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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

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EXCIPLEXES & RADICAL PAIRS: FORMATION & PROPERTIES

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RADICAL PAIR PROPERTIES

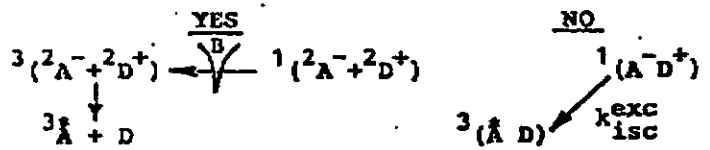
$(^2A^- + ^2D^+)$	(A^-D^+)
rip	exc
radical ion pair	exciplex
SSIP	CIP
$a_o \approx 7$ Å	$d \approx 3$ Å

Back Transfer of the Electron

non-radiative	radiative
	$(k_r \approx 10^7 s^{-1})$

Magnetic Field Effect on Triplet Formation

by radical pair separation and reencounter	by exciplex intersystem crossing



Hyperfine Coupling Interaction, ΔE_{hfc}:

$$2\,\frac{B_a^2 + B_d^2}{B_a + B_d} < 10^{-6}\ \text{eV}$$

$$(B_I^2 = \sum_k a_{Ik}^2 I_k(I_k+1))$$

Exchange Interaction $J(r) = J_o \exp(-\alpha r)$:

$J(a_o) > 10^{-4}$eV
$J(\infty) = 0$

$J > 10^{-2}$eV

EXCIPLEXES AND RADICAL PAIRS

Photoinduced electron transfer reactions taking place between electron-donor (D) and electron-acceptor molecules (A) lead to the formation of high energy intermediates[1]: exciplexes, (A^-D^+), with an interplanar separation $d \approx 3$ Å and radical-ion pairs, $(^2A^- + ^2D^+)$, with a centre-to-centre distance $a \approx 7$ Å. The free energies above the completely separated donor and acceptor molecules in the ground state, $\Delta G^{\epsilon}_{exc}$ and $\Delta G^{\epsilon}_{exc}$, strongly depend on solvent polarity, ϵ, such that generally radical-ion pairs are favoured in polar, exciplexes in nonpolar solvents.[2]

There is a close connection with the classical ion pair nomenclature in that the exciplexes (exc) and radical-ion pairs (rip) correspond to the contact ion pairs (CIP) and the solvent separated ion pairs (SSIP), respectively. It is, however, on the basis of their distinctly different properties that exciplexes, whose back electron transfer is radiative[3], can be distinguished from radical-ion pairs which, in turn, exhibit a magnetic field effect on molecular triplet formation in systems where according to

$$^1\Delta E^*_{0,0} > \Delta G^{\epsilon}_{rip} > {}^3\Delta E^*_{0,0}$$

the radical pair free energy is lower than the zero-zero transition energy, $^1\Delta E^*_{0,0}$, of the lowest locally excited singlet state $^1A^*$ or $^1D^*$, but higher than that of the lowest triplet state $^3A^*$ or $^3D^*$. It is in these cases that singlet exciplexes and/or radical-ion pairs in the overall singlet state are the primarily formed intermediates and that the two possible ways of triplet formation: intersystem crossing in the exciplex:

$$^1(A^-D^+) \xrightarrow{k_{isc}} {}^3(A^*D) \longrightarrow {}^3A^* \text{ or } {}^3D^*$$

and geminate recombination of the radical-ion pair:

$$^1(^2A^- + {}^2D^+) \xrightarrow{k_{S\to T}(D)} {}^3(^2A^- + {}^2D^+) \longrightarrow {}^3A^* \text{ or } {}^3D^*$$

