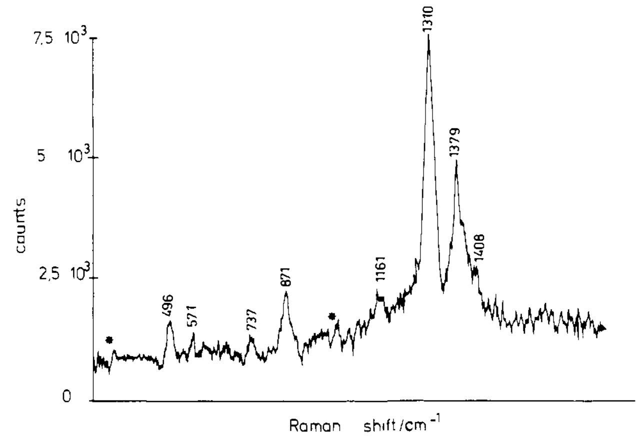

Figure 7. Laser-induced transient resonance Raman spectrum of 2-naphthaldehyde in acetonitrile at Δt = 100 ns and with excitation at 435 nm, attributed to a $\pi\pi^*$ triplet state. The asterisks mark the positions of the residual solvent lines.

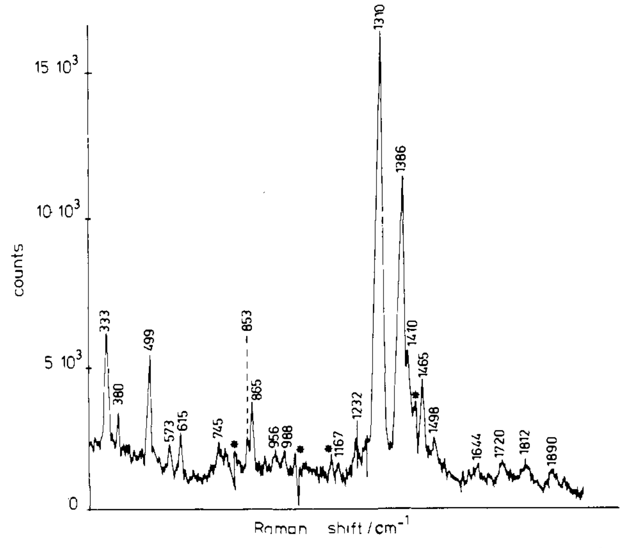

Figure 8. Laser-induced transient resonance Raman spectrum of 2-naphthaldehyde in cyclohexane at Δt = 100 ns and with excitation at 435 nm, attributed to a $\pi\pi^*$ triplet state. The asterisks mark the positions of residual solvent lines.

observed transient lines are given in Table I. Neither of them appear when either the excimer laser or the dye laser is used alone. The solutions of 2-naphthaldehyde are not changed chemically in the course of the signal accumulation which is required to obtain a good signal-to-noise ratio in the transient Raman spectra. The obtained transient Raman spectra can therefore not be attributed to intermediates in a photochemical reaction.

Figure 9 shows a semilogarithmic plot of $I(t)$ as a function of time Δt. In the case of the solution in acetonitrile the lifetime τ^r has been determined for the lines at 1310 and 1379 cm^{-1}. They have the same lifetime, namely τ^r = (235 ± 20) ns. In the case of the solution in cyclohexane, τ^r could be determined for the lines at 333, 449, 1310, and 1386 cm^{-1} and all of these have τ^r = (340 ± 20) ns. For each of the two solutions the value of τ^r for the transient Raman lines (with excitation at λ = 435 nm) lies between the values τ_1^a and τ_2^a.

Table I[a]

2-naphthaldehyde (S_0)	2-naphthaldehyde (T_0) cyclohexane	2-naphthaldehyde (T_0) acetonitrile
	333 m	
	380 w	
515 m	499 m	496 w
	573 w	
	615 w	
768 m	745 w	737 w
	853 sh	
	865 m	871 m
	956 w	
	988 w	
1021 w		
1117 w		
1155 sh		
1170 m	1167 w	1161 w
1212 w	1232 w	
	1310 s	1310 s
1383 s	1386 s	1379 s
1402 sh	1410 sh	1408 sh
1443 m		
1467 m	1465 m	
1495 vw		
1574 m		
1594 m		
1625 s		
1650 m	1644 w	
1695 s		
	1720 w	
	1812 w	
	1890 w	

[a] s = strong; m = medium; w = weak; vw = very weak; sh = shoulder on neighboring band.

