Determination of Delayed Fluorescence of Tetraphenylethylene in Solvents Less Viscous and Less "Polar" than Hexane. A Study in Near-Critical Liquid Ethane and Carbon Dioxide

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Abstract: Fluorescence spectra and quantum yields of tetraphenylethylene (TPE) are determined in near-critical liquid ethane, CO_2, and their mixtures with hexane at room temperature. Because of the low viscosity and small dielectric constant of the solvent, which suppresses the prompt fluorescence and enhances the delayed fluorescence, the observed emission band in ethane is the delayed fluorescence spectrum of TPE. The results provide strong evidence for the delayed fluorescence mechanism of TPE and for the proposed zwitterionic character of the twisted excited state.

Introduction

The photophysics and photochemistry of stilbene, which serve as an excellent model for photoisomerization, have attracted considerable attention.[1] In an attempt to examine other arylalkene systems related to stilbene, there have been a number of recent photophysical studies of tetraphenylethylene (TPE)[2-8] whose excited state processes are also characteristic. Upon ultraviolet excitation the vertically excited state of TPE in solution is short lived (5-15 ps),[3] presumably due to a fast twisting of the central bond to form an excited state intermediate $^1p^*$ with the perpendicular geometry (Figure 1). The fluorescence of TPE is weak in a room-temperature solution ($\Phi_F = 2 \times 10^{-3}$ in hexane)[9] and consists of prompt and delayed emissions. It was proposed that the prompt fluorescence is from both the vertically excited state and a nearly planar excited state,[7] and the delayed fluorescence is due to a thermal repopulation of the nearly planar excited state from the twisted state $^1p^*$.[7,8] The thermally delayed process is facilitated by the long $^1p^*$ state lifetime in nonpolar solvents (1.7 ns in pentane and 1.5 ns in hexane). However, because the $^1p^*$ state is most likely zwitterionic[4-6,8] (as a result of polarization through twisting),[10] its lifetime decreases dramatically in a polar solvent.[4] The decrease of the $^1p^*$ state lifetime can be rationalized by an increase in the radiationless decay rate due to a reduced energy gap between the $^1p^*$ and twisted ground states.[4]

Even in a solvent such as benzene, the thermally delayed process becomes negligible.[8] Because the prompt fluorescence competes with the twisting process and a more viscous solvent hinders the
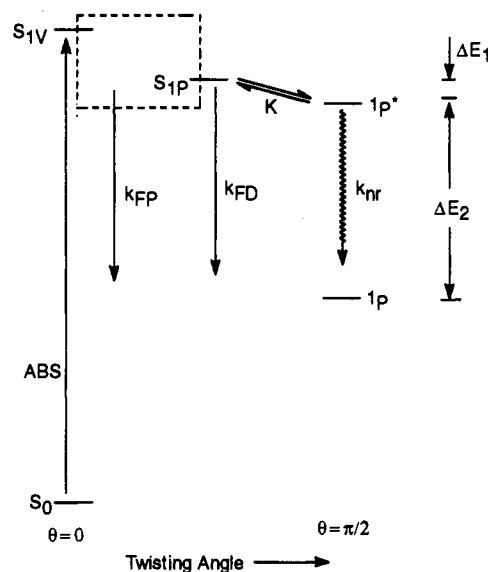

Figure 1. A schematic energy diagram for the photophysics of TPE, where k_{FP} and k_{FD} denote prompt and delayed emissions, respectively. Although relaxation of the phenyl groups plays an important role, it is not included for simplicity.

twisting motion, the yield of the prompt emission increases with increasing solvent viscosity. While a determination of the prompt fluorescence spectrum can readily be accomplished by studying TPE in a polar and, preferably, viscous solvent,[8] an isolation of the delayed fluorescence band from observed spectra in commonly employed nonpolar solvents is not straighforward. In order to determine experimentally the delayed fluorescence spectrum of TPE, a solvent that is less "polar" and less viscous than hexane or pentane is required. A lower "polarity" enhances the thermally activated process and a smaller solvent viscosity suppresses the prompt emission. In this regard, a supercritical or subcritical fluid serves as a unique vehicle for such an investigation. For near-critical liquid ethane at 20 °C and 1000 Psia, the dielectric constant (1.49) and viscosity (0.04 cP)[11] are only 78% and 13% of those of hexane, respectively.

