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Picosecond Transient Absorption Study of the Twisted Excited Singlet State of Tetraphenylethylene in Supercritical Fluids

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Abstract: Picosecond transient absorption spectra and decay kinetics are described for the twisted excited state $^1p^*$ of tetraphenylethylene (TPE) in supercritical fluid–cosolvent mixtures. Microscopic solvation is probed by monitoring fluorescence of the TICT state of ethyl (*N*,*N*-dimethylamino)benzoate. The decay rate constant of the TPE $^1p^*$ state correlates well with solvent-induced changes in the excited-state–ground-state energy gap, as predicted by radiationless relaxation theories.

Introduction

A characteristic property of ethylene and substituted ethylenes is their photoisomerization.[1] Upon excitation the bond order of the olefinic carbon–carbon bond in these molecules is substantially reduced, and the excited singlet relaxes by twisting about the central bond to form an intermediate $^1p^*$ state at a perpendicular geometry. The $^1p^*$ state then decays to the ground-state energy surface, yielding both cis and trans isomers.

The character of the $^1p^*$ state in simple olefinic molecules has been the subject of debate.[1a,2] It seems established that the $^1p^*$ state in ethylene and simple alkenes is zwitterionic, a result of "sudden polarization".[3] However, this notion may not be equally applicable to longer chain polyenes or aryl-substituted ethylenes because in such compounds an excited diradical state could cross the zwitterionic surface to represent the lowest energy state at the perpendicular geometry.[1a,4] In the most extensively studied disubstituted ethylene, stilbene, the assignment of the electronic character of the $^1p^*$ state is inconclusive at best[1a] because experimental determination has been hindered by the very short lifetime of the $^1p^*$ state.[5] An understanding of the polar character of the excited states of extended polyenes is particularly important in understanding third-order nonlinear optical properties of such systems.

In tetraphenylethylene (TPE), another extensively studied substituted ethylene,[6-8] a polar $^1p^*$ state has been established by a recent report[7] of a strong dependence of the $^1p^*$-state lifetime on solvent polarity. It was proposed[7] that the decreasing $^1p^*$-state lifetime with increasing solvent polarity was consistent with radiationless relaxation theories,[9] provided that the $^1p^*$ state was zwitterionic. In that context, the decrease of the $^1p^*$-state lifetime was attributed to a decrease in the $^1p^*$–^1p energy gap (where ^1p is the twisted ground state), resulting from dipolar stabilization of the polar $^1p^*$ state in polar solvents.

The notion of a zwitterionic $^1p^*$ state in TPE is also supported by a recent picosecond optical calorimetry study.[8] A decrease in the $^1p^*$-state lifetime of TPE (from 1.68 ns in pentane to 91 ps in tetrahydrofuran, THF) is accompanied by an energy gap decrease from 66.8 ± 1.1 to 65.3 ± 1.7 kcal/mol. However, the relatively small change in $^1p^*$ energy with solvent change and the relatively large reported experimental uncertainties make this interpretation less conclusive than desirable.

Since supercritical fluids are known as nearly tunable media with their polarity varying continuously with density,[10] they are particularly amenable to studies of polarity effects on chemical processes. In fact, supercritical fluids,[11] mixtures of supercritical fluids,[12] and supercritical fluid–cosolvent systems[13] have been widely used in this regard.

In addition to its tunable nature, a supercritical fluid also imposes a very special local solvent effect on some solutes, known as solute–solvent clustering.[11,14] It has been shown[15,16] that this unusual clustering behavior has a profound impact on the formation and decay of the twisted intramolecular charge-transfer state (TICT) in molecules like (*N*,*N*-dimethylamino)benzonitrile (DMABN) and ethyl (*N*,*N*-dimethylamino)benzoate (DMAEB).[17]

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(1) For reviews, see: (a) Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (b) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415. (c) Allen, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691. (d) Ross, D. L.; Blanc, J. In *Photochromism*; Brown, G. H., Ed.; Wiley: New York, 1971; p 471.

