Department of Chemistry
Florida State University

Elementary Photophysical Transitions and Photochemical Reactions

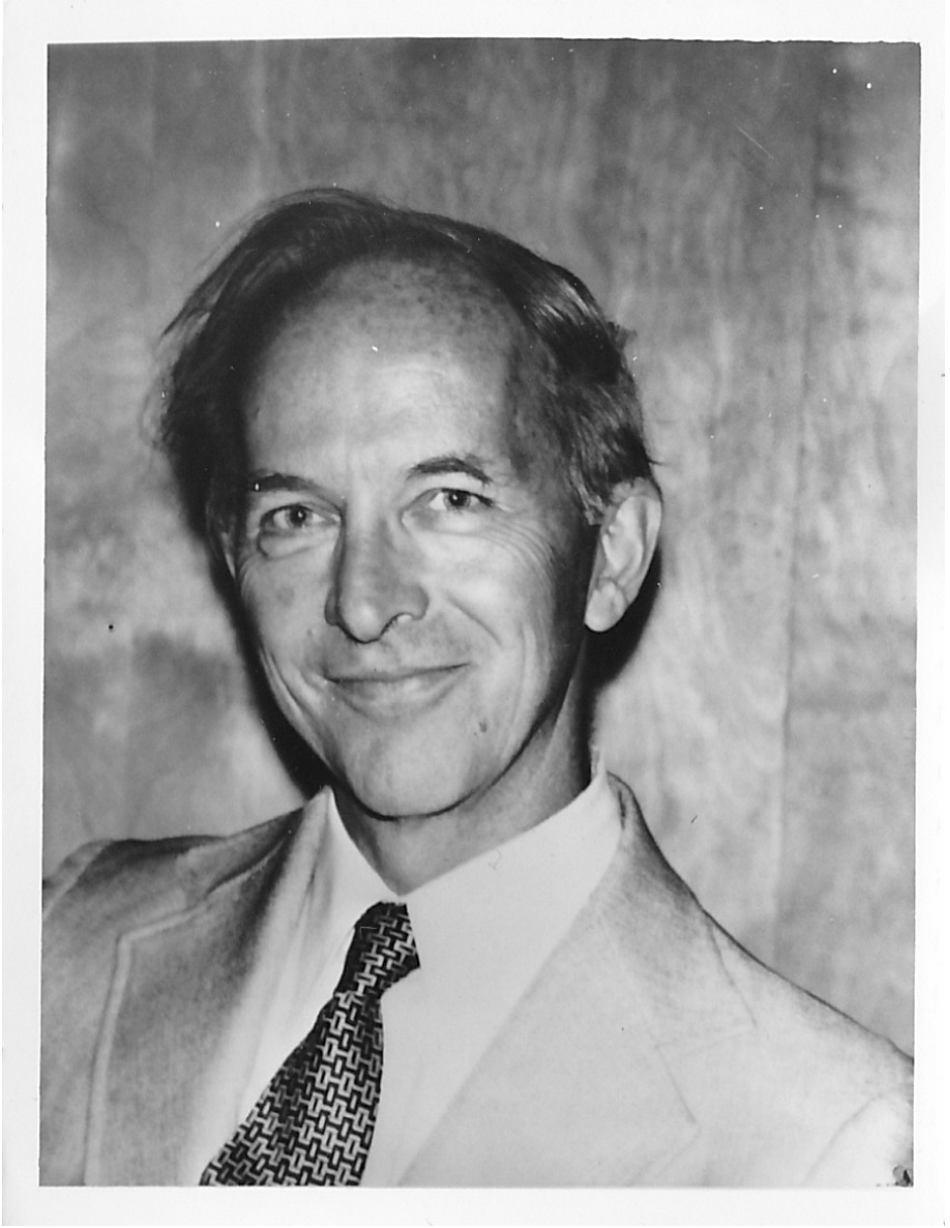
NSF REU June 09, 2023

Photochemistry's Icons Why I am here.

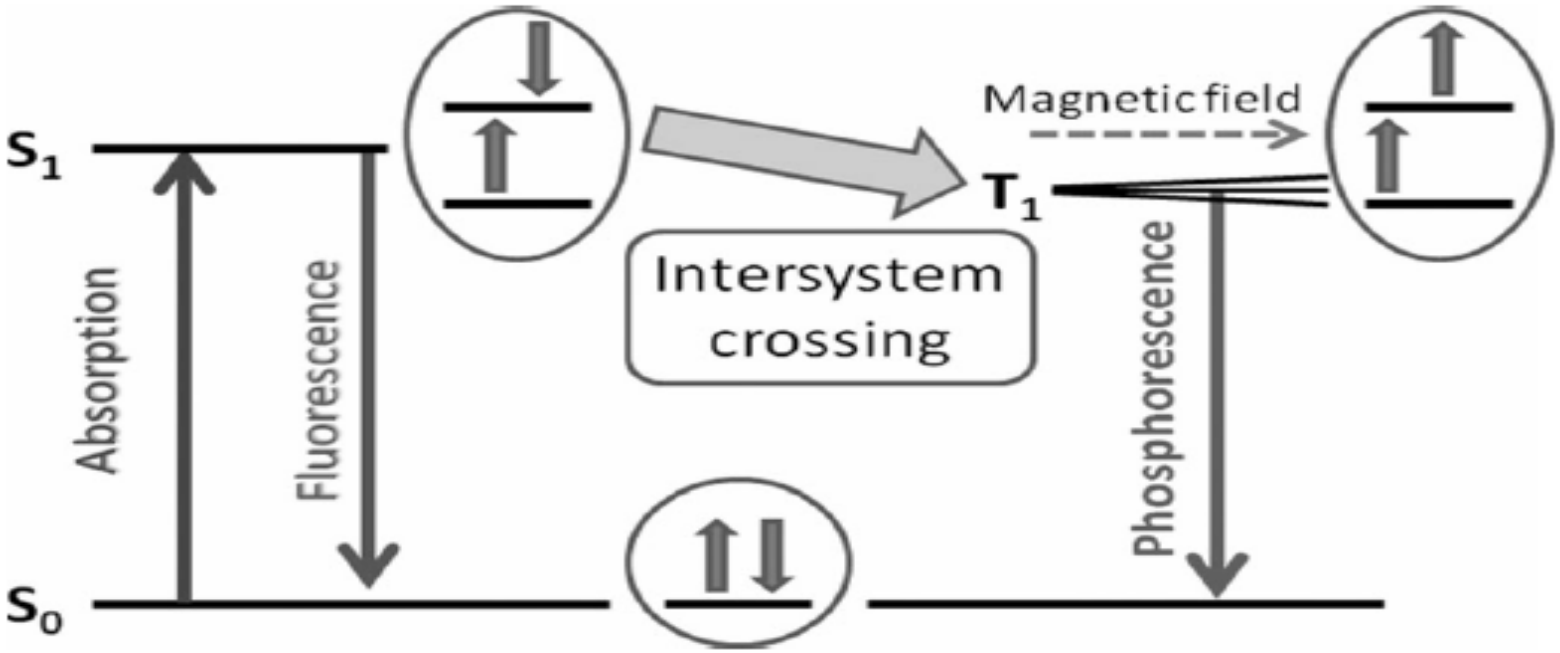
Figure 1-3. Some of photochemistry's icons. Upper (from left to right): Giacomo Ciamician (1857–1922), Theodor Förster (1910–1974), Michael Kasha (1920). Lower: George Hammond (1921–2005), George Porter (1920– 2002), Ahmed Zewail (1946).

From Photochemistry of Organic Compounds by Peter Klán and Jakob Wirz, 2009

Photo by Lilli Kasha ca. 1970



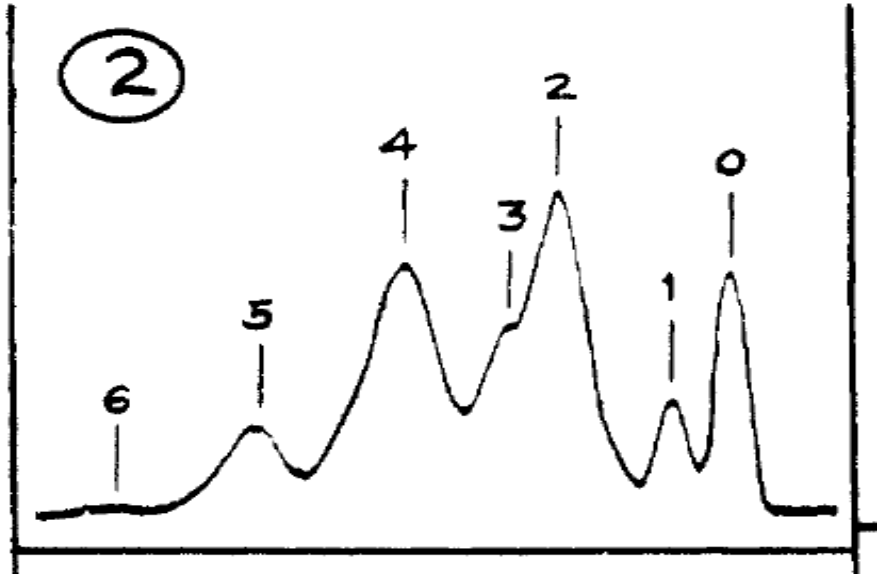
Intersystem Crossing



Demchenko, A. P. *et al. Angew. Chem. Int. Ed.* 2014, *53*, 2-11.