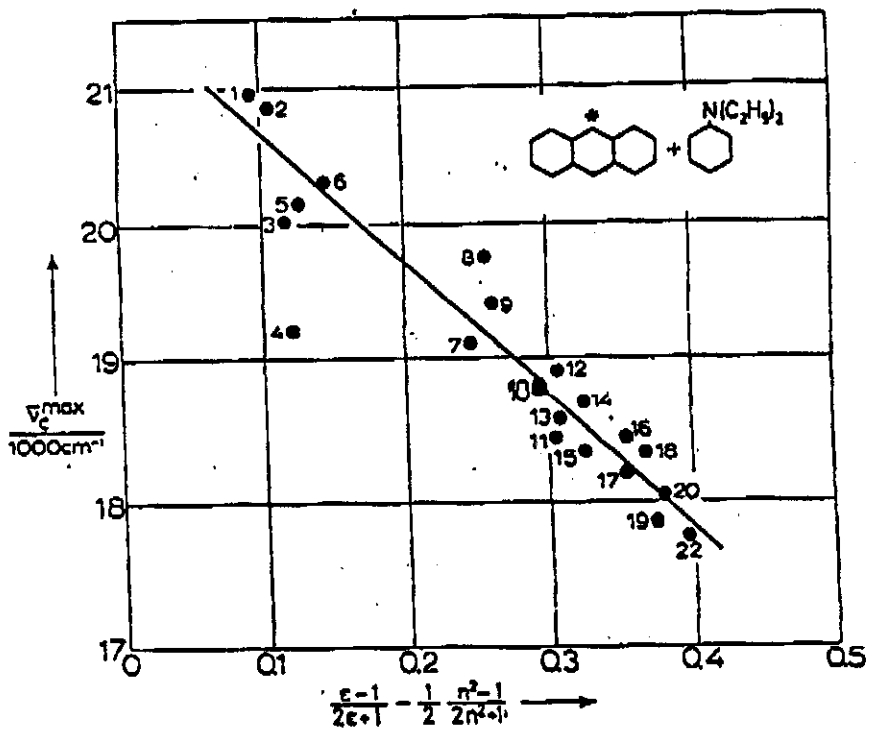
can be distinguished with the aid of the magnetic field effect.

Emission characteristics and dipole moments of a great variety of molecular complexes formed in the excited state are investigated. The results show that molecular complex formation in the excited state is a very general phenomenon ranging from excited charge-transfer complexes, which involve molecules with quite different electronic structures, to excimers involving identical molecules. This whole range is qualitatively discussed in terms of a description which takes into account interaction among charge-transfer and locally excited states.

One further characteristic of typical charge-transfer emission bands is their wavelength sensitivity to the polarity of the solvent. The red shift of $\tilde{\nu}_e^{max}$ which is observed when the solvent polarity is increased can be related to the dipole moment, μ_e, of the excited complex by:

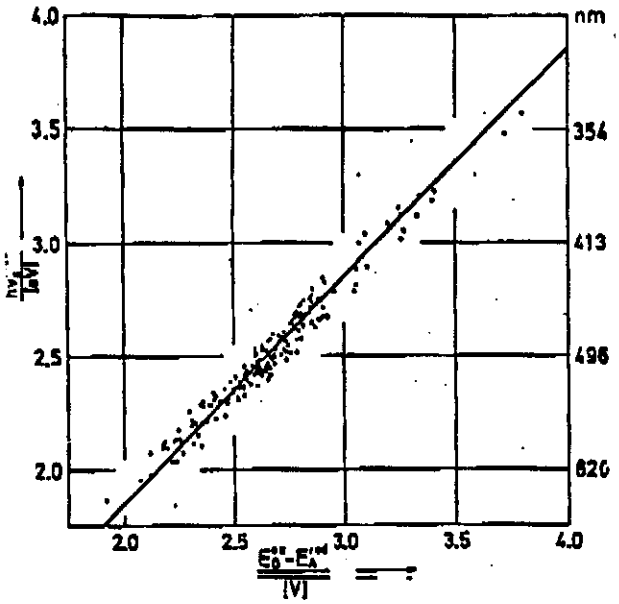
$$\tilde{\nu}_e^{max} = \tilde{\nu}_e^{max}(0) - \frac{2\mu_e^2}{hc\varrho^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{1}{2}\,\frac{n^2-1}{2n^2+1}\right),$$

where ε is the dielectric constant, n the refractive index, and ϱ the equivalent sphere radius of the complex volume.



