Twisted Intramolecular Charge Transfer of Ethyl *p*-(*N,N*-Diethylamino)benzoate in the Gas Phase and in Low-density Non-polar Supercritical Fluids. A Quantitative Spectral Resolution Using Principal Component Analysis and Self Modelling

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Twisted intramolecular charge transfer (TICT) is observed for ethyl *p*-(*N,N*-diethylamino)benzoate in the gas phase and in low-density supercritical ethane, and the emission bands of the locally excited and TICT states and their relative contributions to observed fluorescence spectra are determined using principal component analysis–self modelling spectral resolution.

Twisted intramolecular charge transfer (TICT) is often observed in polar solvents.[1–3] For the classical TICT molecule, *p*-(*N,N*-dimethylamino)benzonitrile (DMABN), and derivatives, there have been a number of studies of isolated molecules or in solvent clusters in a supersonic jet expansion.[3–9] No TICT state formation was observed except in those DMABN derivatives which are already partially twisted in the ground state.[3,6] This implies that the solvent clusters involving water, methanol or acetonitrile in a supersonic jet expansion fail to provide an environment polar enough for the formation of a TICT state. However, TICT state emission has been reported for ethyl *p*-(*N,N*-diethylamino)benzoate (DEAEB) in non-polar solvents such as methylcyclohexane–methylcyclopentane[10] and hexane.[11] In this communication, we report an observation of TICT state emission of DEAEB in the gas phase and in low-density supercritical ethane, a solvent less 'polar' than hexane. Contributions of TICT emission to observed fluorescence spectra are confirmed by a quantitative spectral resolution using principal component analysis and self modelling.

Fluorescence spectra of DEAEB in the gas phase and in supercritical ethane as a function of density at 53 °C are shown in Fig. 1. They are generally narrower than the spectrum obtained in hexane. The band width (fwhm) decreases with decreasing ethane density (Table 1), corresponding to a decreasing TICT contribution. However, even in the gas phase the band width is larger than that of the locally excited (LE) state emission, which can be obtained in highly polar solvents such as methanol and water[11,12] or at low temperature.[10] The observed fluorescence spectrum of DEAEB in the gas phase apparently consists of emissions from both the LE and TICT states. Their relative contributions can be determined from a quantitative spectral resolution.

Table 1 Fluorescence spectral parameters of DEAEB in supercritical ethane at 53 °C

Density/mol dm^{-3}	ε	*n*	Band-width/ cm^{-1}	x_{TICT} (%)
Gas phase			4810	26.6
0.26	1.009	1.004	5170	37.3
0.55	1.019	1.009	5240	40.2
0.87	1.030	1.015	5170	40.5
1.23	1.042	1.021	5370	43.0
1.64	1.056	1.028	5590	47.2
2.13	1.073	1.036	5590	50.5
2.73	1.095	1.047	5720	52.3
3.52	1.124	1.060	5790	53.5
4.71	1.168	1.081	5790	51.0
6.49	1.236	1.113	5790	48.3
Hexane (room temp.)	1.890	1.375	5810	
Methanol (room temp.)	32.63	1.329	3590[a]	
Absorption band[b]			3930	

[a] The width for the LE band only. [b] DEAEB in ethane at 2 mol dm^{-3} and 53 °C.

The principal component analysis–self modelling spectral resolution (PCA–SMSR) method has been described in detail elsewhere.[13–16] The input data matrix consisted of 70 experimental fluorescence spectra over the wavelength range 293–450 nm with 1 nm increments. PCA treatment of the matrix gave eigenvalues corresponding to a two-component system. Shown in Fig. 2 are coefficients for the experimental spectra represented in a two-dimensional eigenvector coordinate. The limiting coefficients for the LE and TICT bands were determined using a self modelling spectral resolution method.[14–17] While the LE band was readily obtained according to the Lawton–Sylvestre constraint[14] by using the longer wavelength region in which the TICT emission has contribution but the LE emission does not, the same application to the TICT band was assisted by an additional requirement that the TICT band should be best represented by a Gaussian function. Shown in Fig. 3 are the results from PCA–SMSR.