In this paper, we report a fluorescence study of TPE in near-critical liquid ethane, CO_2, and their mixtures with hexane at room temperature (20 °C). The use of subcritical rather than

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(1) For several recent reviews see: (a) Waldeck, D. H. *Chem. Rev.* **1990**, *91*, 415. (b) Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (c) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691. (d) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford: New York, 1986.

(2) (a) Stegemeyer, H. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 335. (b) Leigh, W. J.; Arnold, D. R. *Can. J. Chem.* **1981**, *59*, 609. (c) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311.

(3) (a) Barbara, P. F.; Rand, S. D.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 2156. (b) Greene, B. I. *Chem. Phys. Lett.* **1981**, *79*, 51.

(4) Schilling, C. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 2296.

(5) Morais, J.; Ma, J.; Zimmt, M. B. *J. Phys. Chem.* **1991**, *93*, 3885.

(6) Sun, Y.-P.; Fox, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 747.

(7) Ma, J.; Zimmt, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 9723.

(8) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; de Haas, M. P.; Vermeulen, M. J. W.; Jager, W. F.; de Lange, B.; Feringa, B. L.; Fessenden, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 3286.

(9) Bunker, C. E.; Hamilton, N. B.; Sun, Y.-P. *Anal. Chem.* **1993**, *65*, 3460.

(10) (a) Dauban, W. G.; Ritscher, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 2925. (b) Salem, L. *Acc. Chem. Res.* **1978**, *12*, 87.

(11) The dielectric constant was calculated from a modified Clausius–Mosotti equation (Younglove, B. A.; Ely, J. F. *J. Phys. Chem. Ref. Data* **1987**, *16*, 577). The viscosity was obtained from the Jossi–Stiel–Thodos method (Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987).
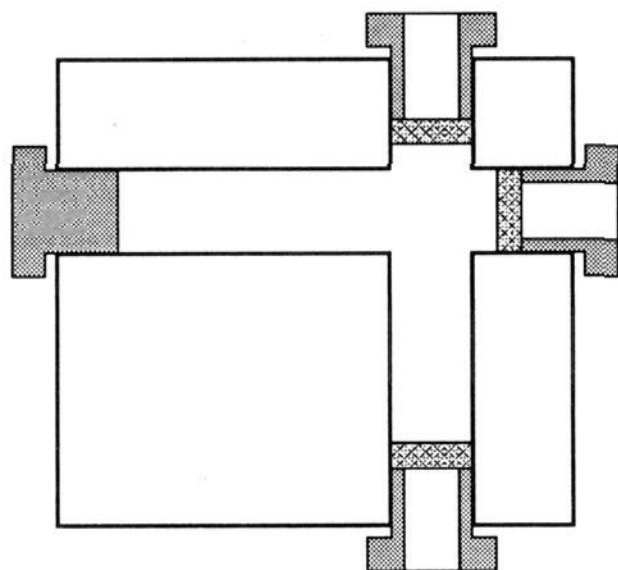
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Figure 2. A schematic diagram of the high-pressure optical cell.

supercritical fluids is to maintain the room-temperature condition, so that the results can be compared with those from normal room-temperature solutions. The delayed fluorescence spectrum and quantum yield of TPE are determined. The results provide strong evidence in support of the proposed delayed fluorescence mechanism of TPE.[7,8]

Experimental Section

Materials. TPE (Aldrich 98%) was repeatedly recrystallized from hexane and ethanol. Spectrophotochemistry grade hexane, cyclohexane, THF, dichloromethane (all from Burdick & Jackson), and ethanol (Curtin Matheson Scientific) were used as received. Ethane (Air Products 99%), CO_2 (Air Products, 99.9999%), and trifluoromethane (MG Industries, >98%) were purified by being passed through a column filled with silica gel and activated carbon and an oxygen trap (Alltech).