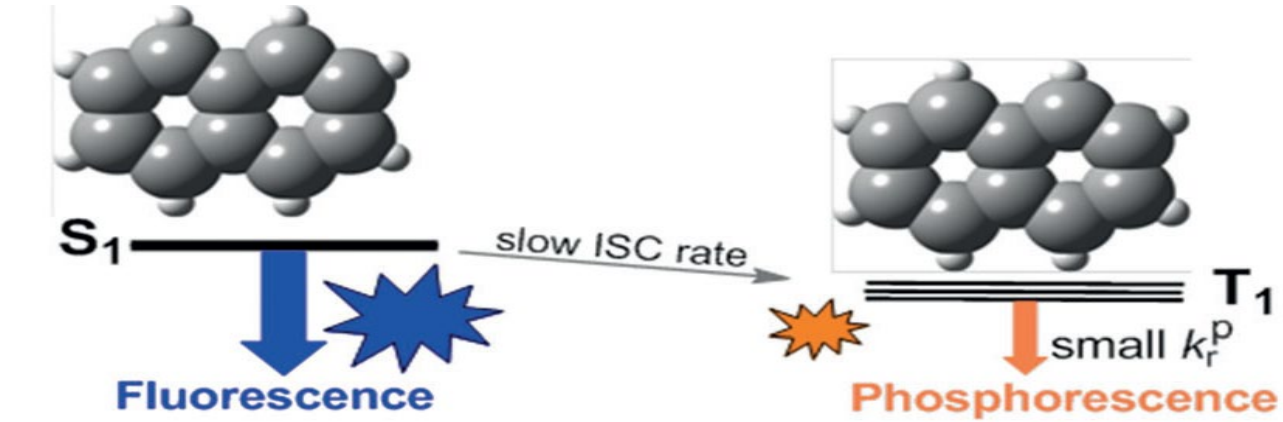
Phosphorescence and the Triplet State

Gilbert N. Lewis , M. Kasha *J. Am. Chem. Soc.* **1944**, *66*, 2100-2116

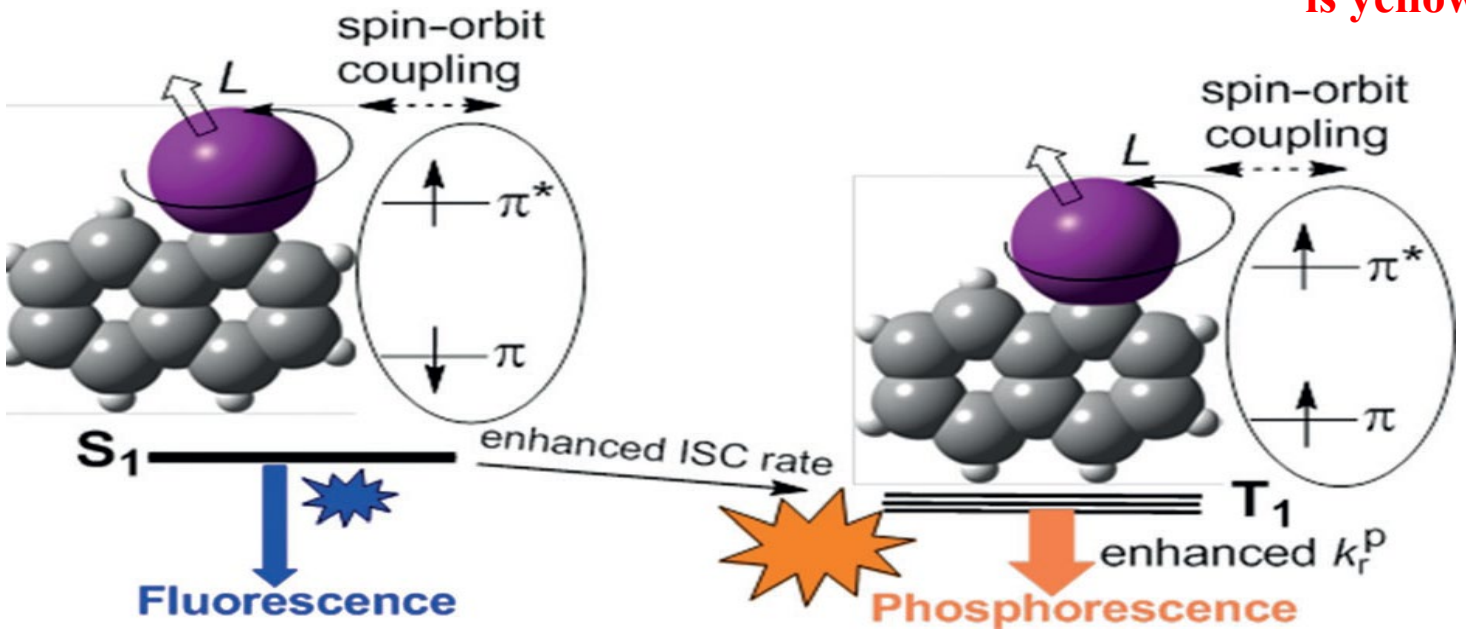


Naphthalene phosphorescence – triplet energies

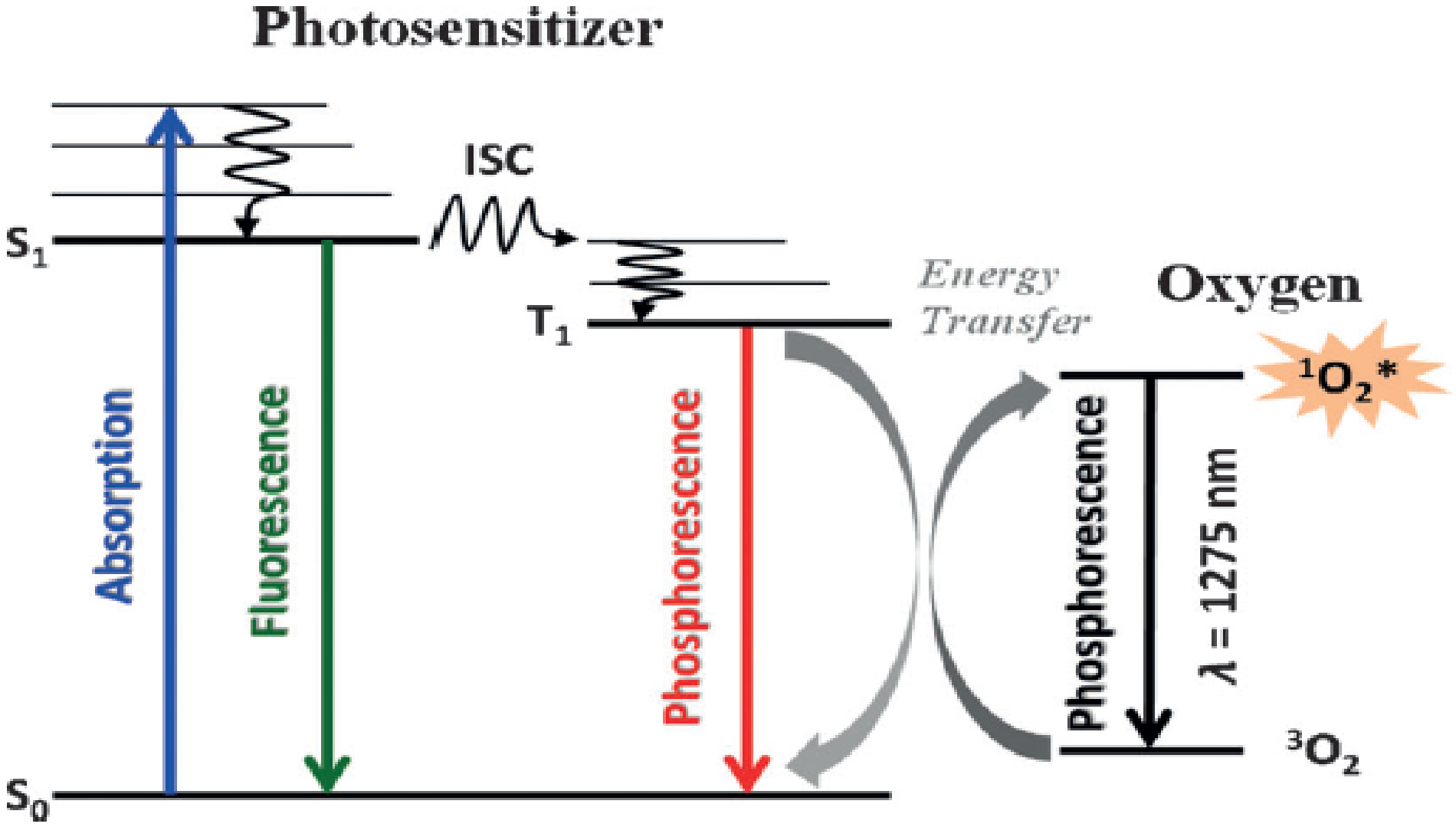
External and Internal Heavy Atom Effects