The LE band from the spectral resolution is in excellent agreement with that obtained in highly polar solvents (Fig. 3), which implies that the band shape is probably only weakly solvent dependent. There is also a mirror-image relationship between the absorption and fluorescence spectra (Fig. 3), indicating that the molecular geometries of the absorbing and emitting states should be quite similar. The results of PCA–SMSR provide strong evidence for the presence of

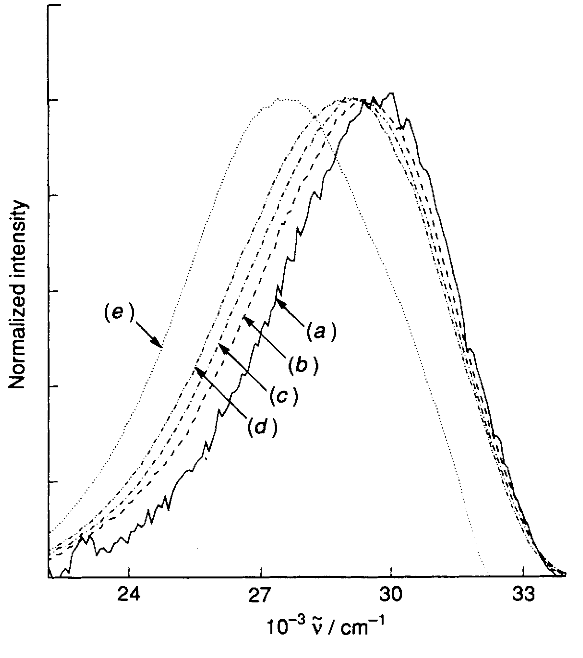

Fig. 1 Representative experimental fluorescence spectra (corrected) of DEAEB (*a*) in the gas phase and in supercritical ethane at 53 °C at a density of (*b*) 0.87, (*c*) 1.64 and (*d*) 3.52 mol dm^{-3} (280 nm excitation). The spectrum in hexane is also shown for comparison (*e*).

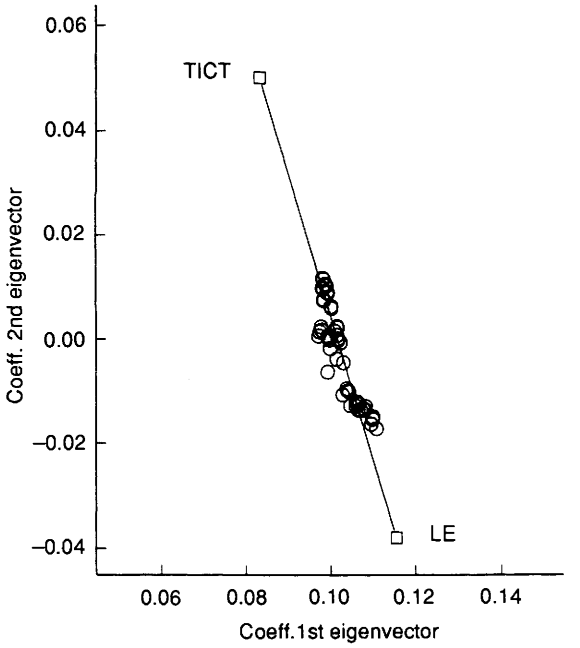

Fig. 2 Combination coefficients for experimental fluroescence spectra of DEAEB in supercritical ethane (○), with the limits (□) from self modelling spectral resolution. The line is the normalization line.