Measurements. Absorption spectra were obtained using a computer-controlled Shimadzu UV-2101PC UV/vis spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source and a R928 photomultiplier tube. The measurements were made in a right-angle geometry using a high-pressure optical cell (Figure 2). The cell body was made from stainless steel. Three quartz windows (12.7 mm diameter and 5 mm thick) on the cell were sealed with Teflon O-rings. The optical paths of the cell for fluorescence and absorption measurements were 7.5 and 35 mm, respectively. System pressure was generated by a syringe pump and was monitored by a pressure gauge (Heise 901A). All fluorescence spectra were corrected for nonlinear instrument response[12] (different intensities of the light source and different sensitivities of the monochromators at different wavelengths) using predetermined correction factors. Fluorescence quantum yields were determined using integrated spectral area. Because TPE undergoes photochemical reactions,[9,13-15] special efforts were made to protect the sample from excessive irradiation by using a small excitation slit width (0.5 mm) and by recharging the optical cell after each fluorescence scan.

Under our experimental conditions, ethane–hexane, ethane–ethanol, and CO_2–hexane mixtures always remain single phase.[16]

Results and Discussion

The fluorescence spectrum of TPE in ethane at room temperature is shown in Figure 3. It is expected that the spectrum is due exclusively to the delayed emission. In room-temperature hexane, an equilibrium between the emitting nearly planar and
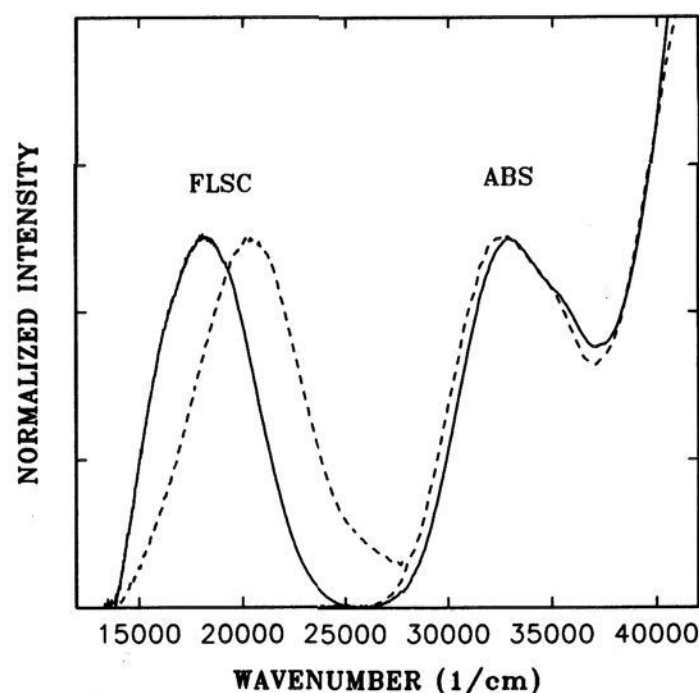
(12) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.

(13) As reported in ref 9, fluorescence of the photoproduct 9,10-diphenylphenanthrene can be observed after irradiation of TPE in a single fluorescence scan.

(14) Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094.

(15) Olsen, R. J.; Buckles, R. E. *J. Photochem.* **1979**, *10*, 215.

(16) (a) Schneider, G. M. In *Extraction with Supercritical Gases*; Schneider, G. M., Stahl, E., Wilke, G., Eds.; Verlag Chemie: Weinheim, 1980; p 45. (b) Zais, E. J.; Silberberg, I. H. *J. Chem. Eng. Data* **1970**, *15*, 253. (c) Shenderei, E. R.; Ivanovskii, F. P. *Khim. Prom.* **1964**, *7*, 506.