(2) (a) Tavan, P.; Schulten, K. *Chem. Phys. Lett.* **1978**, *56*, 200. (b) Orlandi, G.; Palmieri, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492. (c) Hohlneicher, G.; Dick, B. *J. Photochem.* **1984**, *27*, 215. (d) Hicks, J. M.; Vandersall, M. T.; Sitzman, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1987**, *135*, 413.

(3) (a) Dauben, W. G.; Ritscher, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 2925. (b) Dauben, W. G.; Kellog, M. S.; Seeman, J. I.; Wietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 197. (c) Salem, L. *Acc. Chem. Res.* **1978**, *12*, 87. (d) Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170.

(4) (a) Malrieu, J. P.; Nebot-Gil, I.; Sanchez-Marin, J. *Pure Appl. Chem.* **1984**, *56*, 1241. (b) Nebot-Gil, I.; Malrieu, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 3320.

(5) (a) Doany, F, E.; Hochstrasser, R. M.; Greene, B. I.; Millard, R. R. *Chem. Phys. Lett.* **1985**, *118*, 1. (b) Repinec, S. T.; Sension, R. J.; Szarka, A. Z.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 10380.

(6) (a) Greene, B. I. *Chem. Phys. Lett.* **1981**, *79*, 51. (b) Barbara, P. F.; Rand, S. D.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 2156. (c) Stegemeyer, H. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 335. (d) Leigh, W.; Arnold, D. R. *Can. J. Chem.* **1981**, *59*, 3061. (e) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311.

(7) Schilling, C. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1987**, *110*, 2296.

(8) Morais, J.; Ma, J.; Zimmt, M. B. *J. Phys. Chem.* **1991**, *95*, 3885.

(9) (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.

(10) For reviews, see: (a) Paulaitis, M. E.; Krukonis, V. J.; Kurnik, R. T.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1*, 179. (b) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction—Principles and Practice*; Butterworths: Boston, 1986. (c) Johnston, K. P.; Kim, S.; Combes, J. *Am. Chem. Soc. Symp. Ser.* **1989**, *406*, 52. (d) Shaw, R. W.; Briil, T. B.; Clifford, A. A.; Eckert, C. A. *Chem. Eng. News* **1991**, *69* (51), 26 and references therein.

(11) (a) Brennecke, J. F.; Eckert, C. A. *Am. Chem. Soc. Symp. Ser.* **1989**, *406*, 14. (b) Brennecke, J. F.; Tomasko, D. L.; Peshkin, J.; Eckert, C. A. *Ind. Eng. Chem. Res.* **1990**, *29*, 1682. (c) Smith, R. D.; Frye, S. L.; Yonker, C. R.; Gale, R. W. *J. Phys. Chem.* **1987**, *91*, 3059. (d) Betts, T. A.; Bright, F. V. *Appl. Spectrosc.* **1990**, *44*, 1196, 1203. (e) Hrnjez, B. J.; Mehta, A. J.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1989**, *111*, 2662. (f) O'Shea, K. E.; Kirmse, K.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1991**, *95*, 7863. (g) O'Shea, K. E.; Combes, J. R.; Fox, M. A.; Johnston, K. P. *Photochem. Photobiol.* **1991**, *54*, 571.

(12) (a) Sun, Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *Anal. Chem.* **1992**, *64*, 1763. (b) Sun, Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* In press.

(13) (a) Johnston, K. P.; Peck, D. G.; Kim, S. *Ind. Eng. Chem. Res.* **1989**, *28*, 1115. (b) Kim, S.; Johnston, K. P. *AIChE J.* **1987**, *33*, 1603. (c) Dobbs, J. M.; Wong, J. M.; Lahiere, R. J.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 56.

(14) (a) Kim, S.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 1206. (b) Brennecke, J. F.; Eckert, C. A. *AIChE J.* **1989**, *35*, 1409. (c) Brennecke, J. F.; Tomasko, D. L.; Eckert, C. A. *J. Phys. Chem.* **1990**, *94*, 7692. (d) Cochran, H. D.; Lee, L. L. *Am. Chem. Soc. Symp. Ser.* **1989**, *406*, Chapter 3. (e) Debenedetti, P. G.; Mohamed, R. S. *J. Chem. Phys.* **1989**, *90*, 4528. (f) Shing, K. S.; Chung, S. T. *J. Phys. Chem.* **1987**, *91*, 1674.