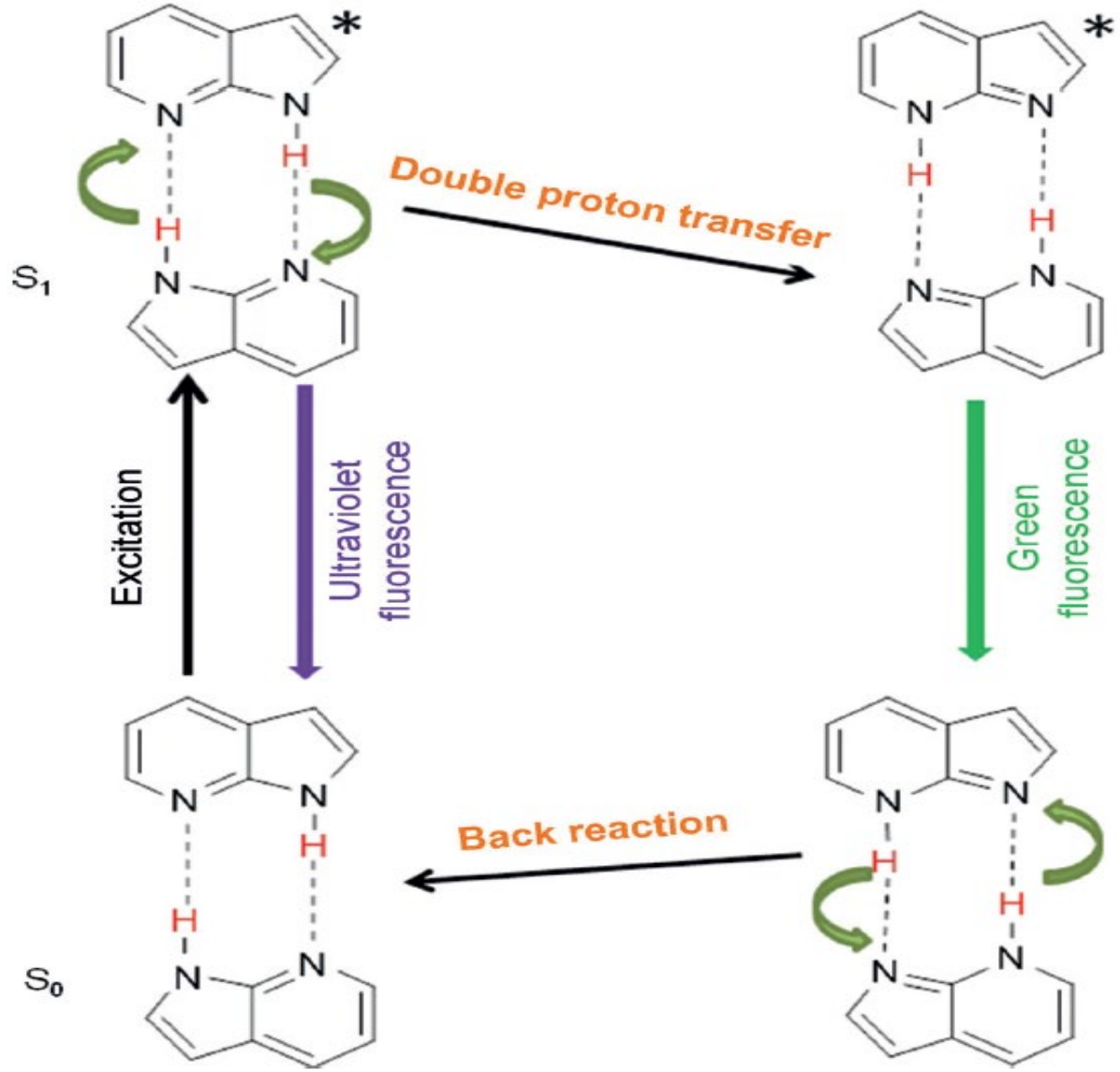
α-Chloronaphthalene is yellow in EtI, JCP, 1952



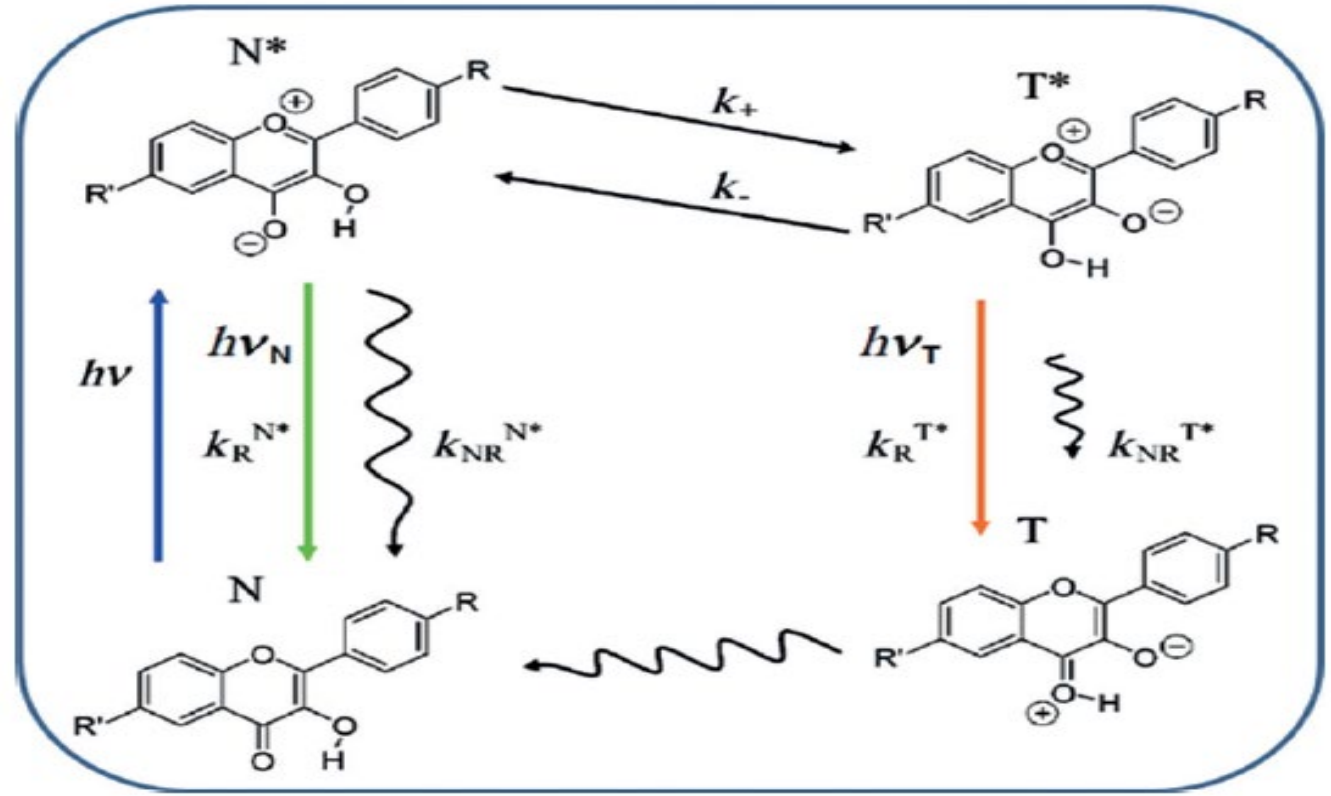
Singlet O_2 in Chemiluminescence and in Triplet Energy Transfer