Maximum emission frequency of anthracene-diethylaniline exciplex in different solvents (ε = dielectric constant, n = refractive index) ranging from 1,n-hexane to 22, methanol.

$h\nu_e^{max}$ (hex) = $E_D^{ox} - E_A^{red} - 0.15 \pm 0.10$ eV



Plot of maximum energy of exciplex fluorescence $h\nu_e^{max}$, measured in n-hexane at room temperature, against the difference between donor oxidation and acceptor reduction potentials, $E_D^{ox} - E_A^{red}$.

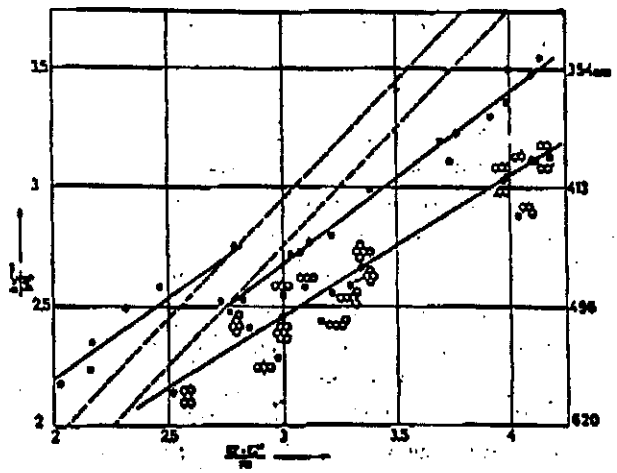
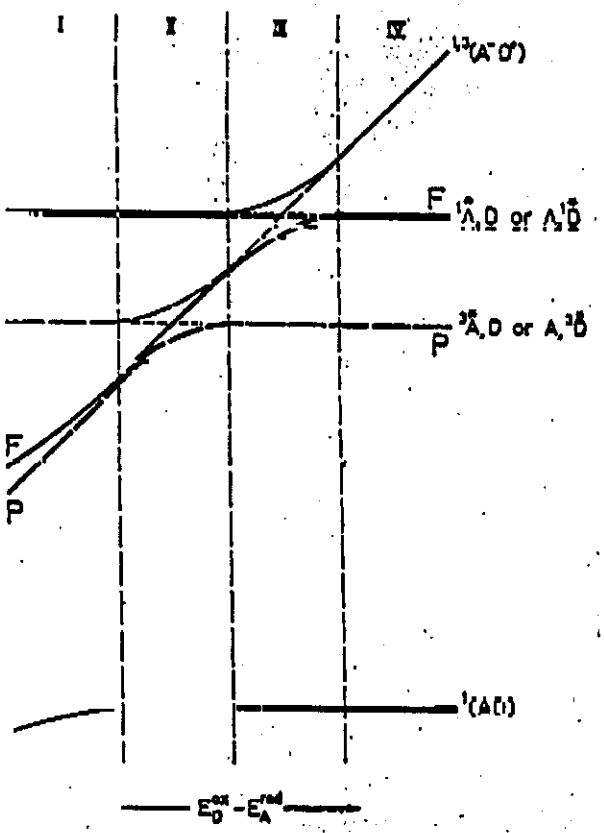


Fig. 1. Plot of maximum energy of exciplex fluorescence $h\nu_e^{max}$, measured in n-hexane at room temperature, against the difference between donor oxidation and acceptor reduction potentials, $E_D^{ox} - E_A^{red}$. The two dashed lines give the limits for charge-transfer singlet exciplexes

● *Excited EDA complexes;* ● *mixed excimers;*

○ *excimers.*



Singlet State (F) and Triplet State (P) Exciplexes.