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

(16) (a) Kajimoto, O.; Futakami, M.; Kobayashi, T.; Yamasaki, K. *J. Phys. Chem.* **1988**, *92*, 1347. (b) Morita, A.; Kajimoto, O. *J. Phys. Chem.* **1990**, *94*, 6420.

(17) (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. (b) Lippert, E.; Rettig, W.; Bonačić-Koutecký, V.; Heisel, F.; Miehé, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.

0002-7863/93/1515-747$04.00/0

Because of solute–solvent clustering in supercritical fluids, solvent effects on the TICT state show a very characteristic density dependence. In supercritical mixtures, emission of the TICT state is also very sensitive to the composition of the mixtures.[12]

The twisted excited state $^1p^*$ in TPE should be very similar to the well-known TICT states in donor–acceptor-substituted molecules like DMABN or DMAEB if the zwitterionic assignment for the $^1p^*$ state is correct. A study of the characteristics of the twisted excited state of TPE in supercritical fluids will allow us to further understand the nature of the twisted intermediate. In this paper, we report a picosecond transient absorption study of TPE in two supercritical fluid–cosolvent systems. DMAEB is employed as a molecular probe, and the results of solvent effects on the $^1p^*$ state of TPE are compared with those on the TICT state of DMAEB in the same media.

Experimental Section

Materials. Tetraphenylethylene (TPE, Aldrich) was used without further purification. Ethyl (dimethylamino)benzoate (DMAEB, Aldrich) was repeatedly recrystallized from ethanol/water before being stored under vacuum for at least 12 h. Tetrahydrofuran (THF, Aldrich, HPLC grade) and *n*-hexane (Baker, Photrex reagent) were used as received. Carbon dioxide (Liquid Carbonic, 99.99%) and trifluoromethane (MG industries, etching grade) were purified on a freshly packed column of activated carbon.

Measurements. The picosecond transient absorption measurements were conducted at the Center for Fast Kinetic Research at the University of Texas at Austin. The experimental setup has been described in detail elsewhere.[19] The excitation source was the third harmonic (355 nm, ~30-ps pulse) of a Quantel YG402 mode-locked Nd:YAG laser. Part of the laser fundamental (1064 nm) was focused through a cell containing a D_2O solution of deuterated phosphoric acid to generate a coherent continuum pulse. A right-angle geometry for the excitation and probing beams was used. The detection unit consisted of two fiber optic conduits connected to photodiode arrays which were balanced before each measurement. Each measurement is an average of 80–150 laser shots.

Steady-state fluorescence spectra of DMAEB were measured on a computer-interfaced SLM Aminco SPF-500C emission spectrophotometer equipped with a 300-W Xe lamp using a right-angle geometry. For spectra of low intensity, the multiple-averaging mode of the instrument was used to minimize noise. The TICT emission band of DMAEB was resolved from the dual fluorescence spectra of the molecule on the basis of a least-squares curve resolution method.[12a]

Both the transient absorption and the steady-state fluorescence measurements were conducted in a high-pressure optical cell which has been described in detail previously.[15,20] Because of difficulties associated with circulation of the sample solution in such a high-pressure optical cell, the transient absorption measurements were made without continuous sample renewal. Possible photodecomposition of the sample by excitation light was minimized by generating a fresh sample for each measurement.

Results

TPE in *n*-Hexane. Upon flash excitation of TPE in *n*-hexane, a transient absorption band ($\lambda_{max} \approx 416$ nm) was observed immediately after the pulse (355 nm, ~30-ps pulse). This band is assigned to the absorption of the $^1p^*$ state of TPE. The band at 630 nm reported earlier[6a] for the nearly planar excited singlet state of TPE is apparently too short-lived (5 ± 1 ps in *n*-hexane)[6a] to be observed under our conditions. The 416-nm transient decays with a time constant of 1.3 ± 0.1 ns.

