

Medium Effect on Charge Transfer Emission Spectra of Biomolecules as Donors & Tetracycline & Oxytetracycline as Acceptors

JYOTIRMAY LAHIRI & RAMA BASU*

Department of Pure Chemistry, University College of Science,
92A P C Road, Calcutta 700 009

Received 2 January 1985; revised and accepted 4 April 1985

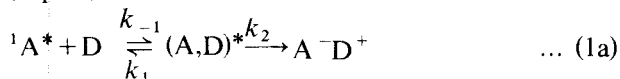
Emission spectra of charge transfer (CT) complexes of purines, pyrimidines and amino acids (as donors) and tetracycline and oxytetracycline (as acceptors) have been determined in highly polar solvents. The CT fluorescence peak undergoes pronounced red shift with considerable decrease in emission intensity within the group as the polarity of the solvent increases. The excited CT state dipole moments of adenine, guanine, xanthine, hypoxanthine, thymine, cytosine, phenylalanine, tyrosine, histidine and tryptophan complexes have been estimated using Onsager and Lippert-Mataga models.

A number of excited state charge transfer (CT) complexes are known in the literature¹⁻⁵. However, no systematic work has been done on emission from CT complexes of nucleic acid bases with antibiotics, such as tetracycline and oxytetracycline. In this connection, Labianca *et al.*⁶ showed that the excited molecule interacted with the donor to give an exciplex in a reversible process which decayed to give the products. The exciplex (¹AD*) was stabilized by resonance structures (see Eq. 1), assuming that



excitation wavelength corresponded to the absorption of the acceptor.

A mechanism similar to that proposed by Evan⁷ (Eq. 1a)



was suggested by the authors⁸ for fluorescence quenching effect on tetracycline and oxytetracycline by purines, pyrimidines and amino acids in highly polar solvents. The title investigation is in continuation of our earlier studies⁸. The excited state dipole moments of complexes of purine and pyrimidine bases and of amino acids with the antibiotics have been evaluated using Onsager model of liquid dielectrics.

All the purines, pyrimidines, and amino acids were obtained from E Merck, BDH and Loba Chemicals (Austria). Their purity was checked by usual

procedure. The solvents used were dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and propylene glycol (PG) (all from E Merck) and water. The water had a conductivity of $3.4\Omega^{-1}$ and the other three solvents were carefully dried and freshly distilled. Tetracycline and oxytetracycline were obtained from Sigma Chemiscals (USA) and their purity was checked by usual procedure. Fluorescence spectra were recorded at 23°C with the fluorimeter instrument designed and described earlier⁸. The concentration of donors used were 10^{-2} mol dm⁻³ and those of acceptors were of 10^{-5} mol dm⁻³.

Using Onsager model of liquid dielectrics, the energy change involved in the transfer of a dipole from vacuum to a medium of dielectric constant (ϵ) and refractive index (n) could be calculated by Eq. (2).

$$\Delta E = \frac{2\mu^2}{a^3} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad \dots (2)$$

where a is the radius of a circular cavity surrounding the molecule. This is normally equal to molecular radius calculated from molecular volume. So if we know fluorescence frequency (ν_s) in the solvent of dielectric constant (ϵ) and that in the vacuum (ν_v), then the change in energy is given by Eq. (3).

$$\Delta E = h\Delta\nu \quad (\text{where } \Delta\nu = \nu_s - \nu_v) \quad \dots (3)$$

or

$$h\Delta\nu = \frac{2\mu^2}{a^3} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$

or

$$h\Delta\nu = h(\nu_s - \nu_v) = \frac{2\mu^2}{a^3} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$

or

$$h\nu_s = h\nu_v + \frac{2\mu^2}{a^3} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$

A plot of $h\nu_s (= h\nu_{CT})$ versus $\left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$ should, therefore, be linear if the solute-solvent interaction is small and from the slope of this curve μ , the dipole moment can be evaluated. Since the completely charge-separated dative state should have a dipole moment of 15.35D, it is thus possible to calculate the degree of excited state CT from the shift in the fluorescence spectra in media of different dielectric constants. On the other hand, using the Lippert-Mataga⁹⁻¹¹ method, the dipole moment of the CT state has been estimated from the knowledge of values of $\Delta\mu = (\mu_{CT} - \mu_g)$, where μ_{CT} and μ_g represent the