Double Proton Transfer in 7-Azaindole
Proton Transfer Spectroscopy

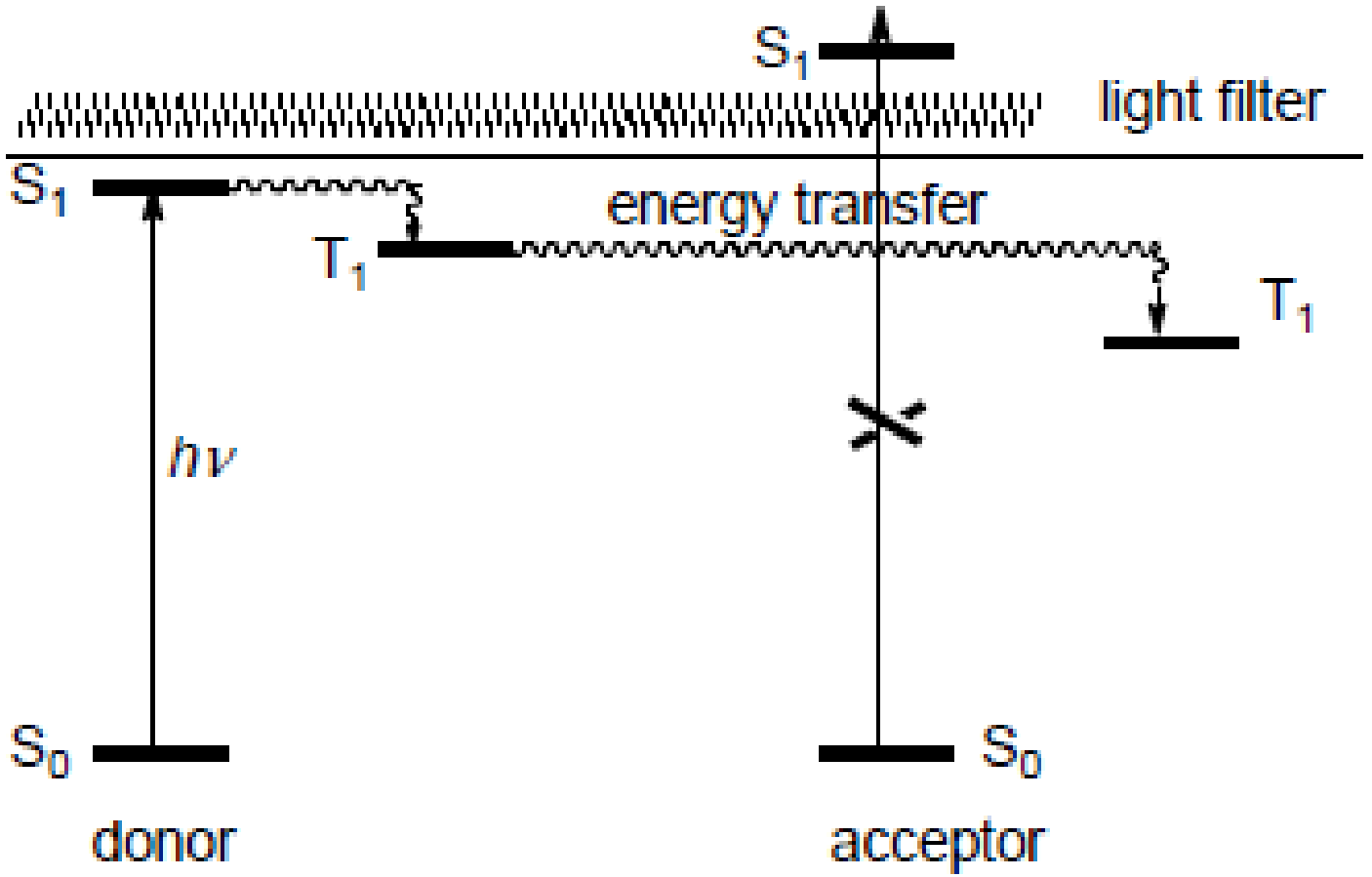


The Blue Daylily and Intramolecular S_1 Proton Transfer in Flavonoids

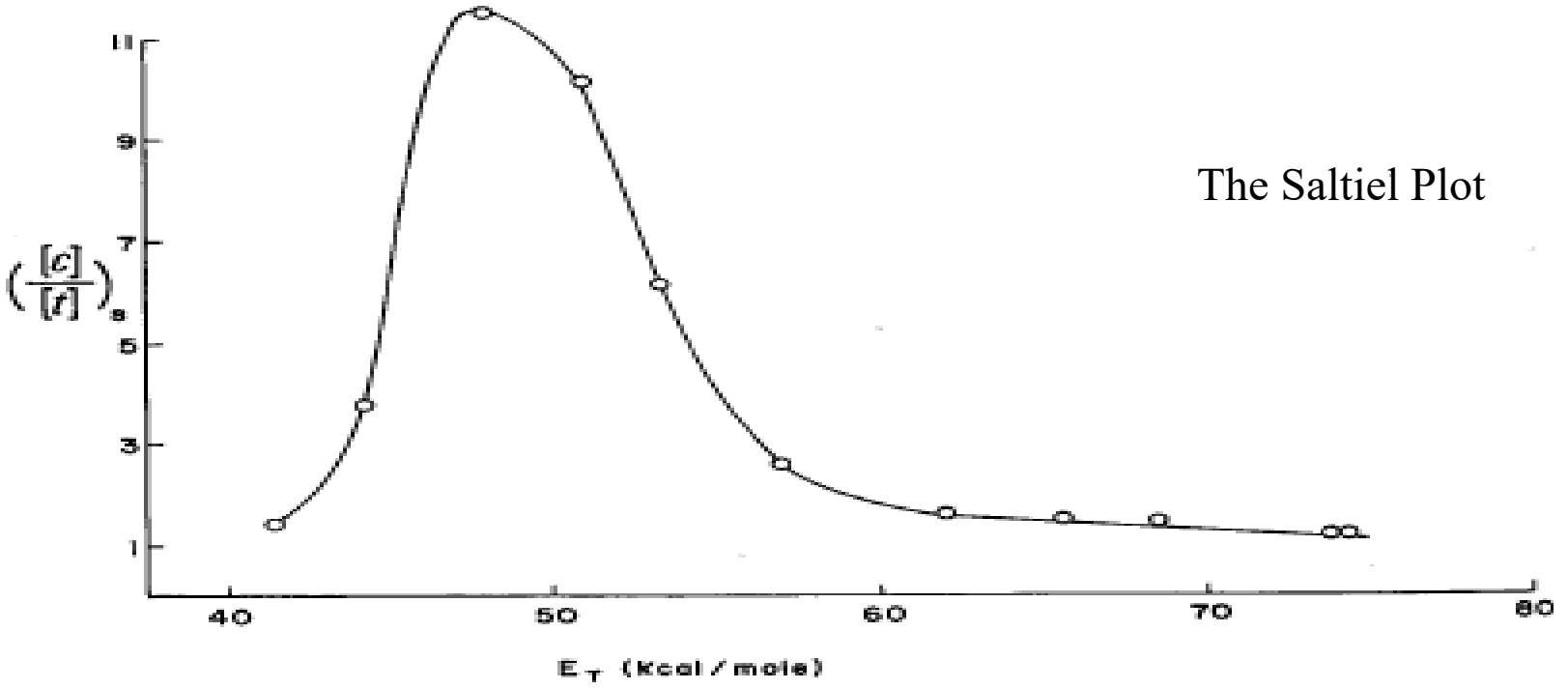


The Kasha Guitar

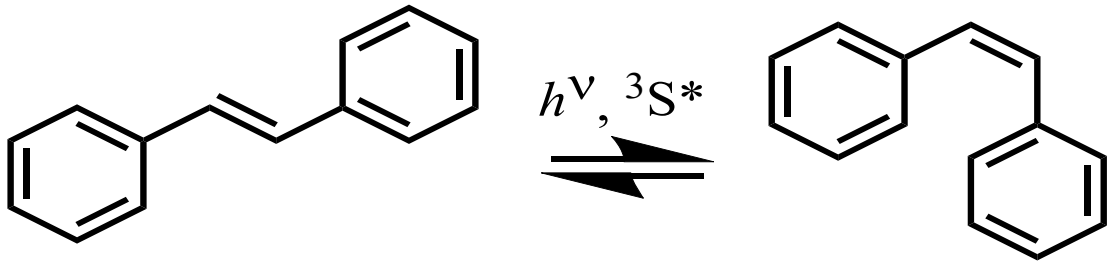
Triplet Sensitization



Triplet Sensitized Stilbene Photoisomerization



The Saltiel Plot



Hammond, G. S.; Saltiel, J. *J. Am. Soc. Chem.* **1962-1964.**

The Photostationary State

^{1}t-St + ^{3}S* → ^{3}t* + ^{1}S*

^{3}t* ⇌ ^{3}p*

^{3}p* → α^{1}t + (1-α)^{1}c

^{1}c-St + ^{3}S* → ^{3}c* + ^{1}S*

$$\frac{d[^1t]}{dt} = -k_t[^3S^*][^1t] + \alpha k_d[^1p^*] = 0$$