TPE in CHF_3–*n*-Hexane. Under our experimental conditions, the solubility of TPE at 60 °C in either CO_2 or CHF_3 is low, even at high fluid densities. Since our excitation wavelength (355 nm) is at the red edge of the TPE absorption band, the optical density at the excitation wavelength for TPE in pure supercritical CO_2 or CHF_3 is small, making it nearly impossible to use the setup available to us to conduct a transient absorption measurement. Therefore, a cosolvent was introduced in order to increase solubility.

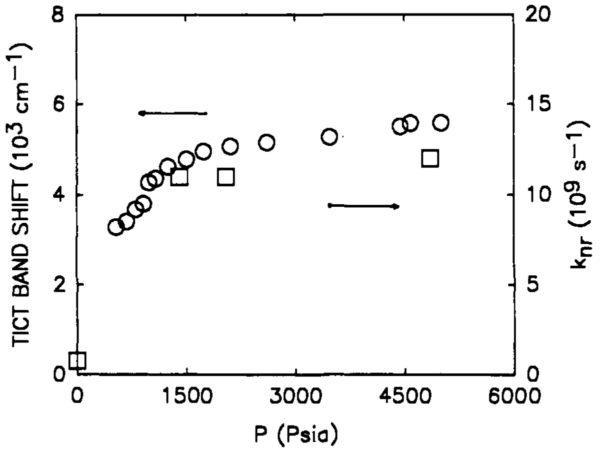

Figure 1. Total pressure dependencies of the radiationless decay rate constant of the $^1p^*$ state in TPE (□) and the bathochromic spectral shifts of TICT emission band maximum in DMAEB (○) in supercritical CHF_3–*n*-hexane mixtures at 60 °C.

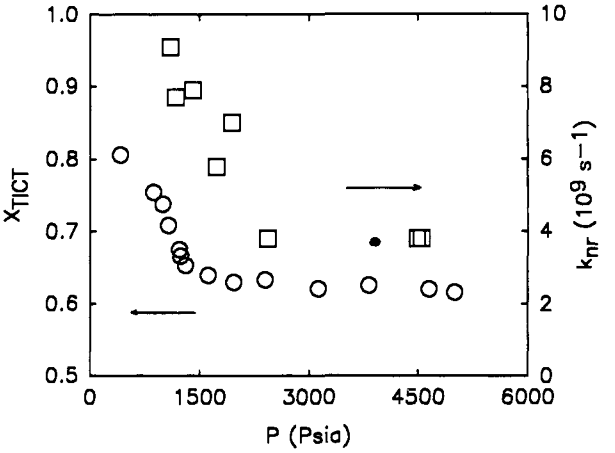

Figure 2. Total pressure dependencies of the radiationless decay rate constant of the $^1p^*$ state in TPE (□) and the relative fluorescence quantum yield of the TICT state in DMAEB (○) in supercritical CO_2–THF mixtures at 60 °C.

For supercritical CHF_3 (highly polar), the nonpolar *n*-hexane was employed as cosolvent. In each measurement, a 1-mL solution of TPE in *n*-hexane (optical density = 2 at 355 nm) was added to the optical cell (3-mL capacity). At 60 °C, CHF_3 was added to the cell using a syringe pump, generating a CHF_3–*n*-hexane cosolvent mixture with defined total pressure. Transient absorption spectra of TPE in this mixture were measured at a series of time delays following an excitation pulse to obtain a decay rate constant. The decay is expected to be dominated by a radiationless transition of the $^1p^*$ state to the twisted ground state ^1p.[6-8]

The $^1p^*$-state lifetime depends on the composition of the CHF_3–*n*-hexane mixtures. Transient absorption spectra and decay kinetics were obtained for TPE in a series of CHF_3–*n*-hexane mixtures corresponding to different total pressures. Upon addition of CHF_3 to the optical cell containing *n*-hexane, the lifetime of the $^1p^*$ state decreases very rapidly from 1.3 ns in neat *n*-hexane to ~90 ps in a CHF_3–*n*-hexane mixture with a total pressure of ~1400 psia, Figure 1. Further addition of CHF_3 hardly changes the $^1p^*$ lifetime at all, and a plateau is formed in the high-pressure region.