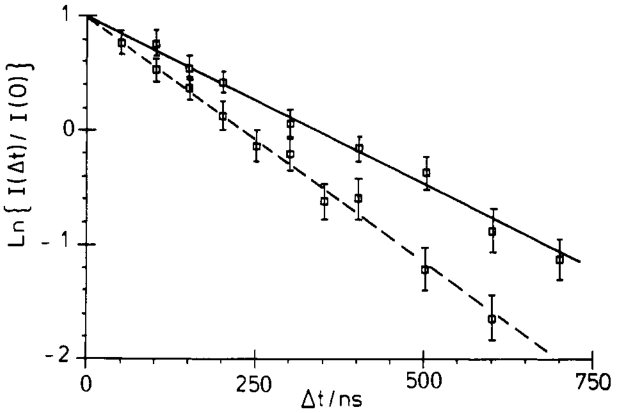

Figure 9. Time dependence of the intensity $I(t)$ of the transient Raman line at 1310 cm^{-1} of the solution of 2-naphthaldehyde in cyclohexane (—) and in acetonitrile (---).

Note that the signal-to-noise ratio in the transient resonance Raman spectrum of the solution in acetonitrile is small compared to that of the solution in cyclohexane. By measuring the intensity of the transient Raman line at 1310 cm^{-1} relative to the intensity of the 992 cm^{-1} Raman line of benzene, it has been found that the transient line of the solution in acetonitrile is a factor of 2 weaker than the corresponding line of the solution in cyclohexane. There are two causes for this difference in intensity of the transient Raman scattering, namely a difference in concentration of the transient species at the time of observation (Δt = 100 ns), due to unequal decay times, and a difference in the extinction coefficient.

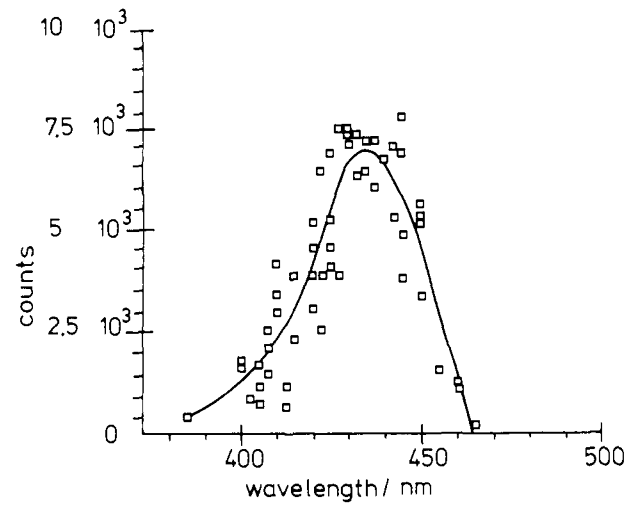

Figure 10. Excitation profile of the transient Raman line at 1310 cm^{-1} of 2-naphthaldehyde in acetonitrile. The experimental points are marked with an open square.

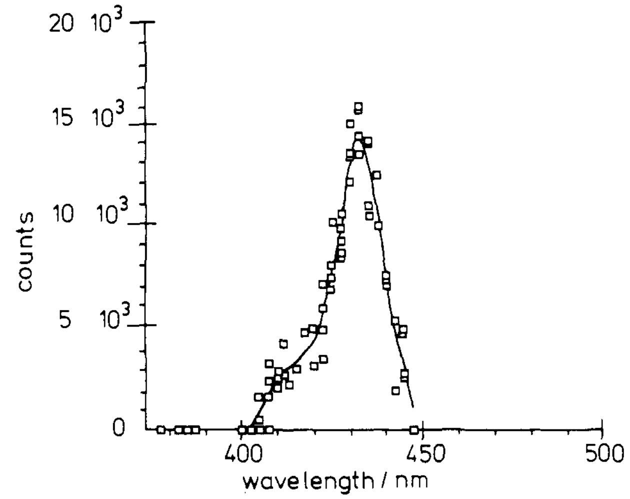

Figure 11. Excitation profile of the transient Raman line at 1310 cm^{-1} of 2-naphthaldehyde in cyclohexane. The experimental points are marked with an open square.