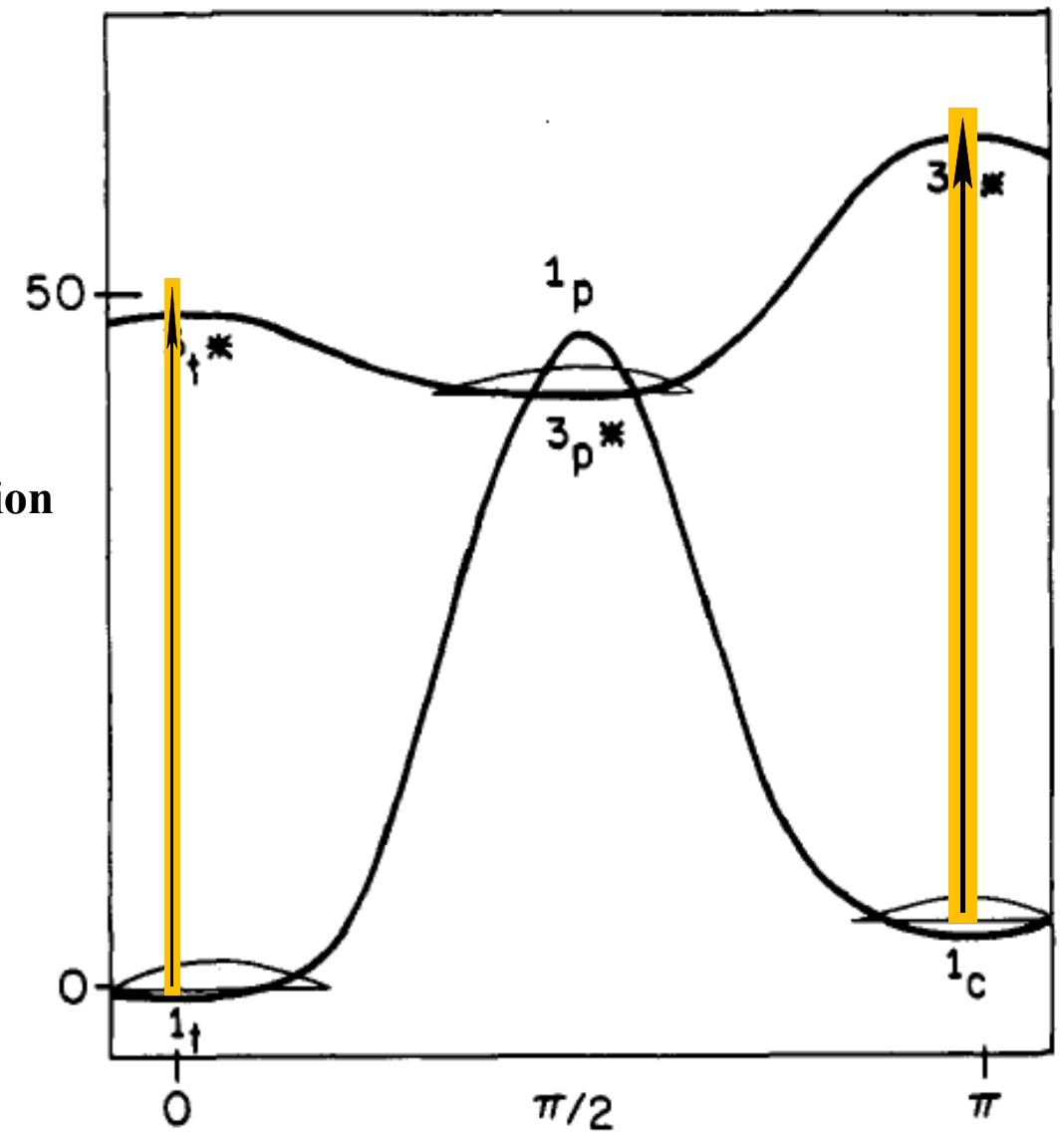
$$\frac{d[^1c]}{dt} = -k_c[^3S^*][^1c] + (1-\alpha)k_d[^1p^*] = 0$$

$$k_t[^3S^*][^1t] = \alpha k_d[^1p^*]$$

$$k_c[^3S^*][^1c] = (1-\alpha)k_d[^1p^*]$$

$$\left[\frac{[^1c]}{[^1t]}\right]_{PSS} = \frac{[k_t]}{[k_c]}\frac{(1-\alpha)}{\alpha}$$

49 kcal/mol
Vertical Excitation



62 kcal/mol

57 kcal/mol
Vertical Excitation

5 kcal/mol

Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in S_0 and T_1.

Nonvertical Triplet Energy Transfer

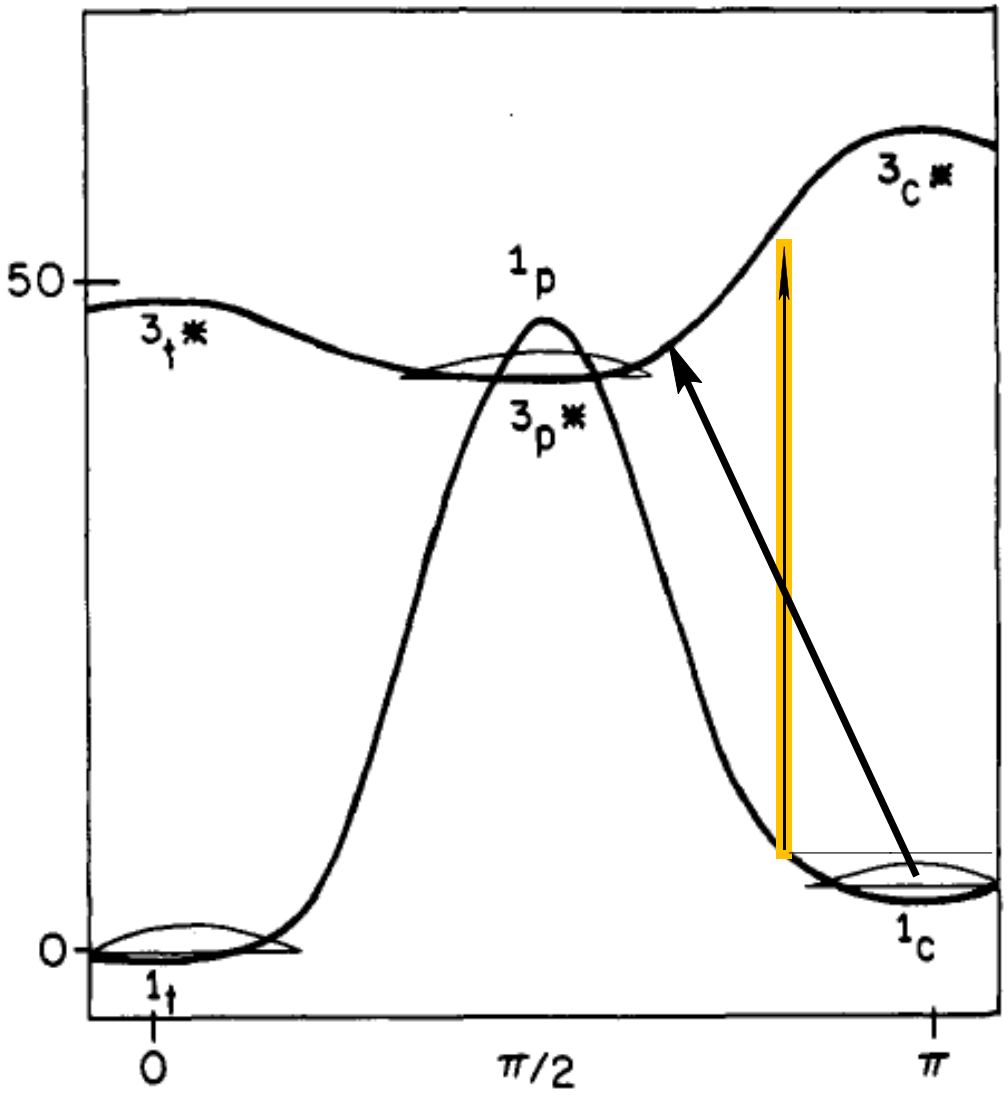
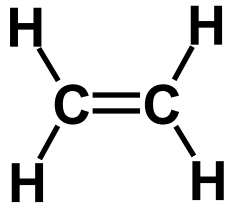
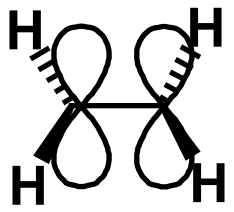


Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in S_0 and T_1.