TPE in CO_2–THF. In the relatively nonpolar supercritical fluid CO_2, THF was used as cosolvent. For each mixture, 1 mL of an *n*-hexane solution of TPE (optical density = 2 at 355 nm) was introduced into the optical cell. The *n*-hexane was then evaporated with a slow purge of N_2 gas. Next, 0.6 mL of THF was added to the cell before CO_2 was injected via a syringe pump at a cell temperature of 60 °C. Transient absorption spectra and decay

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(18) (a) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. (b) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970. (c) Lippert, E. *Ber. Bunsenges. Phys. Chem.* **1957**, *61*, 962. (d) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 115, 465.

(19) Atherton, S. J.; Hubig, S. M.; Callan, T. J.; Duncanson, J. A.; Snowden, P. T.; Rogers, M. A. *J. Phys. Chem.* **1987**, *91*, 3137.

(20) Yazdi, P. T.; McFann, G. J.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1990**, *94*, 7224.

kinetics of TPE in these mixtures were obtained as above. Shown in Figure 2 is a plot of the ^{1}p*-state decay rate constant against the total pressure.

The ^{1}p*-state lifetime is again dependent on the total pressure. However, the observed dependency is very different from that of TPE in CHF_3–*n*-hexane mixtures. In neat THF, the ^{1}p* state has a lifetime of ~90 ps,[7,8] significantly shorter than that in *n*-hexane. Upon the addition of CO_2, the ^{1}p*-state lifetime increases rapidly to a value of ~260 ps at a total pressure of ~2000 psia. Further increases in total pressure caused by the addition of more CO_2 have very little effect on the ^{1}p*-state lifetime, corresponding to a plateau in the high-pressure region.

Molecular Probe DMAEB in the Mixtures. Since DMAEB is well-known to form a TICT state in supercritical fluids[12,15] and mixtures of supercritical fluids,[12] it can be used as a molecular probe for microscopic solvation of the supercritical fluid–cosolvent mixtures. This TICT state is very polar and is therefore sensitive to changes in solvent properties. The band maximum and relative quantum yield of the TICT emission depend sensitively on the composition of the mixtures.

In the same CHF_3–*n*-hexane mixtures as those studied in the transient absorption measurements of TPE, the relative fluorescence quantum yield of DMAEB TICT state increases with increasing amount of CHF_3 in a mixture until a near plateau is reached at a total pressure of ~1200 psia. A very similar total pressure dependence of the bathochromic shift of the TICT emission band is also observed. As shown in Figure 1, bathochromic shifts of the DMAEB TICT emission band depend on total pressure in the same pattern as the radiationless decay rate constant of TPE in the same mixtures.

Similar measurements were made for DMAEB in CO_2–THF mixtures. In contrast to the effects induced by adding CHF_3 to *n*-hexane, the addition of CO_2 to THF causes a decrease of overall medium polarity. As total pressure increases, corresponding to mixtures containing more and more CO_2, both the bathochromic spectral shifts and the relative quantum yields of DMAEB TICT emission decrease in the same pattern as the observed decreases of radiationless decay rates of TPE in the same mixtures (Figure 2).

Discussion

The transient absorption band for the ^{1}p* state of TPE in *n*-hexane agrees well with the spectrum reported in the literature.[6a,7] However, the lifetime of the transient (1.3 ± 0.1 ns) obtained in our experiment is somewhat shorter than the earlier value of 3.0 ± 0.5 ns[6a] but comparable to a recent value of 1.62 ± 0.05 ns.[8] This is also close to the value of 1.4 ± 0.2 ns obtained in cyclohexane.[7] Therefore, it is likely that the lifetime of the ^{1}p* state of TPE in nonpolar solvents (*n*-hexane and cyclohexane) is around 1.5 ± 0.2 ns.