The Mixing of the zero-order States

$NB_o \leftrightarrow CT_o \leftrightarrow LE_o$

leads to destabilization and stabilization of the charge-transfer state

INTERACTION OF ZERO-ORDER COMPLEX STATES

The interaction of the Charge-Transfer exciplex state (A^-D^+) with

No-Bond ground state	Locally Excited states
$(AD)_o$ —— $(A^*D^*)_o$	$(\overset{*}{A}D)_o$ —— $(A^*D^*)_o$ —— $(A\overset{*}{D})_o$
leads to destabilization by U_{dest}	leads to stabilization by U_{stab}

of the "pure" charge-transfer exciplex state, so that

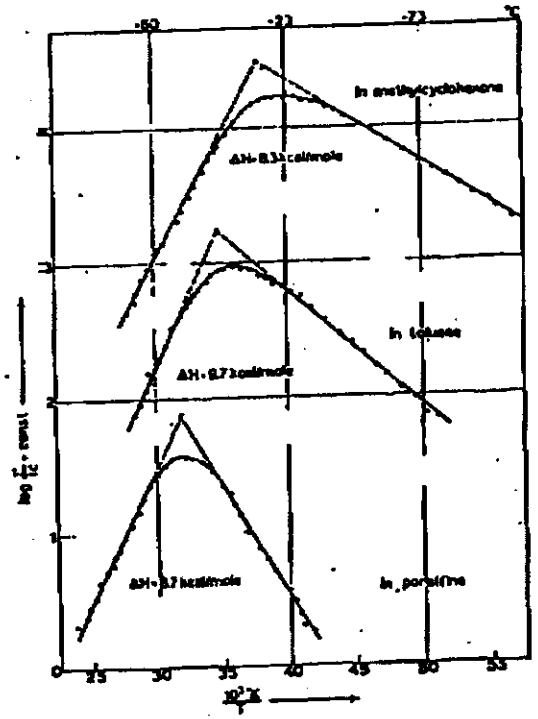
$$\Delta G_{ex}^c = E_D^{ox} - E_A^{red} - \frac{u^2}{\rho 3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - 0.19\right) + (U_{dest} - U_{stab}) + 0.38 \text{ eV}$$

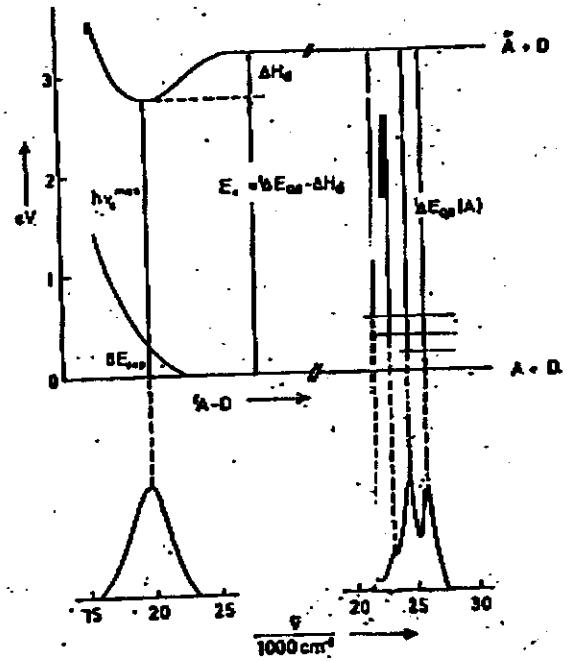
LE —— $E_{LE}^o = \overset{*}{A}E_{0,0}$ (lowest)

CT —— $U_{dest} - U_{stab} = \frac{(CT|V|NB)^2}{E_{CT}^o - E_{NB}^o} - \frac{(LE|V|CT)^2}{E_{LE}^o - E_{CT}^o}$

