

## Spectral Shifts in the Triplet–Triplet Absorption Spectrum of Anthracene in Supercritical Fluids

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Spectral shifts are observed in the triplet–triplet absorption bands of anthracene in supercritical fluids compared to those observed in normal liquids and are attributed to London dispersion forces and local solvent density enhancements.

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We have recently demonstrated<sup>1,2</sup> that the investigation of time-resolved chemical reactivity by laser flash photolysis (LFP) is an effective means of studying solute–co-solvent dynamics in supercritical fluids (SCFs). In our current pursuit of the use of LFP and well-defined photophysical probes to elucidate the nature of solute–solvent interactions in SCFs, we

have observed significant shifts in the triplet–triplet (T–T) absorption spectra of nonpolar aromatic hydrocarbons under SCF conditions. In this communication, we report the T–T absorption spectra of anthracene in SC CO<sub>2</sub> and ethane and their spectral dependence on SC solvent density and refractive index. The application of LFP transient absorption technique

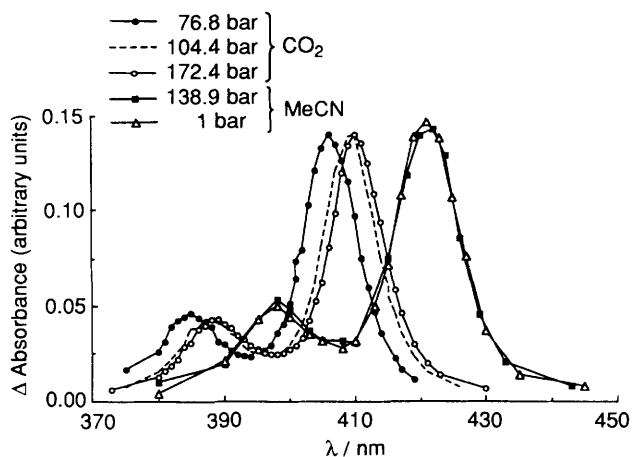


Fig. 1 T-T absorption spectra of anthracene in supercritical CO<sub>2</sub> and MeCN at the indicated pressures

to SCF samples has recently been described in detail.<sup>1,2</sup> In these experiments, 355 nm Nd:YAG laser excitation (*ca.* 8 mJ; pulse width *ca.* 6 ns) was provided perpendicular to a pulsed 1000 W xenon lamp monitoring source. The critical pressure and temperature of CO<sub>2</sub> and ethane are 73.8 bar; 31.0 °C and 48.7 bar (1 bar = 10<sup>5</sup> Pa); 32.2 °C, respectively.

It has been well documented in spectroscopic studies<sup>3-5</sup> that anthracene undergoes excited state level crossing under high (Kbar) pressure in organic liquid,<sup>3</sup> polymeric<sup>4</sup> and crystalline<sup>5</sup> media. The perturbation of excited state energy levels with application of pressure results in bathochromic shifts in the T-T absorption spectrum. To determine the importance of the pressure effect under the pressure conditions of this study, LFP of anthracene in liquid MeCN was investigated up to 172.4 bar. Fig. 1 demonstrates that there is no observable shift in the T-T absorption spectra ( $\lambda_{\max} = 420$  nm) over this pressure range, and therefore we conclude that state switching is insignificant under the current SCF conditions. In fact a shift opposite to that expected for the application of pressure if there had been state switching is observed in the SCF experiments.

LFP of anthracene in SC CO<sub>2</sub> at 35 °C and 172.4 bar results in a spectral shift of the primary absorption band to 410 nm (Fig. 1). However, as the fluid pressure is decreased towards the critical pressure of CO<sub>2</sub> the T-T absorption spectrum does continuously shift to shorter wavelengths (Fig. 1). Similar but less dramatic results were observed in SC ethane where the primary absorption band shifted from 412 nm at 118.3 bar to 410 nm at 54.1 bar.

The origin of the 'apparent' blue shift observed in SCFs compared to liquid solvents becomes clear when the triplet spectrum is compared to that measured in the gas phase,<sup>6</sup>  $\lambda_{\max} = 403$  nm. Electronic transitions of molecules in solution are typically lower in energy compared to those of the isolated molecule due to either specific or non-specific solvent interactions.<sup>7</sup> For a nonpolar aromatic hydrocarbon in non-polar solvents only the nonspecific interaction of London dispersion forces need to be considered and spectral shifts should be proportional to a dispersion term that is a function of the refractive index (*n*) of the solvent [ $F = n^2 - 1/(2n^2 + 1)$ ]. Using refractive indices of SC CO<sub>2</sub> and ethane obtained from the Lorentz-Lorentz relationship,<sup>8</sup> the spectral shifts of triplet anthracene are plotted vs. this dispersion term (Fig. 2) and compared to normal liquids.<sup>9</sup> The linearity in Fig. 2 demonstrates the spectral shifts observed in the above SCFs are readily accounted for by nonspecific solvent interaction. It should be noted that the slight upward deviation in the low pressure SCF results (Fig. 2) is attributed to a difference in the

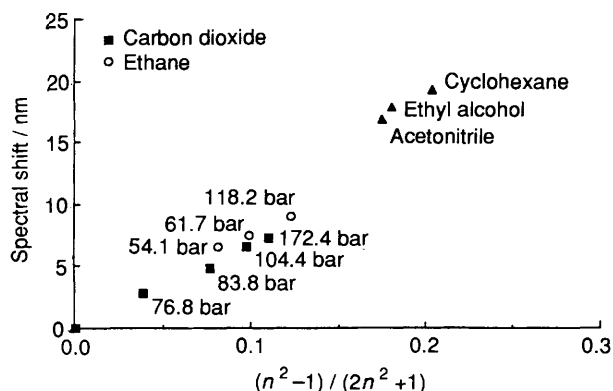


Fig. 2 Plot of the spectral shift in the maximum of the T-T absorption spectrum of anthracene vs. the solvent dispersion term in SC CO<sub>2</sub> and ethane at the pressures indicated compared to normal liquids (see text)

bulk and local refractive indices owing to local solvent density enhancements, a phenomenon extensively studied with efficient solvatochromic probes.<sup>10</sup>

In summary, we have presented the first T-T absorption spectrum of an aromatic hydrocarbon in a SCF and attribute the spectral shifts observed primarily to London dispersion forces. We are currently pursuing the generality of the observations.

It should be noted that initial analysis of the kinetic fate of triplet anthracene is similar to that in normal liquids when changes in fluid viscosity are accounted for. Similar kinetic results have been observed for the diffusion-controlled termination reactions of triplet benzophenone and benzyl free radical in SC CO<sub>2</sub> and ethane.<sup>11</sup>

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