CH_3-CH_3

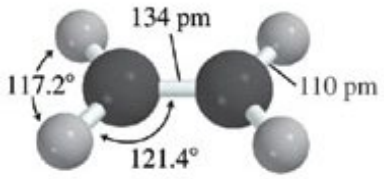


Average bond energies

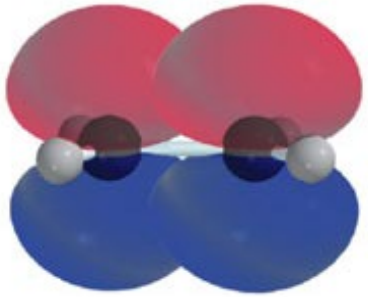
C-C 83 kcal/mol

C=C 146 kcal/mol

π bond ~ 63 kcal/mol

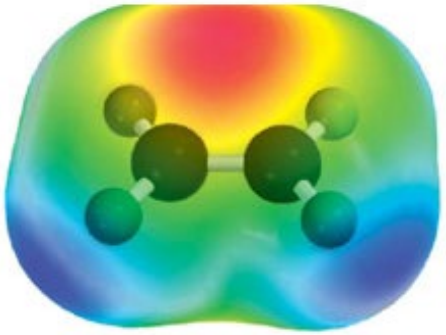


(a)

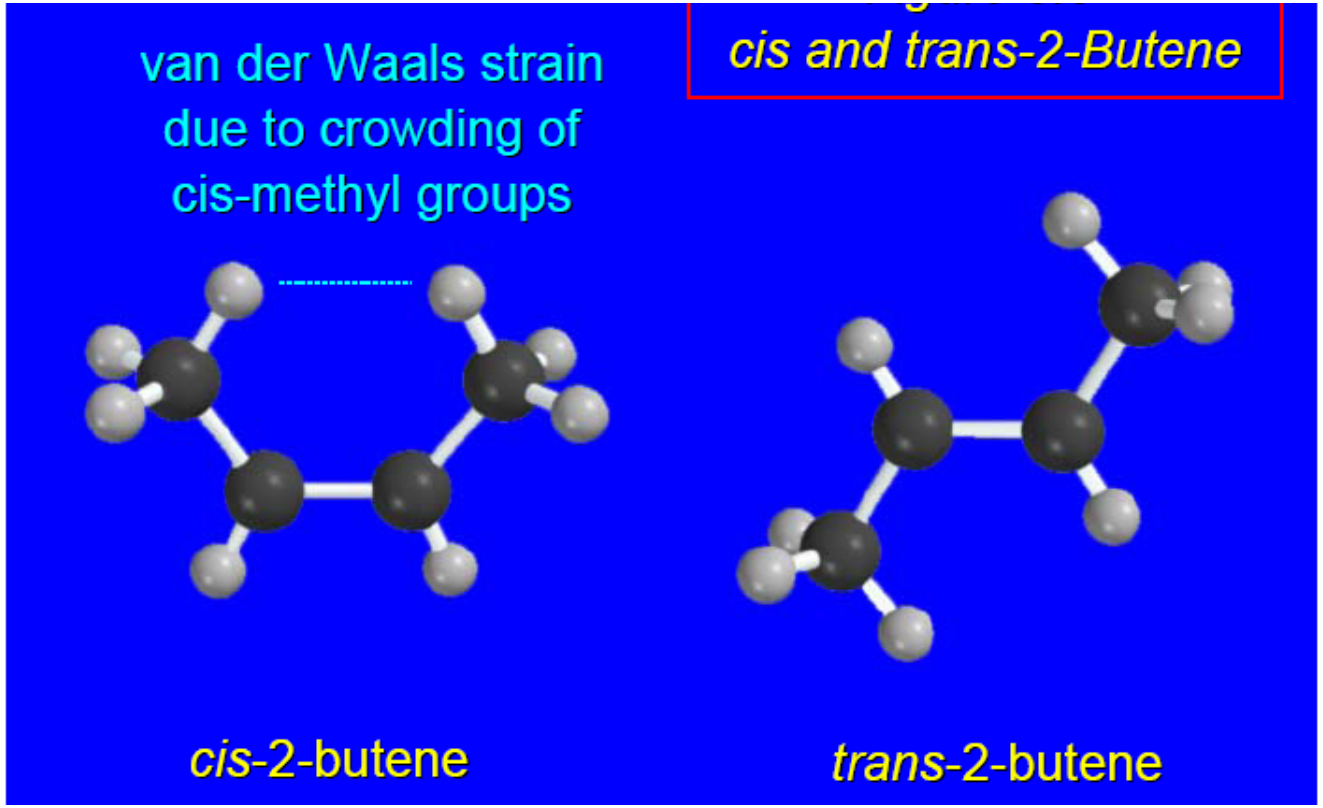


(b)

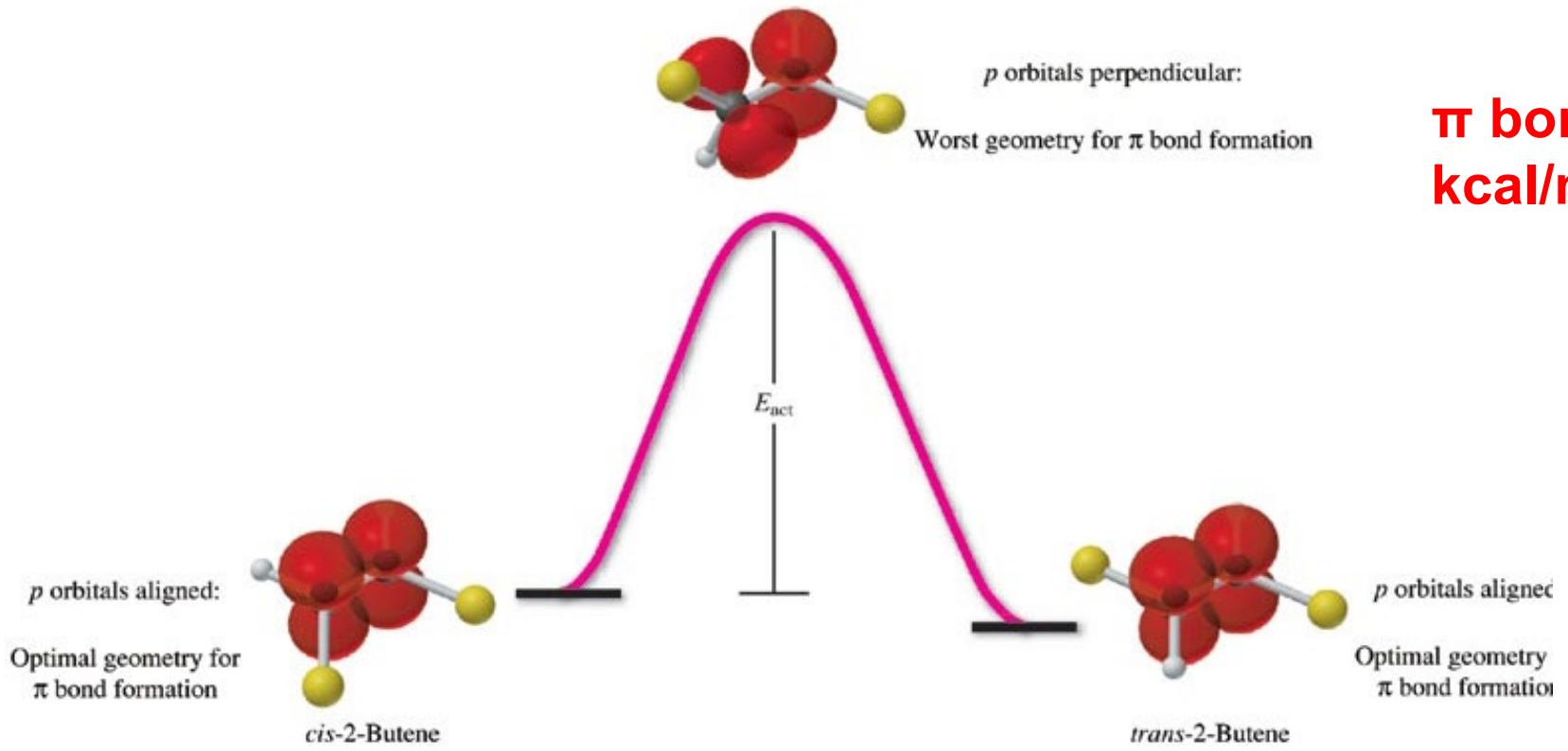
(c)



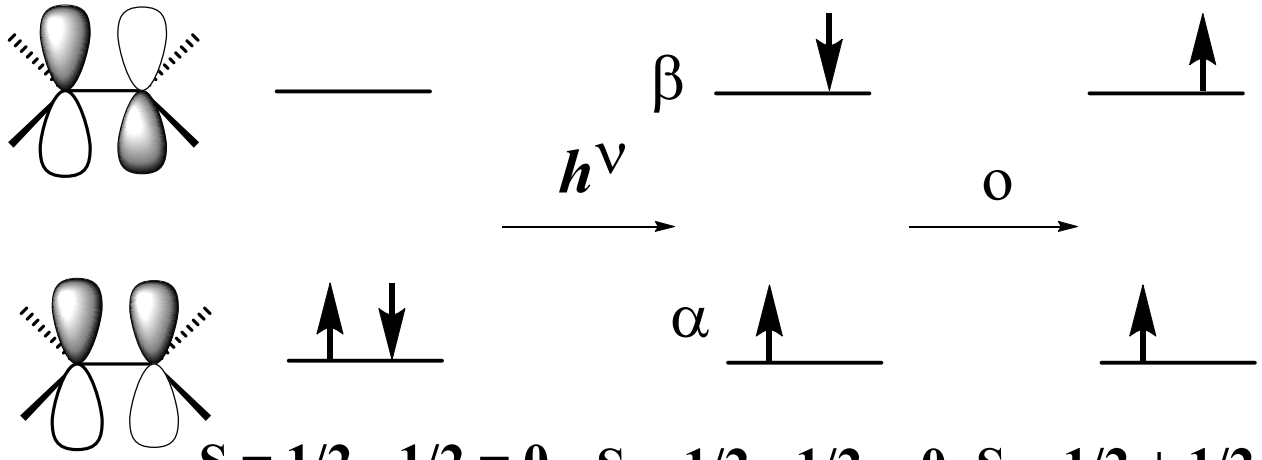
(d)


van der Waals strain
due to crowding of
cis-methyl groups
cis and trans-2-Butene
cis-2-butene
trans-2-butene