$E_{CT}^o = E_D^{ox} - E_A^{red} + 0.32$ eV

NB —— $E_{NB}^o = 0$





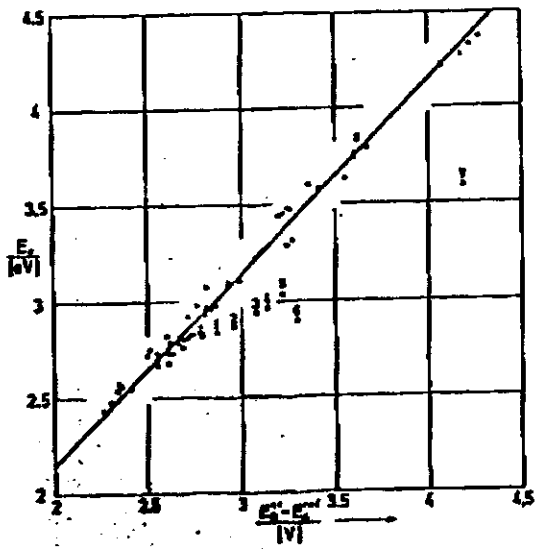


Fig. 2 Plot of singlet exciplex energy, E_e, in aliphatic hydrocarbon solvents against the difference between donor oxidation and acceptor reduction potentials, $E_D^{ox} - E_A^{red}$. Equation of the line: $E_e = E_D^{ox} - E_A^{red} + 0.15$ eV. 1 - 5, mixed excimers; 6, pyrene excimer; 7, naphthalene excimer.

Data on mixed exciers and excimers

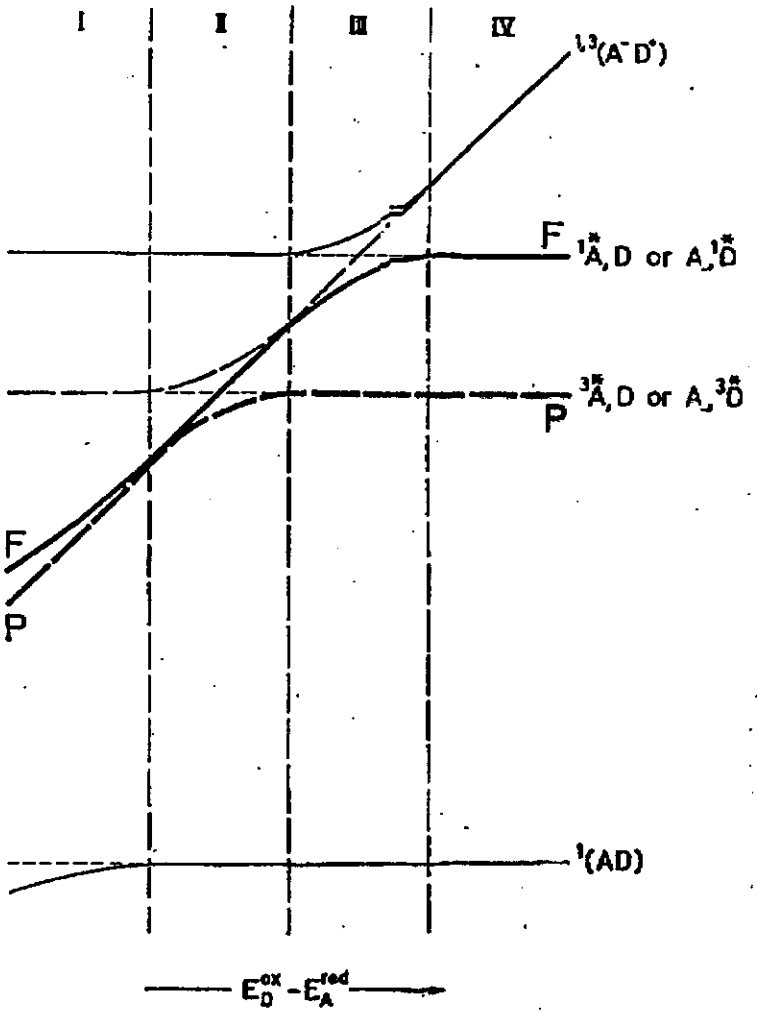
No	Acceptor ($-E^{red}$)[a]	Donor (E^{ox})[a]	E_e (eV)	τ_{stab} (eV)
1	Benz(c)acridine*(1.75 V)	1,2,4-$(MeO)_3C_6H_3$(1.12 V)	2.84	0.25
2	Benz(a)anthracene(2.02 V)	9,10-Me_2-anthracene*(0.94 V)	2.87	0.31
3	Anthracene*(1.96 V)	1,2,4-$(MeO)_3C_6H_3$(1.12 V)	2.94	0.36
4	Benz(a)anthracene*(2.02 V)	1,2,4-$(MeO)_3C_6H_3$(1.12 V)	2.97	0.39
5	Pyrene*(2.10 V)	1,2,4-$(MeO)_3C_6H_3$(1.12 V)	3.04	0.40
6	Pyrene*(2.10 V)	Pyrene(1.20 V)	2.90	0.72
7	Naphthalene*(2.58 V)	Naphthalene(1.60 V)	3.69	0.81