Figure 3. Fluorescence spectra of TPE (λ_{exc} = 340 nm) in ethane at room temperature and 700 Psia (—) and in dichloromethane (- - -), which are the delayed and prompt fluorescence spectra of TPE, respectively. The spectra are corrected for nonlinear instrument response. Their corresponding absorption spectra are also shown for comparison.

the $^1p^*$ states was proposed and contribution of the delayed emission to the observed spectrum was estimated to be 80–85%.[7,8] The yields of prompt and delayed emissions (Figure 1) can be represented as the following:

$$\Phi_{FP} = k_{FP}/(k_{FP} + k_t + k_{cr}) \quad (1)$$

$$\Phi_{FD} = k_{FD}/(k_{FD} + k_{nr,D} + k_{nr}/K) \quad (2)$$

where k_t and k_{cr} are the twisting and chemical reaction rate constants of the vertically excited state, rspectively, and $k_{nr,D}$ is the radiationless decay rate constant for the nearly planar emitting state. The equilibrium constant K is a function of the energy gap ΔE_1 (Figure 1),

$$K = \exp(-\Delta G_1/RT) \approx \exp(-\Delta E_1/RT) \quad (3)$$

where ΔG_1 is the corresponding free energy difference. In terms of radiationless decay theories,[17] the radiationless decay rate constant of the $^1p^*$ state k_{nr} depends on the energy gap ΔE_2 (Figure 1),

$$1/\tau \approx k_{nr} \approx k_0 \exp(-a\Delta E_2) \quad (4)$$

where τ is the $^1p^*$ state lifetime, and k_0 and a are constants. It is obvious from eqs 3 and 4 that small changes in ΔE_1 and ΔE_2 will result in significant changes in K and τ because of exponential functions. A decrease in dielectric constant and refractive index from hexane to ethane causes an increase in $^1p^*$ state energy and, consequently, a decrease of ΔE_1 and an increase of ΔE_2. Both energy gap changes enhance the delayed fluorescence (eq 2) because of an increase in K (eq 3) and a decrease in k_{nr} (eq 4).

Changes in solvent dielectric constant and refractive index may also affect the twisting from the vertically excited state. However, we expect the effects to be small because TPE at geometries of and close to the vertically excited state is much less polar.[3,4] For *trans*-stilbene, it was argued that polarity effects could cause a decrease in the intrinsic energy barrier for twisting

(17) (a) Siebrand, W. *J. Chem. Phys.* **1967**, *46*, 440. (b) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (c) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (d) Casper, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (e) Casper, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. (f) Casper, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

from the vertically excited state to the perpendicular geometry, resulting in a lower fluorescence quantum yield.[1a,b,18] However, such an argument is hardly applicable to TPE because the twisting in TPE is likely not subject to an intrinsic potential energy barrier.[3]

The viscosity of ethane (~0.04 cP) is also much lower than that of hexane, resulting in a significantly smaller prompt fluorescence yield. Considering the combined effects of smaller solvent "polarity" and lower viscosity, it can be concluded that the observed emission band in ethane is the delayed fluorescence spectrum of TPE (Figure 3). In order to further confirm this conclusion, a small amount of ethanol (~10% v/v) was added to the ethane solution to increase solvent polarity while the low viscosity environment was maintained. With the delayed emission completely quenched as a result of the high solvent polarity, the fluorescence spectrum due to residual prompt emission became so weak that it was barely distinguishable from background noise. Because the addition of ethanol to ethane increases the solvent viscosity somewhat, which is in favor of the prompt fluorescence, an even smaller contribution from prompt fluorescence in neat ethane should be expected. For a comparison, significant prompt fluorescence of TPE in a hexane–ethanol mixture was observed. Results from a study of TPE in an ethane–trifluromethane mixture also support the conclusion.