Evidence for the production of two types of triplet species may also be obtained from the excitation profiles (REP) of the resonance Raman lines. The REP of the most intense transient Raman lines has been measured. These are the 1310- and 1386-cm^{-1} lines of the solution in cyclohexane and the 1310-cm^{-1} line of the solution in acetonitrile. The excitation profiles are shown in Figures 10 and 11. The REP's of the 1310- and 1386-cm^{-1} lines of the solution in cyclohexane are identical and do not cover the whole wavelength region of the transient absorption spectrum. The REP of the 1310-cm^{-1} line of the solution in acetonitrile covers also only part of the transient absorption spectrum. Although the inhomogeneously broadened REP for a given Raman line of a molecule and the shape of its electronic absorption spectrum may be different, they cover in general the same spectral region. No transient Raman lines are observed for excitation at 380 and 470 nm, which are both wavelengths outside the region of the REP of the 1310-cm^{-1} line, shown in Figures 10 and 11. This means that the species absorbing at these wavelengths do not show resonance Raman scattering. Since there are two transient species, it must be concluded that in each of the two solutions the transient Raman lines are arising from a single type of species. The transient Raman scatterer must be identified with the triplet species, having the longer lifetime of the two, since the maximum in the REP and that in τ_1^a are observed at approximately the same wavelength.

In the Raman spectrum of 2-naphthaldehyde, in its ground state, the characteristic line of the aldehyde group, due to the C=O stretching vibration, appears with high intensity at 1699 cm^{-1}. The intense lines in this spectrum at 1627 and 1379 cm^{-1} have been attributed to C–C ring vibrations.[11] In the triplet-state resonance Raman spectrum of 2-naphthaldehyde there is not any strong line in the region of 1690 cm^{-1} as in the ground-state Raman spectrum. The most intense lines in the triplet-state Raman spectrum are at 1310 and 1386 cm^{-1}. In this spectral region one might expect to find the wavenumber of the C=O stretching mode for an $n\pi^*$ excited state, since the wavenumber for the C=O stretching mode in the state $S_1(n\pi^*)$ of benzaldehyde is thought to be around 1315 cm^{-1}.[12]

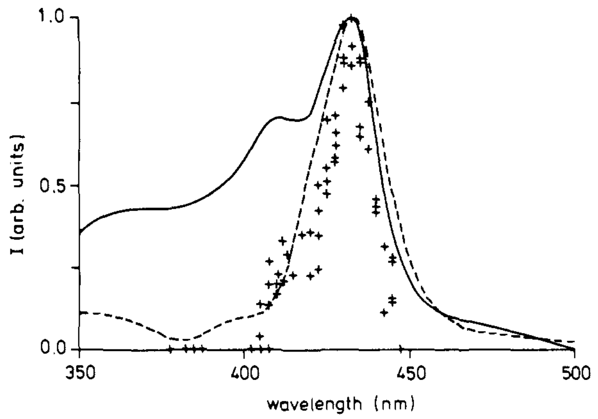

Figure 12. Transient absorption spectrum (—), excitation profile as transform of the former (---), and experimental excitation profile (+) of the 1310-cm^{-1} transient Raman line of 2-naphthaldehyde in cyclohexane.

The lowest triplet state of 2-naphthaldehyde has been characterized as a $^3\pi\pi^*$ state. If one of the two triplet states observed here is a $^3n\pi^*$ state, it will have the shortest lifetime due to stronger spin–orbit coupling with the ground state. Since the transient Raman scattering arises from the triplet state with the longest lifetime, it must be attributed to the state with $\pi\pi^*$ character. The C=O stretching mode is expected to shift much less in going from S_0 to a low-lying $\pi\pi^*$ excited state than in going to the lowest $n\pi^*$ state. A reliable indication of the frequency shift of a stretching mode upon $\pi\pi^*$ excitation is offered by the shift from 1643 cm^{-1} (S_0) to 1440 cm^{-1} (S_1) for the C–C stretching mode in 1,3-butadiene, whose π-electron system is spatially not very extended.[13] Increasing the extension of the π-system over more atoms must lead to a reduction in the shift. The lines at 1310 and 1386 cm^{-1} in the transient spectrum of 2-naphthaldehyde can therefore not be attributed to the C=O stretching mode. They arise from vibrations of the naphthyl group. The line positions correspond to the 1337 and 1395 cm^{-1} lines in the Raman spectrum of naphthalene in its lowest triplet state T_0.[14]

