Short Communication

Notes on excited state charge-transfer interaction

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The energy change associated with charge-transfer (CT) interaction is expressed as [1]:

$$h\nu_{CT} = I_D - E_A - \Delta \tag{1}$$

where ν_{CT} is the charge transfer frequency, I_D is the ionization energy of the donor D, E_A is the electron affinity of the acceptor A, and Δ is the stabilization energy of the ion pair. This relation holds irrespective of whether the charge transfer is taking place in the ground state or excited state; in the former case ν_{CT} refers to absorption frequency while in the latter it is associated with CT emission. It has been well established that in the case of charge transfer absorption ν_{CT} varies linearly with I_D and E_A [1]. But the situation is less clear with CT emission, *i.e.* with charge transfer interaction in electronically excited state. In the case of CT emission from dimethylaniline (DMA)-polynuclear aromatic hydrocarbon [4] systems it has been assumed that DMA acts as donor and the excited hydrocarbon as acceptor. In this case the ν_{CT} emission should vary linearly with electron affinity of the excited hydrocarbon molecule. This quantity is extremely difficult to determine experimentally. Now since in polynuclear hydrocarbons the excited states involved are the $\pi*$ states, the electron affinity of excited hydrocarbon may be estimated from the energy of the highest occupied molecular orbital (Homo). (We should not take the energy of the lowest empty molecular orbital (Lemo) as there is no ground state charge transfer absorption in these systems.) Homo for polynuclear hydrocarbons have been calculated and tabulated by Coulson and Streitwisser [5]. The ν_{CT} for a number of systems were measured in benzene solution with 365 nm exciting light. $h\nu$ in eV was then plotted against orbital energy expressed as $(\alpha - \alpha_0)/\beta$ given by Coulson and Streitwisser. It may be observed (Table 1) that approximate linearity is obtained.

It may be mentioned that correlation between ν_{CT} emission and polarographic oxidation reduction potentials of the donor and acceptor has been proposed [2, 3]. Polarographic method gives the redox potential of the molecules in their ground state. Their correlation with ν_{CT} absorption is straightforward but for ν_{CT} emission any correlation may be purely accidental.

TABLE 1

CT emission from DMA–hydrocarbon systems

Hydrocarbon	ν_{CT}	$h\nu(eV)$	$(\alpha - \alpha_0)/\beta$
1. Perylene	20,000	2.48	0.347
2. 3,4-Benzpyrene	21,276	2.63	0.371
3. Anthracene	21,740	2.69	0.414
4. Pyrene	22,730	2.81	0.445
5. Chrysene	23,530	2.91	0.520

Solvent = benzene.
Exciting light = 365 nm H_g line.

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3 H. Beens and A. Weller, Acta Phys. Polon, 34 (1968) 1.
4 H. Leonhardt and A. Weller, Ber. Bunsenges. Phys. Chem., 63 (1963) 791.
5 C. A. Coulson and A. Streitwisser, Dictionary of electron calculation, Vol. 2, Pergamon Press, New York, 1965.