As in liquid solutions,[7,8] the ^{1}p*-state lifetime of TPE in supercritical fluid–cosolvent mixtures is also very sensitive to changes of medium properties. In CHF_3–*n*-hexane mixtures, as the amount of the polar component CHF_3 in the cell increases (as is induced by an increase of total pressure), the lifetime of the ^{1}p* state becomes shorter as a result of increasing medium polarity. Apparently, the lifetime of the ^{1}p* state is greatly influenced by dipolar solute–solvent interactions, as would be expected with a polar ^{1}p* state.[7,8]

In CO_2–THF mixtures, two opposite effects accompany the addition of the nonpolar component CO_2 to the cell containing a THF solution of TPE. As more and more CO_2 is added, the medium polarity should decrease because of the presence of more and more nonpolar component CO_2. However, the decrease is somewhat offset by an opposite effect caused by an increase in total pressure. It is obvious from Figure 2 that the net result of these two opposite effects must be a decrease of medium polarity, resulting in an increase of the ^{1}p*-state lifetime.

According to radiationless relaxation theories,[9] the radiationless relaxation rate constant k_{nr} between states separated by an energy gap (ΔE) can approximately be expressed as[9,21]

$$\ln k_{nr} = A\Delta E + B \qquad (1)$$

where A and B are treated as ΔE-independent constants.[21] For the ^{1}p* state in TPE in solution, $\Delta E = \Delta E_0 + \Delta E_s$. Here ΔE_0 is the ^{1}p*–^{1}p energy gap in the absence of a solvent, and ΔE_s, the solvent-induced energy gap change, is strongly dependent on the medium polarity.

A quantitative evaluation of the polarity of a supercritical fluid–cosolvent mixture requires information on the density and composition of the mixture. Determination of such parameters for the mixtures used in this study might be possible, at least in principle, by employing a well-behaved equation of state[12b,22] along with an appropriate mixing rule,[22] but the prediction of mixture properties entirely on the basis of properties of individual components can hardly be quantitative. Even if such an approach were successful, the parameters thus obtained would reflect only the macroscopic polarity of a mixture, which is quite different from the microscopic polarity experienced by solutes in the mixtures. In these media, microscopic solvation plays a predominant role in solute–solvent interactions, especially in the near-critical density region.[10,12,15]

Since a direct quantitative characterization of microscopic polarity effects and solvation based on macroscopic properties of the mixtures is very difficult, a well-characterized molecular probe DMAEB was employed in this study to "measure" the microscopic properties of the mixtures used for TPE. We assume that the ^{1}p* state in TPE and the TICT state in DMAEB experience nearly equivalent microscopic solvation in the same supercritical fluid–cosolvent mixtures. A quantitative evaluation of solvent effects on TPE in the mixtures can thus be achieved using DMAEB as a reference.

The pressure dependencies of the bathochromic spectral shift and relative quantum yield of DMAEB TICT emission in both CHF_3–*n*-hexane and CO_2–THF mixtures resemble those observed in neat supercritical CHF_3 and CO_2[15] and their mixtures.[12] Solvation in these mixtures is dictated by both local density[11,15,16] and local composition[12,13,23] effects, resulting in a significant deviation from the dielectric continuum theory.[18]

In the context of the Onsager reaction field model,[18] the solvent-induced energy gap change for ground and excited states with dipole moments μ_g and μ_e, respectively, can be expressed as[16,24]

$$\Delta E_s = \frac{\mu_g^2 - \mu_e^2}{a^3} f'(n) + \frac{2\mu_e(\mu_g - \mu_e)}{a^3}[f(\epsilon) - f(n)] \qquad (2)$$

where $f'(n) = (n^2 - 1)/(2n^2 + 1)$, $f(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$, and $f(n) = (n^2 - 1)/(n^2 + 2)$. ϵ and n are the solvent dielectric constant and refractive index, respectively, and a is the Onsager cavity radius. For TPE, $\mu_g = 0$, so eq 2 can be simplified to

$$\Delta E_s = \frac{-\mu_e^2}{a^3} f'(n) + \frac{-2\mu_e^2}{a^3}[f(\epsilon) - f(n)] \qquad (3)$$

Since n values are generally small for our solvent systems, $f'(n) \approx f(n)$ can be assumed for a first approximation, and eq 3 becomes

$$\Delta E_s = \frac{-2\mu_e^2}{a^3} \Delta f \qquad (4)$$

where $\Delta f = f(\epsilon) - (^1/_2)f(n)$.