The electronic absorption spectrum of a molecule may be transformed theoretically into the REP of any of its chosen Raman lines.[15] Application of a procedure of this kind[16] to the whole transient absorption spectrum of the solution in cyclohexane yields a REP for the 1310-cm^{-1} transient Raman line, which is shown in Figure 12. It has a major band which covers the experimental REP, but which is slightly broader than the latter. A much better fit to the experimental REP may be obtained by transforming the triplet–triplet absorption spectrum of naphthalene, after this is shifted uniformly to lower wavenumbers over a distance of 1000 cm^{-1}. The recorded absorption spectrum of naphthalene in its lowest triplet state is taken to obtain the better fit. The shift is such that the long wavelength maximum in this spectrum and that in the experimental triplet–triplet absorption spectrum of 2-naphthaldehyde in cyclohexane are coincident. The result of the

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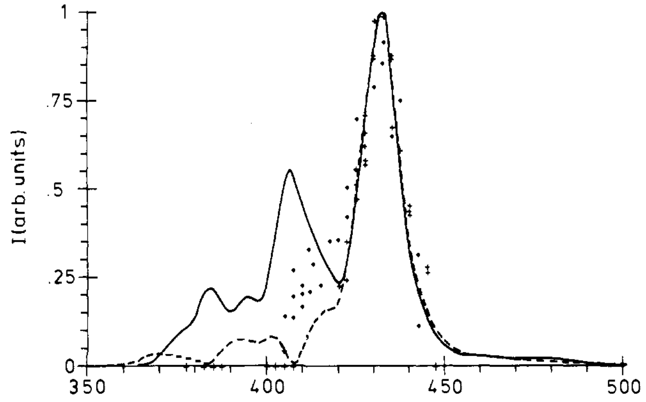

Figure 13. Experimental REP (+) and a theoretical REP (---) of the 1310-cm^{-1} transient Raman line of 2-naphthaldehyde in cyclohexane. The theoretical profile results from transformation of a triplet–triplet absorption spectrum of naphthalene in cyclohexane, shifted uniformly over 1000 cm^{-1} toward the long-wavelength side (—).

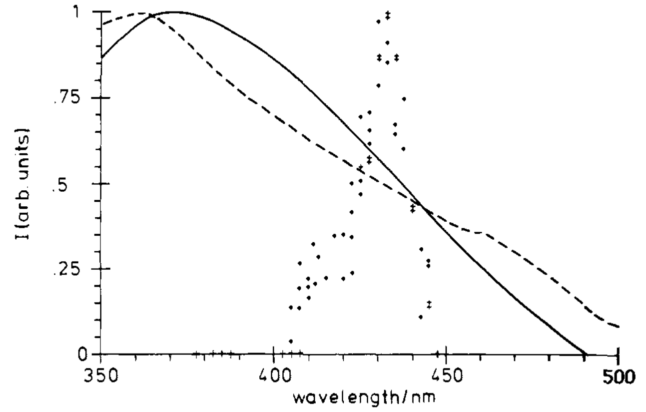

Figure 14. Difference of the total transient absorption spectrum of 2-naphthaldehyde in cyclohexane and the shifted triplet–triplet absorption spectrum of naphthalene in Figure 13 (—). Comparison of the experimental REP of the 1310-cm^{-1} transient Raman line (+) of 2-naphthaldehyde in cyclohexane with the transform of the difference spectrum (---).

transformation of the shifted naphthalene spectrum is shown in Figure 13. It can be seen, from Figures 13 and 14, that the experimental transient absorption spectrum of 2-naphthaldehyde in cyclohexane in Figure 3 may be considered reasonably well as the superposition of the shifted triplet absorption spectrum of naphthalene in cyclohexane and the tail of an absorption, which increases toward short wavelengths. When this tail is transformed into a REP for a 1310-cm^{-1} Raman line the REP shown in Figure 14 is obtained. The REP in Figure 14 predicts an enhancement of the Raman line intensity by a factor of 2 when λ changes from 435 to 380 nm. Since for λ = 380 nm all transient Raman lines have zero intensity, it must be concluded that the scaling factor used to relate the REP to the absolute cross section for Raman scattering[17] is negligibly small for the second type of triplet species.