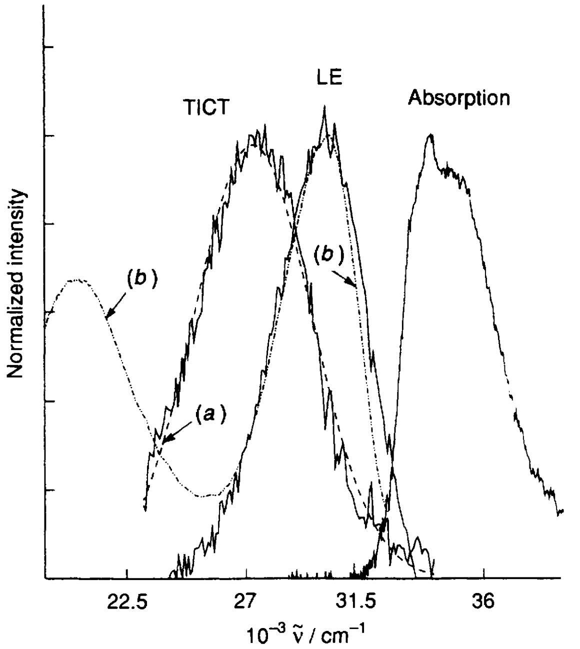

Fig. 3 The LE and TICT emission bands of DEAEB determined using the PCA–SMSR method. The TICT band is fitted well with a Gaussian function (*a*) and the LE band is in excellent agreement with that in methanol (*b*) 1800 cm^{-1} blue-shifted. The absorption spectrum of DEAEB in ethane at a density of 2 mol dm^{-3} and 53 °C is also shown for comparison.

DEAEB TICT emission in the gas phase. This is probably the first example of gas-phase TICT state formation in a planar DMABN-related molecule.[3] For ethyl *p*-(*N*,*N*-dimethylamino)benzoate (DMAEB), a molecule closely related to DEAEB, a broad fluorescence band significantly red-shifted from the LE spectrum was observed in the gas phase with excitation at the red onset of the DMAEB absorption spectrum.[†][4,6,7] The red-shifted band was attributed to the emission of excited DMAEB ground-state complexes.[4,7] However, for DEAEB at the temperature (53 °C) for our measurements, the concentration in the gas phase was very low ($<1 \times 10^{-7}$ mol dm^{-3} according to absorption), precluding the possibility of complexes. The fluorescence spectra of DEAEB were excitation-wavelength-independent, indicating no contribution from any other ground-state species. The Gaussian-like band shown in Fig. 3 is due to the TICT state emission of DEAEB.[‡][18]

As shown in Table 1, the contribution of TICT emission x_{TICT} is *ca.* 27% in the gas phase and is increased to *ca.* 50% at an ethane density of 6.5 mol dm^{-3}, which corresponds to solvent relative permittivity (ε) and refractive index (n) of 1.236 and 1.113, respectively. Assuming that the LE and TICT states are in thermodynamic equilibrium, we have eqn. (1)

$$-(E_{\text{TICT}} - E_{\text{LE}})/RT \approx \ln K = \ln\,[(x_{\text{TICT}}/x_{\text{LE}})(k_{\text{LE}}/k_{\text{TICT}})] \qquad (1)$$

where K is the equilibrium constant and k denotes the fluorescence radiative rate constants. In the gas phase, the energy difference between the two excited states can be calculated from the relative fluorescence contributions [eqn. (2)]. Because $(k_{\text{LE}}/k_{\text{TICT}}) > 1$ can be expected,[1] our results

$$E_{\text{TICT}} - E_{\text{LE}} = 2.8 - 2.8\ln\,(k_{\text{LE}}/k_{\text{TICT}}) \qquad (2)$$

indicate that even in the gas phase the TICT state of DEAEB is either iso-energetic with or below the LE state.

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Footnotes

[†] The red-shifted band is absent for DMAEB in the gas phase at a lower temperature (40 °C) with excitation at the DMAEB absorption band maximum.[18]

[‡] It should also be recognized that unlike DEAEB, DMAEB does not form a TICT state in non-polar solvents such as hexane.

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