In supercritical fluids, an upward deviation from the Onsager reaction field model is usually observed[11,15,16] because local density effects cause the reaction field actually experienced by a solute molecule to be larger than the field calculated on the basis of the bulk dielectric constant and refractive index. Similar upward

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(21) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. *J. Phys. Chem.* **1983**, *87*, 952.

(22) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

(23) Johnston, K. P.; Kim, S.; Wong, J. M. *Fluid Phase Equilib.* **1987**, *38*, 39.

(24) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.

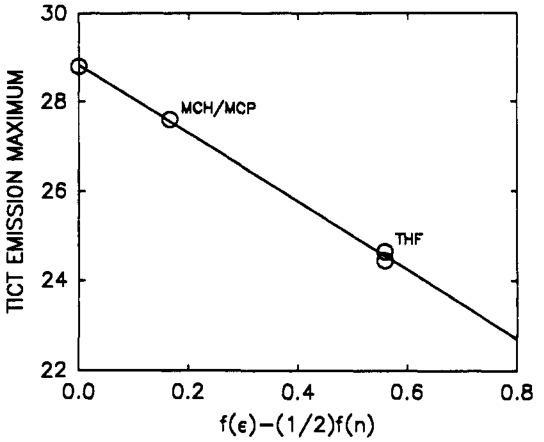

Figure 3. Dependence of TICT emission band maximum in DMAEB on $\Delta f = f(\epsilon) - (^1/_2)f(n)$ (eq 4).[26] The value at $\Delta f = 0$ was obtained by extrapolating the density dependence of TICT spectral shifts in ref 15 to zero density. The line is the best least-squares fit (slope = 21.9 kcal/mol, intercept = 28 830 cm^{-1}).

deviations are expected in our supercritical fluid–cosolvent mixtures[12,13,23] as a result of both local density and composition effects.

A more realistic estimate of the appropriate Onsager reaction field for the mixtures requires an accurate knowledge of local density and composition in the immediate vicinity of a solute molecule, which is obviously very difficult. However, if we choose to discuss microscopic solvent effects within the scope of the Onsager reaction field theory, an average measure of microscopic solvation in the mixtures can be achieved with our molecular probe DMAEB.[12] By denoting Δf^{loc} as a microscopic measure of the Onsager reaction field that takes into account the local effects, ΔE_s in a supercritical fluid–cosolvent mixture becomes

$$\Delta E_s = \frac{-2\mu_e^2}{a^3}\Delta f^{loc} \qquad (5)$$

Since we assume that the zwitterionic excited state $^1p^*$ in TPE experiences the same microscopic solvation as the TICT state in DMAEB in a supercritical fluid–cosolvent mixture, deviations of solvation from those predicted by the Onsager model should also be the same. Therefore, the "microscopic" Onsager field Δf^{loc} for the $^1p^*$ state in TPE can be determined on the basis of bathochromic spectral shifts of DMAEB TICT emission in the same mixtures.

Since $\mu_e \gg \mu_g$ for DMAEB twisted states,[25] the dependence of the TICT fluorescence spectral shifts on solvent dielectric properties can also be described by eqs 4 and 5 for normal liquids and supercritical fluids, respectively. A plot of the TICT emission band maximum against Δf for DMAEB in normal liquids is shown in Figure 3, yielding a slope $(-2\mu_e^2/a^3)$ and an intercept $(\tilde{\nu}_{max,0})$ of −21.9 kcal/mol and 28 830 cm^{-1}, respectively. Using a = 4 Å, the same as the value for DMABN,[16a] we obtain μ_e = 7 D for the DMAEB TICT state, which is in general agreement with the results of transient dielectric loss studies.[25] By assuming that when Δf^{loc} is used the same linear equation shown in Figure 3 applies for DMAEB in the supercritical fluid–cosolvent mixtures, Δf^{loc}s for the mixtures can be calculated from experimental values of bathochromic shifts using the plot in Figure 3 as a standard curve.