The agreement between the transformed shifted triplet naphthalene spectrum and the experimental REP, shown in Figure 13, leads to the conclusion that the transient Raman scatterer resembles triplet-state naphthalene in a spectroscopic sense.

A number of possible explanations for the resemblance will be discussed by referring to the initial and final electronic state of the triplet–triplet absorption band of 2-naphthaldehyde as T_i and T_f, respectively. The enhancement in resonance Raman transition probability for a particular vibrational mode arises when two conditions are met simultaneously. These are the requirement of a large oscillator strength of the transition from T_i to T_f and non-zero Franck–Condon factors for the specified mode. The latter condition is equivalent to the requirement of a displacement of the normal coordinate and/or a frequency change of the mode, in going from T_i to T_f. The absence of the aldehyde vibrational modes in the resonance Raman spectrum of triplet-state 2-naphthaldehyde means that the latter condition is not satisfied for these modes. There are two situations in which this may happen and in which a triplet–triplet absorption spectrum resembling that of naphthalene will be observed. The electronic excitation has to be localized on the naphthyl group both in the state T_i and in the state T_f, and the molecular geometry must be the same in the two states, since otherwise the oscillator strength for the transition between these states would be negligable. In one situation the molecule is fully planar and in the other one the naphthyl group and the aldehyde group are mutually perpendicular. A quantum chemical calculation may help to discriminate between these two possibilities.

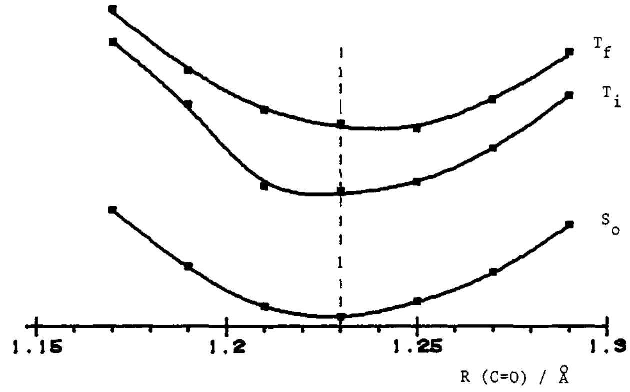

Figure 15. Calculated potential energy curve for the C=O stretching mode in the electronic ground state and the initial (T_i) and final (T_f) state of the triplet–triplet absorption band of planar 2-naphthaldehyde.

The energy spacing and the oscillator strengths for transitions between states in the triplet manifold of fully planar 2-naphthaldehyde have been calculated with the semiempirical CNDO/S-CI program.[18] Sixty singly excited configurations are included in the configuration interaction. The lowest triplet state is found to be a $\pi\pi^*$ state, which may be identified with T_i. The first two higher lying triplet states which carry nonnegligable oscillator strength are calculated to be about 3.6 and 3.7 eV above T_i. They carry oscillator strength of 0.24 and 0.18, respectively, at a C=O distance of 1.23 Å and they will be referred to as T_f and $T_{f'}$. The potential energy curve for the C=O stretching mode in the electronic ground state has been calculated with the semiempirical MNDO program.[19] The potential energy curves for this mode in the states T_i, T_f, and $T_{f'}$, are obtained by adding the energy of the ground state to the calculated energy spacings between the ground state and the triplet states. The experimental value of the C=O equilibrium bond distance for the ground state is reproduced by the MNDO calculation. Since all the potential energy curves (Figure 15) are displaced and distorted relative to each other, none of the excited states may be regarded as a state with the excitation localized on the naphthyl ring. The changes in bond length are not small compared to, e.g., the change of 0.04 Å in the C–C bond length in benzene, when it is brought from the ground state to its first excited singlet state.[20] Therefore the situation of non-coplanarity must be the one that is actually encountered in the states T_i and T_f. This conclusion may be verified by inspecting the variations in the oscillator strength of the T_i–T_f transition with variations of the C=O and C—C bond lengths in both the planar and nonplanar forms of 2-naphthaldehyde. In the planar form the oscillator strength changes 7% with a 5% change in the length of the C=O bond and it changes 1% with a 1% variation in all the C—C bond lengths in the naphthyl group. In the nonplanar form the corresponding vari-

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ations in the oscillator strength are 0% and 0.7%, respectively.

