

points, even if the departures from a Boltzmann population that he finds among certain individual levels are real.

Why, then, does Lambert's value of the colour excess differ from mine? This results less from his use of a more rigorous method than from the fact that, in order to apply this method, it is necessary to use the sharp-line components measured from coude spectra (and normalized to the scanner data) by Aller and Dunham<sup>3</sup>, because the scanner measurements themselves have less resolution and so do not give enough unblended lines. An independent treatment of the sharp components of lines whose upper terms are  $b^4F$ ,  $b^4P$  and  $a^6S$  (omitting the two faint and very discrepant lines  $\lambda 4,533.0$  and  $\lambda 4,470.3$  which Lambert has also apparently rejected) with the method I used before gives  $E_{B-V} = 1.9 \pm 0.3$  m, in very good agreement with Lambert's value.

The difference between the values of  $E_{B-V}$  given by the total line fluxes and the sharp components is an interesting phenomenon, and it suggests that the region from which the sharp components are emitted (presumably the  $1.5''$  central nucleus<sup>4,5</sup>) may be still more heavily reddened than the object as a whole (observed photoelectrically with diaphragms typically  $10''$  to  $20''$  in diameter). Alternatively, there might be a wavelength-dependent instrumental effect in the resolution of sharp and diffuse components, for example, as a result of atmospheric dispersion across the slit of the coude spectrograph. In either case, the value  $E_{B-V} = 1.2$  m derived previously seems the right one for discussions of the continuum and emission lines observed with photoelectric scanners.

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## Solvent Effects on Charge-transfer Fluorescence Bands

CHARGE-TRANSFER (CT) transitions in complexes with an ionic ground state, leading as they do to annihilation of the charge, are particularly sensitive to the polarity of the solvent. Such transitions have been used to derive the empirical solvent polarity parameters  $Z$  (ref. 1) and  $E_T$  (ref. 2) which correlate well with the transition energies of other complexes with charged ground states<sup>3-5</sup>. Complexes in which the ground state is non-ionic show, on the other hand, little correlation between the energy of the charge-transfer transition and  $E_T$  (or  $Z$ ), because of the Franck-Condon restriction on reorganization of the solvent during the transition. The CT fluorescence transitions in such complexes should, however, correlate well with  $Z$  and  $E_T$  provided that the lifetime of the excited state is sufficient to allow reorganization of the solvent. The energy of the CT fluorescence transition should thus

Table 1. POSITION OF THE CT FLUORESCENCE BAND MAXIMUM ( $\text{cm}^{-1}$ ) IN VARIOUS SOLVENTS FOR THE COMPLEX, HEXAMETHYLBENZENE-TETRACHLOROPHTHALIC ANHYDRIDE

Solvent	Benzene	Toluene	Benzene-butyl ether (50:50)	Butyl ether	Xylene	Carbon tetrachloride-butyl ether (50:50)
$\bar{\nu}$ ( $\text{cm}^{-1}$ )	18650	18720	18660	18800	18810	19240
Solvent	Carbon disulphide	Carbon tetrachloride	Carbon tetrachloride-cyclohexane (50:50)	Cyclohexane	n-Hexane	
$\bar{\nu}$ ( $\text{cm}^{-1}$ )	19180	19220	19400	19620	19880	

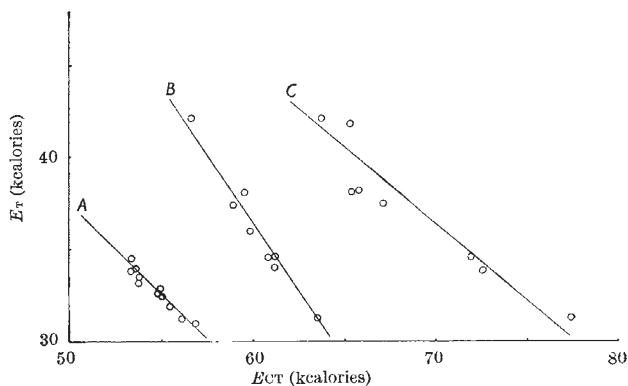


Fig. 1. Energy of the CT fluorescence band maximum,  $E_{CT}$ , as a function of the solvent polarity parameter,  $E_T$ , for the complex hexamethylbenzene-tetrachlorophthalic anhydride (A) and the excited state complexes, dimethylnaphthylamine-methylbenzoate (B) (data taken from ref. 10) and biphenyl-diethylaniline (C) (data taken from ref. 8).

decrease with an increase in solvent polarity, the reverse of the trend observed for the absorption process. Few complexes have been found to fluoresce in fluid solution<sup>6,7</sup>, and these only in a few solvents, mainly of very low polarity. The fluorescence band maxima measured in a range of solvents using a Baird-Atomic SF100 spectrofluorimeter for the complex hexamethylbenzene-tetrachlorophthalic anhydride are shown in Table 1, and Fig. 1 is a plot of the fluorescence band energy,  $E_{CT}$ , against the solvent polarity parameter,  $E_T$ . A good straight line with a slope close to unity (0.91) is obtained, showing that solvent stabilization of the excited state is very similar to that of the ground state in ionic complexes.

In addition to complexes which exist in the ground state, owing to the changes in ionization potential and electron affinity on excitation, complexes may be formed only in the excited state with little or no ground state stability, being similar in this respect to contact complexes<sup>8</sup>. Such complexes, for example, those formed between  $N,N$ -dialkylanilines and aromatic hydrocarbons, cause quenching of the hydrocarbon fluorescence and also give rise to a new fluorescence band at longer wavelength attributed to charge-transfer fluorescence of the excited complex<sup>9-12</sup>. These bands also exhibit considerable solvent sensitivity<sup>9,10</sup>, as expected for a transition arising from an ionic state. Plots of the fluorescence band energy against  $E_T$  for such complexes all yield good straight lines with slopes close to unity, two examples being shown in Fig. 1. The charge-transfer nature of the transition and the fact that the excited state is ionic are thus confirmed, and such plots provide a simple diagnostic test for these transitions. Only in solvents of low polarity is charge-transfer fluorescence observed in fluid solution, suggesting that only contact ion-pairs can fluoresce. More polar solvents give rise to solvent separated ion-pairs, and those of very high polarity to solvated ions, both these situations being non-fluorescent although quenching may still occur<sup>9</sup>.

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