Table 1—Excited State Dipole Moments of CT Complexes

Donor	Solvent*	$\nu_{CT} \times 10^{-3}$ (cm ⁻¹)		$h\nu_{CT}$ (eV)		Dipolemoment (D)	
		Tetra-cycline	Oxytetra-cycline	Tetra-cycline	Oxytetra-cycline	Tetra-cycline	Oxytetra-cycline
Adenine	a	20.00	19.38	2.482	2.405		
	b	20.16	19.61	2.502	2.433		
	c	20.32	19.84	2.522	2.462	13.72	10.18
	d	22.32	22.62	2.770	2.808		
Guanine	a	21.74	21.28	2.698	2.641		
	b	22.02	22.83	2.734	2.833		
	c	22.22	23.25	2.758	2.886	12.39	9.92
	d	22.72	23.47	2.821	2.913		
Xanthine	a	19.92	21.74	2.472	2.698		
	b	22.62	22.22	2.808	2.758		
	c	22.72	22.47	2.821	2.789	9.83	10.60
	d	22.83	22.72	2.833	2.821		
Hypoxanthine	a	19.23	19.23	2.387	2.387		
	b	19.61	19.38	2.433	2.405		
	c	19.96	19.92	2.477	2.472	13.85	13.14
	d	20.40	20.00	2.533	2.482		
Thymine	a	18.42	18.52	2.285	2.298		
	b	19.01	18.87	2.359	2.342		
	c	19.05	19.38	2.364	2.405	13.78	12.94
	d	19.16	19.53	2.377	2.424		
Uracil	a	18.52	18.70	2.298	2.320		
	b	18.87	19.05	2.342	2.364		
	c	19.23	19.23	2.387	2.387	13.14	12.47
	d	19.31	19.38	2.396	2.405		
Phenylalanine	a	19.42	19.53	2.410	2.424		
	b	19.61	19.68	2.433	2.443		
	c	19.80	19.80	2.457	2.457	12.47	11
	d	21.27	20.92	2.640	2.596		
Tyrosine	a	19.53	19.61	2.424	2.433		
	b	20.16	19.76	2.502	2.453		
	c	20.40	20.00	2.533	2.482	13.14	12.47
	d	20.49	20.32	2.543	2.522		
Histidine	a	19.38	19.16	2.405	2.377		
	b	19.61	19.68	2.433	2.443		
	c	20.00	19.84	2.482	2.462	11.75	11.52
	d	20.16	20.00	2.502	2.482		
Tryptophan	a	19.23	19.38	2.387	2.405		
	b	20.16	19.53	2.502	2.424		
	c	20.49	19.68	2.543	2.443	12.29	11.23
	d	20.83	20.66	2.585	2.564		

*a=water, b=DMSO, c=DMF, d=propylene glycol; the corresponding dielectric constants (ϵ) are 78.54, 48.90, 36.70, 32.00 and the refractive indices (n) are 1.02606, 1.4780, 1.4295, 1.4320.

dipole moments of the excited CT state and ground state, respectively of the form

$$\Delta\bar{\nu}_{CT} = \text{Const.} + \frac{2F(\epsilon, n) (\Delta\mu)^2}{hca^3}$$

where

$$\Delta\bar{\nu}_{CT} = \bar{\nu}_{ab}^m - \bar{\nu}_{CT}^m$$

$$F(\epsilon, n) = \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right)$$

A plot of $\Delta\bar{\nu}_{CT}$ as a function of $F(\epsilon, n)$ is linear from the slope of which $\Delta\mu$ value may be obtained.

The results of the present investigation are given in Table 1. It may be observed that for all the systems studied the emission peak undergoes red shift as the polarity of the medium is increased. The dipole moments estimated from Eq. (3) are found to be $11 \pm 2D$. The Onsager radii range is of 3 to 4 Å in these calculations. Similar results were obtained using

Lippert-Mataga equation. All calculations are based on method of least squares.

Since the completely charge-separated state has a dipole moment of 15.35 D and the no-bond structure has no moment, the charge transfer in these systems was calculated to be in the range of 64 to 90%. Thus the overall wavefunction of the state becomes

$$\Psi = \Psi_{(D-A)^*} + \lambda \Psi_{(D^+ + A^-)} \quad \dots (5)$$

where the first term denotes the CT resonance contribution and the second term represents the CT contribution. It appears, therefore, that the CT resonance contribution is in the range of 36 to 10% in these systems.

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