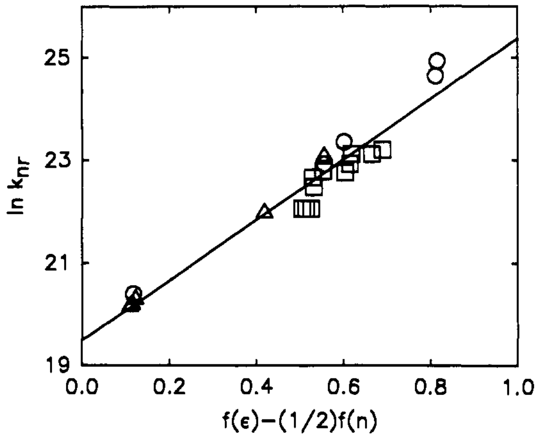

Figure 4. Dependence of radiationless decay rate constant of the $^1p^*$ state in TPE on the medium-induced $^1p^*$–^1p energy gap change in the supercritical fluid–cosolvent mixtures (□) and in normal liquids (○,[7] △[8]). The line is the best least-squares fit (slope = 5.9, intercept = 19.5).

By substituting eq 5 into eq 1, we obtain

$$\ln k_{nr} = A(-2\mu_e^2/a^3)\Delta f^{loc} + C \qquad (6)$$

where $C = A\Delta E_0 + B$ is a solvent-independent constant. For normal liquids $\Delta f^{loc} = \Delta f$. A plot of eq 6 for TPE in the supercritical fluid–cosolvent mixtures and in normal liquids is shown in Figure 4. Apparently, the results for TPE in the mixtures fall on the same line as those for TPE in normal liquids. A best least-squares fit yields slope $A(-2\mu_e^2/a^3) = 5.9$ and intercept C = 19.5. Since the central carbon–carbon bond length of the $^1p^*$ state in TPE is expected to be somewhere between those of carbon–carbon single (1.53 Å) and double (1.34 Å) bonds in hydrocarbons, this corresponds to a dipole moment of the charge-separated $^1p^*$ state in the range of 7.34–6.43 D. Using a = 4.27 Å,[8] we obtain an A value in the range of −0.3 to −0.39, which corresponds nicely with those obtained for many other systems.[21,27]

The above analysis further confirms that solvent effects on the radiationless decay rate of the $^1p^*$ state in TPE can, indeed, be related to solvent-induced $^1p^*$–^1p energy changes, consistent with predictions of radiationless relaxation theories. It also indicates that the $^1p^*$ state in TPE is very likely to have characteristics similar to those of the highly polar TICT state in DMAEB, although quantitative details of specific clustering may be different for TPE and the TICT molecule in a supercritical fluid.

Our results again demonstrate that solvation in a supercritical fluid–cosolvent mixture is complicated by local density and composition effects. Classical models of dipolar solute–solvent interactions can be applied only when a microscopic solvent-imposed reaction field is used. We have shown that an average measure of microscopic solvation properties in the mixtures can be achieved using a well-characterized molecular probe. This approach is expected to have a significant impact on other supercritical fluid investigations.

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(25) (a) Visser, R. J.; Weisenborn, P. C. M.; Varma, C. A. G. O. *Chem. Phys. Lett.* **1985**, *113*, 330. (b) Weisenborn, P. C. M.; Varma, C. A. G. O.; de Haas, V. M. P.; Warman, J. M. *Chem. Phys. Lett.* **1986**, *129*, 562. (c) Weisenborn, P. C. M.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1895.

(26) (a) Wermuth, G. *Z. Naturforsch.* **1983**, *38A*, 641. (b) Rettig, W.; Wermuth, G. *J. Photochem.* **1985**, *28*, 351.

(27) Siebrand, W. *J. Chem. Phys.* **1967**, *46*, 440.