***cis*- and *trans*-2-butenes are stable separable isomers. They have the same connectivity and are stereoisomers. Rotation about a double bond occurs only at very high *T* or following light absorption.**

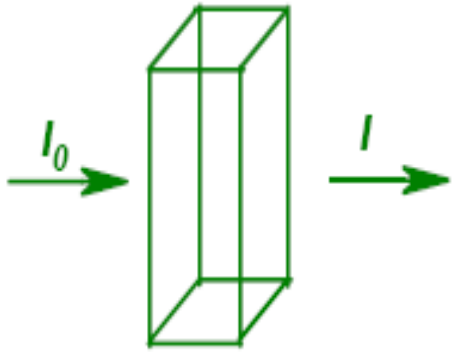


π bond ~ E_{act} = 66 kcal/mol



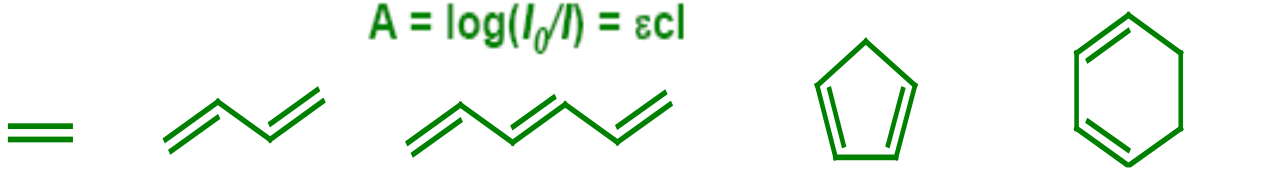
Spin States $\alpha\alpha$, $\beta\beta$, $\sqrt{1/2}(\alpha\beta + \beta\alpha)$, $\sqrt{1/2}(\alpha\beta - \beta\alpha)$

T T T S



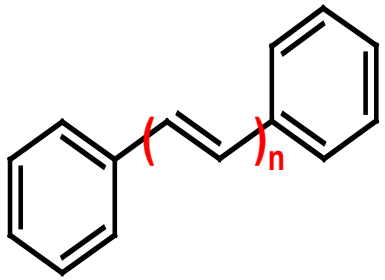
Absorbance

$A = \log(I_0/I) = \varepsilon c l$



170 nm	217 (21,000)	263 (52,500)	239 (3,400)	256 (8,000)

λ_{max} (ε_{max})



n	λ_{max}, nm	ε_{max} x 10^{-3}, $M^{-1}cm^{-1}$
1	294.1	28
2	328	53
3	348	80
4	404	86

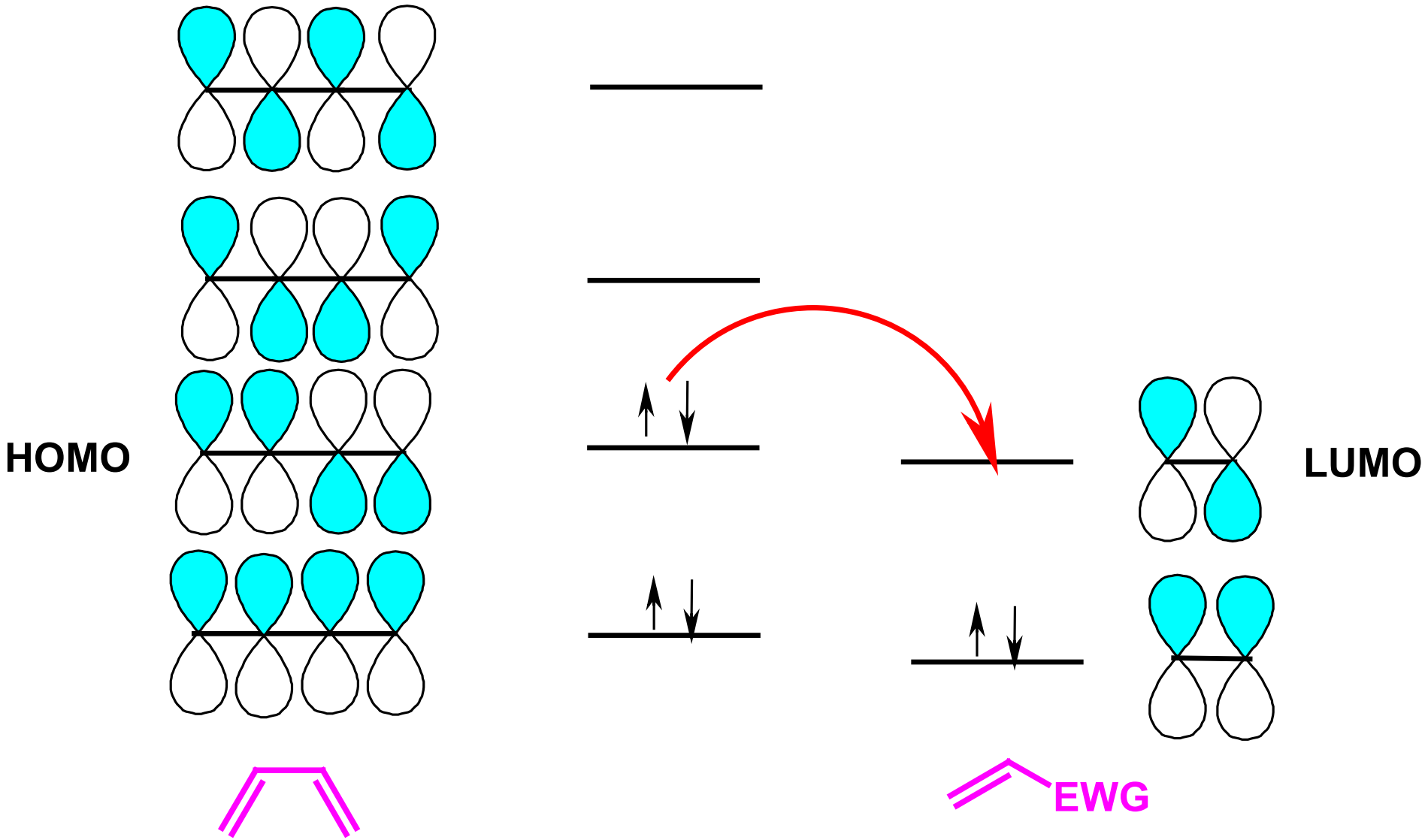
Effect of Conjugation

Molecular Orbital Analysis of the Diels-Alder Reaction

The diene is the electron donor and the dienophile is the electron acceptor. The concerted nature of the D-A reaction can be understood by considering the interaction of the HOMO of the diene with the LUMO of the dienophile (Fukui/Kyoto, Woodward/Harvard, Hoffmann/Harvard now Cornell---Nobel prize in Chemistry)