Fluorescence quantum yields in ethane and ethane–hexane mixtures were determined in reference to TPE in a hexane solution in order to examine gradual changes of TPE emission properties with decreasing solvent viscosity and "polarity" (Figure 4). Measurements of the reference were also made in the high-pressure cell in order to maintain the same experimental conditions. After a correction for refractive index according to the following equation,[12]

$$\Phi_{F,ethane}/\Phi_{F,hexane} = (F_{A,ethane}/F_{A,hexane})(n_{hexane}/n_{ethane})^2 \quad (5)$$

where F_A is the ratio between the integrated fluorescence spectral area and the optical density at the excitation wavelength, the yield in ethane is ~10% higher than that in hexane. This corresponds to a 30–40% increase of delayed fluorescence yield from hexane to ethane. The increase is a combined result of a longer $^1p^*$ state lifetime and a smaller energy gap between the emitting nearly planar and the $^1p^*$ states, consistent with the conclusion discussed above. As the composition of hexane increases in an ethane–hexane mixture, the yield quickly approaches the value in neat hexane. It seems that the polar excited state $^1p^*$ is preferentially solvated by hexane molecules in an ethane–hexane mixture. The quantum yield results at two different pressures follow the same trend, indicating that effects due to a change of pressure are small under our expermental conditions.

Fluorescence quantum yields of TPE were also determined in CO_2 and CO_2–hexane mixtures (Figure 4). Although the dielectric constant of CO_2 (1.5 at 20 °C and 2000 Psia) is close to that of ethane, the fluorescence yields are quite different. As the composition of CO_2 in the mixtures increases, the fluorescence yield decreases significantly. The yield in neat CO_2 is less than 20% of that in hexane. It seems that CO_2 behaves like a polar solvent, stabilizing a polar twisted excited state. Such unusual solvent effects of CO_2 have also been observed in systems that form a twisted intramolecular charge transfer state (TICT). For ethyl p-(N,N-dimethylamino)benzoate, TICT state formation can be observed in condensed CO_2 but not in hexane.[19] For ethyl p-(N,N-diethylamino)benzoate, solvent effects on TICT state formation in supercritical ethane and CO_2 are also quite different,

ETHANE–HEXANE
(HEXANE %)
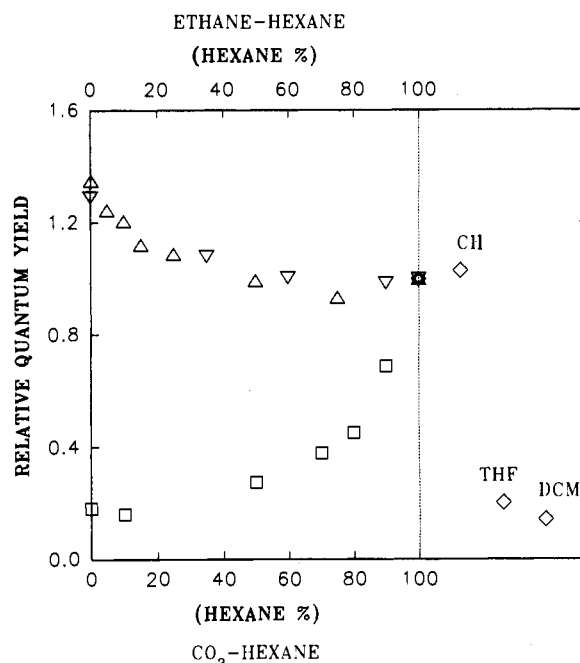
Figure 4. Relative fluorescence quantum yields of TPE (λ_{exc} = 340 nm) in ethane and ethane–hexane mixtures (▽, 700 Psia; △, 2000 Psia) and in CO_2 and CO_2–hexane mixtures (□, 2000 Psia) at room temperature (20 °C). Results in cyclohexane (CH), THF, and dichloromethane (DCM) are also shown for comparison. The quantum yield values are not corrected for the difference in solvent refractive index because an estimation of refractive indexes of the mixtures is hindered by local composition effects.