The fact that there are two metastable triplet states, which are not in thermal equilibrium at 300 K, must be interpreted as a consequence of a high potential energy barrier, separating a planar and a twisted form of the triplet-state molecule.

Transient Dielectric Loss Measurements. In order to find out whether or not the triplet with the nonplanar geometry has to be characterized as a twisted intramolecular charge-transfer state,[21] its contribution to the transient dielectric loss of the solution has been investigated. A small laser-induced transient dielectric loss of a solution of 2-naphthaldehyde in cyclohexane is observed at 10.04 GHz. The decay time of the signal is (360 ± 50) ns, which is equal to τ_1^a, i.e., the lifetime of the triplet-state Raman scatterer. The transient dielectric loss must therefore arise from the latter type of species. The signal is small compared to that encountered for similar concentrations of transient species, which have similar dipole relaxation times, but transient changes of molecular dipole moments of 10 D.[22] The difference $\Delta\mu$ between the dipole moment μ_T in the triplet state and μ_G in the ground state is evaluated in the usual manner.[8] A value $\Delta\mu \leq 4$ D is obtained by taking the relaxation time τ equal to 60 ps and the triplet quantum yield $\phi_T = 0.7$.[10] This means that the state does not have charge-transfer character. The lack of charge-transfer character is in agreement with the large difference between the observed transient absorption spectrum and the spectra of the radical cation and radical anion of naphthalene.[23]

Conclusion

Two electronic triplet states of 2-naphthaldehyde get populated at 300 K by optical excitation into the singlet manifold. One of these states resembles the lowest triplet state of naphthalene and it is considered to be a $\pi\pi^*$ state with the excitation localized on the naphthyl group. The resonance Raman spectrum of the molecule in this state does not reveal the C=O stretching vibration, because of non-coplanarity of the aldehyde and the naphthyl group.

A forthcoming paper will discuss the effect of isotopic substitutions in the triplet-state resonance Raman spectra of 2-naphthaldehyde.

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Kinetic Analysis of Association Processes between Oppositely Charged Polymer Latex Particles

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Abstract: The association processes between oppositely charged polymer latex particles could be directly studied by using an ultramicroscope connected to an image-processing system and also spectrophotometric techniques. The relaxation times obtained by the two methods were in good agreement. The forward rate constants (k_f) of the association of latex particles obtained from the slope of the plots of the reciprocal relaxation time vs. concentration of latex particles in excess were unexpectedly close to, but slightly smaller than, the theoretical values for the diffusion-controlled association process of neutral species. The k_f values were obviously in disagreement with the theoretical values calculated by the theory developed on the point charge approximation. The disagreement persisted even when the counterion association is taken into consideration. The enthalpy and entropy of activation were larger than the theoretical values calculated for diffusion-controlled processes.

The kinetic studies of chemical reactions in general have been performed by measuring the time changes of parameters associated with the reactions. The spectrophotometry is, for example, based on the change of absorbance of reactants and/or products in the course of the reactions. The underlying assumption is that the absorbance is strictly proportional to the concentration of the species in consideration. This assumption would be intrinsically correct in dilute regions. Although we are not questioning the validity of this assumption, it would be quite interesting if we could study various kinetic laws without introducing the assumption. In the present paper, we take the advantage of polymer latex particles being large enough to be seen by an ultramicroscope and carry out a kinetic (naked-eye) study of the association between oppositely charged latex particles as the first of the series of our investigation.

This study also has another significance in colloid science. Polymer latices have been widely used in the diagnosis of various kinds of diseases,[1-3] and even in the therapy of cancers.[4] In the actual diagnosis of diseases, the recognition and estimation of specific compounds in biological samples can be carried out with agglutination methods. Agglutination of latex particles with many electric charges by the increase in ionic strength has been studied extensively.[5,6] However, the basic nature of the association

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