[a] measured in acetonitrile or dimethylformamide against S.C.E.

* asterisk denotes primarily excited species.

The results plotted in figure 2 show that most of the exciplexes investigated obey the relation

$$E_e = E_D^{ox} - E_A^{red} + 0.15 \pm 0.10 \text{ eV} \qquad [11]$$



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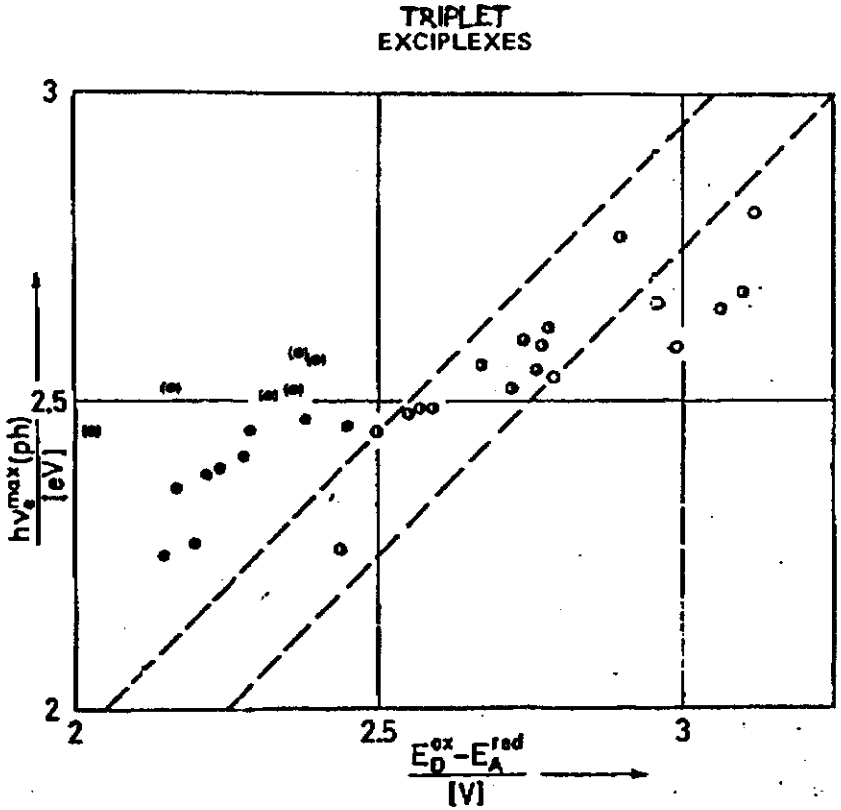

Plot of maximum energy of exciplex phosphorescence, $h\nu_e^{max}(ph)$, measured in rigid glass solution at 77 K against the difference between donor oxidation and acceptor reduction potentials, $E_D^{ox} - E_A^{red}$. The two dashed lines give the limits found for charge-transfer singlet-state exciplexes