Table 1. Absorption and Fluorescence Spectral Parameters

solvent	ν_{max}^{ABS} (cm^{-1})^a	ν_{max}^{FLSC} (cm^{-1})	fwhm (cm^{-1})^b
ethane	32800	18200	5650
hexane	32400	17900	5800
dichloromethane	33000	20400	6100

^{a} First absorption band maximum. ^{b} Full width at half maximum of the fluorescence band.

with CO_2 again acting like a polar solvent.[20] These results are in general agreement with what can be expected on the basis of $E_t(30)$ values of CO_2 and hexane.[21] The large quadrapole moment of CO_2 may have played a role in the solute–solvent interactions.[22]

It is also interesting that the prompt and delayed fluorescence spectral shapes are rather similar (Figure 3), suggesting that the geometries of their corresponding emitting states are close. The emitting states are probably shallow minima on the excited state potential energy surface, which are subject to solvent friction effects.

While the delayed fluorescence is red shifted from the prompt fluorescence in a spectral mixture,[7,8] the spectrum in ethane (due to delayed emission) is actually slightly blue shifted from the spectrum in hexane, which consists of both delayed and prompt emissions (Table 1). It suggests that the delayed fluorescence spectrum blue shifts with decreasing solvent viscosity, similar to the prompt fluorescence band.[8] The shifts cannot be explained by a change in the degree of hindrance to the rotational relaxation of the phenyl groups because less hindrance as a result of lower solvent viscosity should result in a spectral red shift.[3] Although a determination of the causes for the characteristic shifts is probably difficult, one rationalization could be made according to a viscosity enhanced barrier model, in which solvent effects are treated empirically as a modification to the intrinsic potential

(18) (a) Hicks, J. M.; Vandersall, M. T.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1987**, *135*, 413. (b) Sundström, V.; Gillbro, T. *Chem. Phys. Lett.* **1984**, *109*, 538. (c) Akesson, E.; Bergström, H.; Sundström, V.; Gillbro, T. *Chem. Phys. Lett.* **1986**, *126*, 385.

(19) Sun, Y.-P.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1992**, *114*, 1187.

(20) Bunker, C. E.; Bowen, T. L.; Sun, Y.-P. Manuscript in preparation.
(21) Reichardt, C. *Solvent and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.
(22) Hirshfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; John Wiley & Sons: New York, 1954.

energy surface.[23,24] As viscosity decreases, the solvent induced changes to the excited state energy surface cause a slight shift of the emitting state minimum away from the twisted geometry. While a shift of excited state energy due to such a small geometry change is probably trivial, a change in the energy gap between excited and ground states is significant because of the steep slope of the ground state energy surface around the emitting state geometry. A blue shift of the emission band is thus observed.

In conclusion, near-critical liquid ethane as a truly nonpolar room-temperature solvent serves as a unique medium for the determination of the TPE delayed fluorescence spectrum. The results provide strong evidence not only for the delayed fluorescence mechanism of TPE but also for the proposed zwitterionic character of the twisted excited state.

(23) (a) Dellinger, B.; Kasha, M. *Chem. Phys. Lett.* **1975**, *36*, 410, **1976**, *38*, 9. (b) Henry, B. R.; Mohammadi, M. A.; Thomson, J. A. *J. Chem. Phys.* **1981**, *75*, 3165.

(24) (a) Saltiel, J.; Sun, Y.-P. *J. Phys. Chem.* **1989**, *93*, 6246. (b) Sun, Y.-P.; Saltiel, J.; Hoburg, E. A.; Park, N. S.; Waldeck, D. H. *J. Phys. Chem.* **1991**, *95*, 10336.