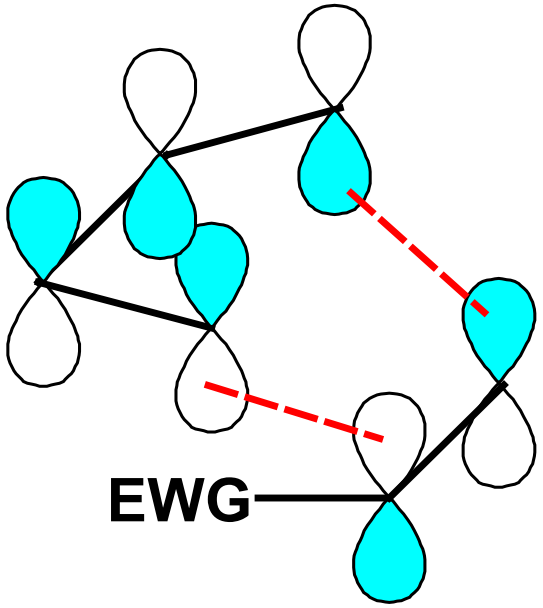
1965

1981


HOMO
LUMO
EWG

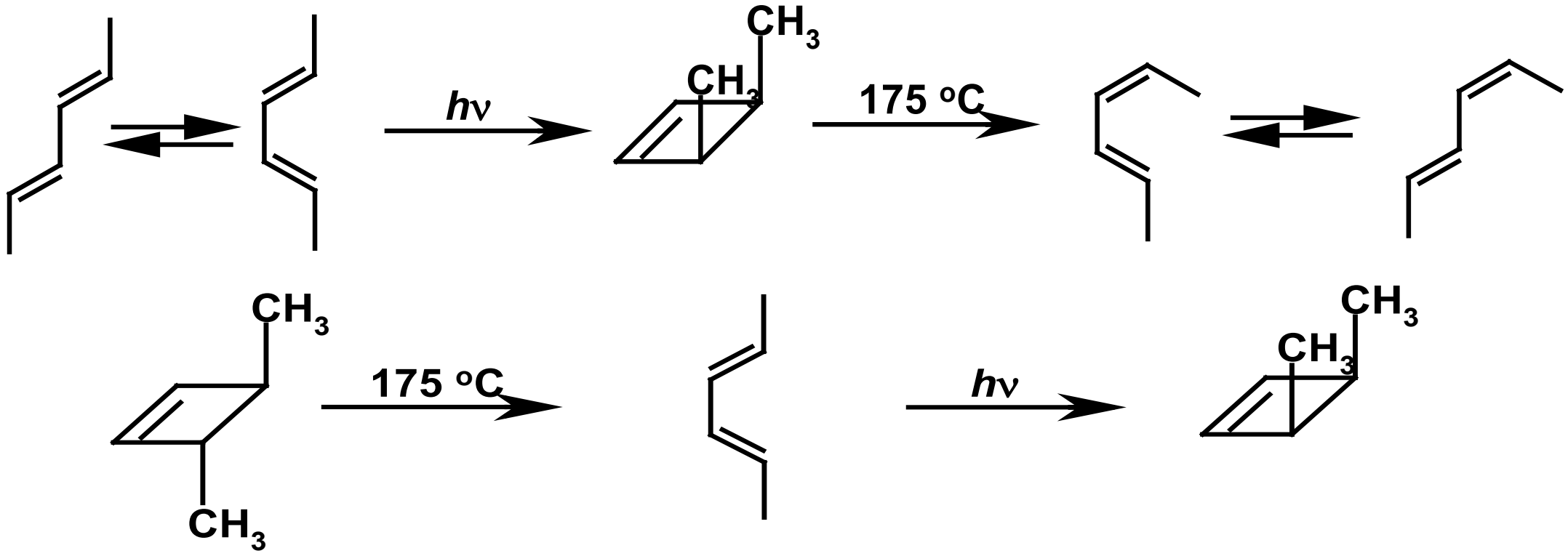
Frontier Orbital Control of Diels-Alder Reaction

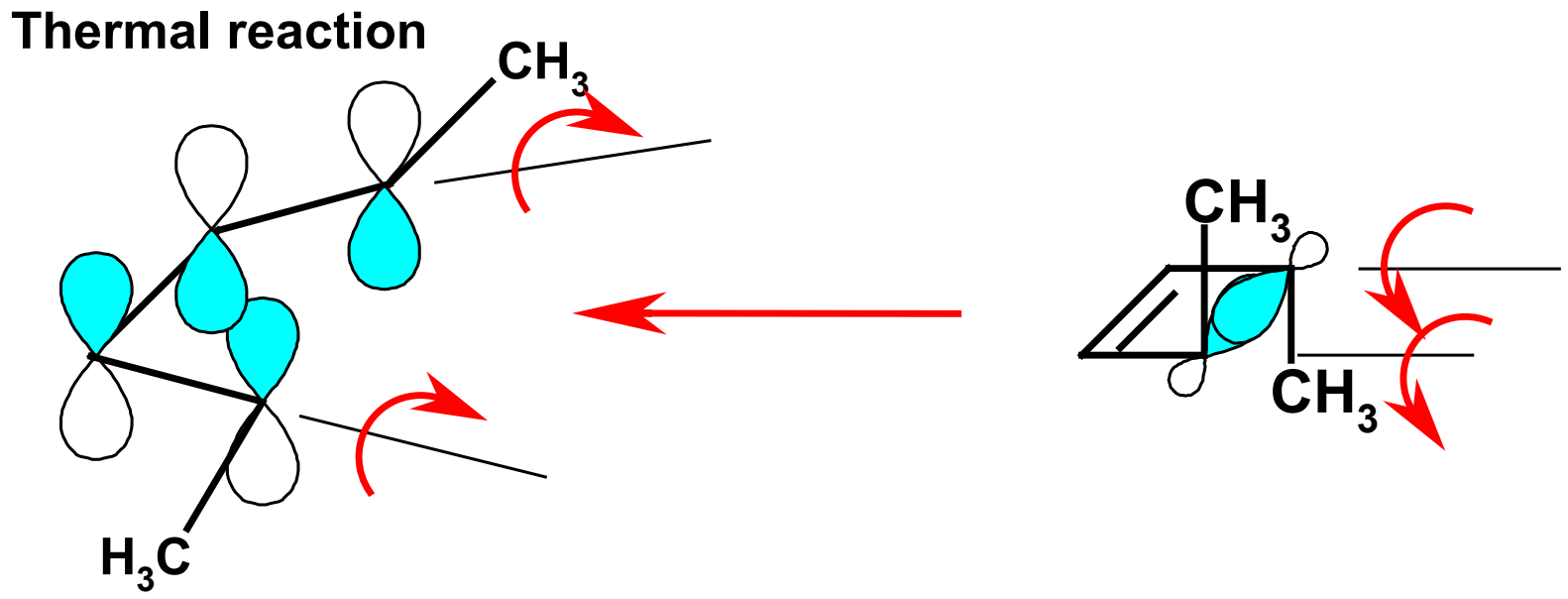
HOMO Donor



LUMO Acceptor

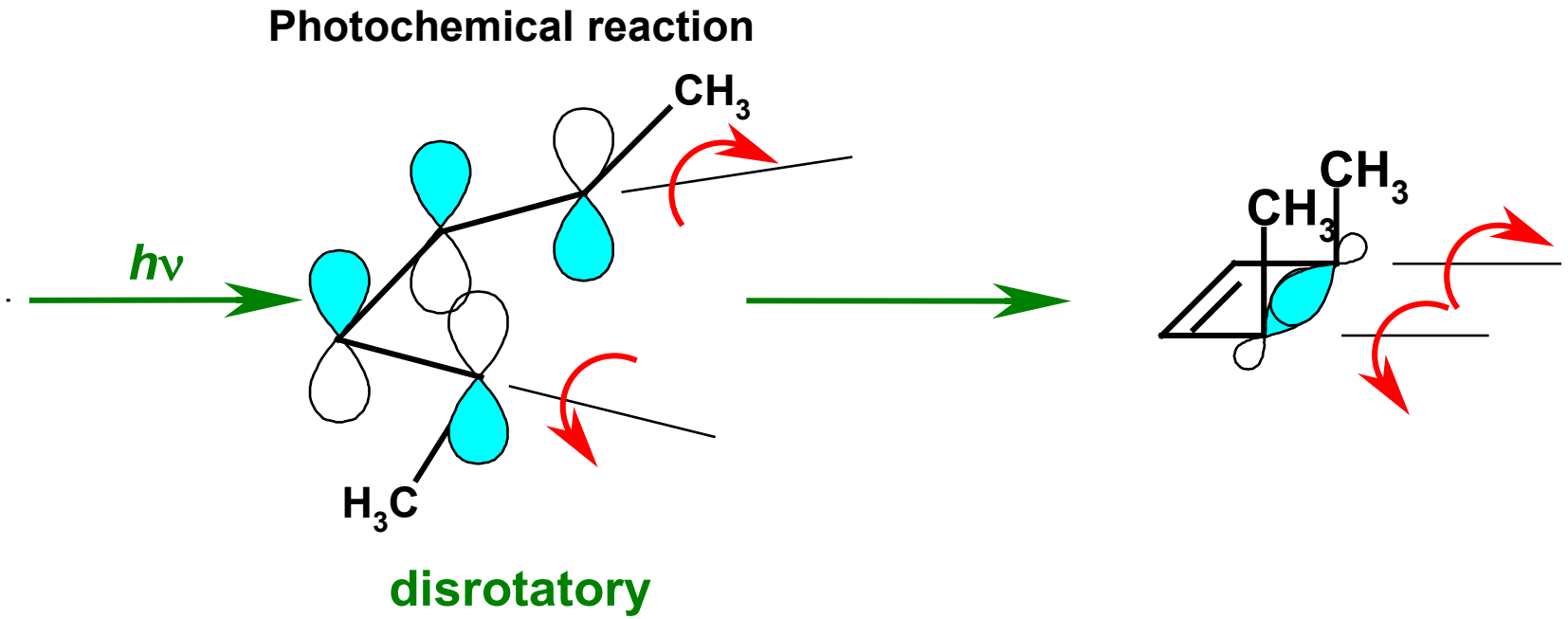
Electrocyclic reactions are stereospecific





conrotatory

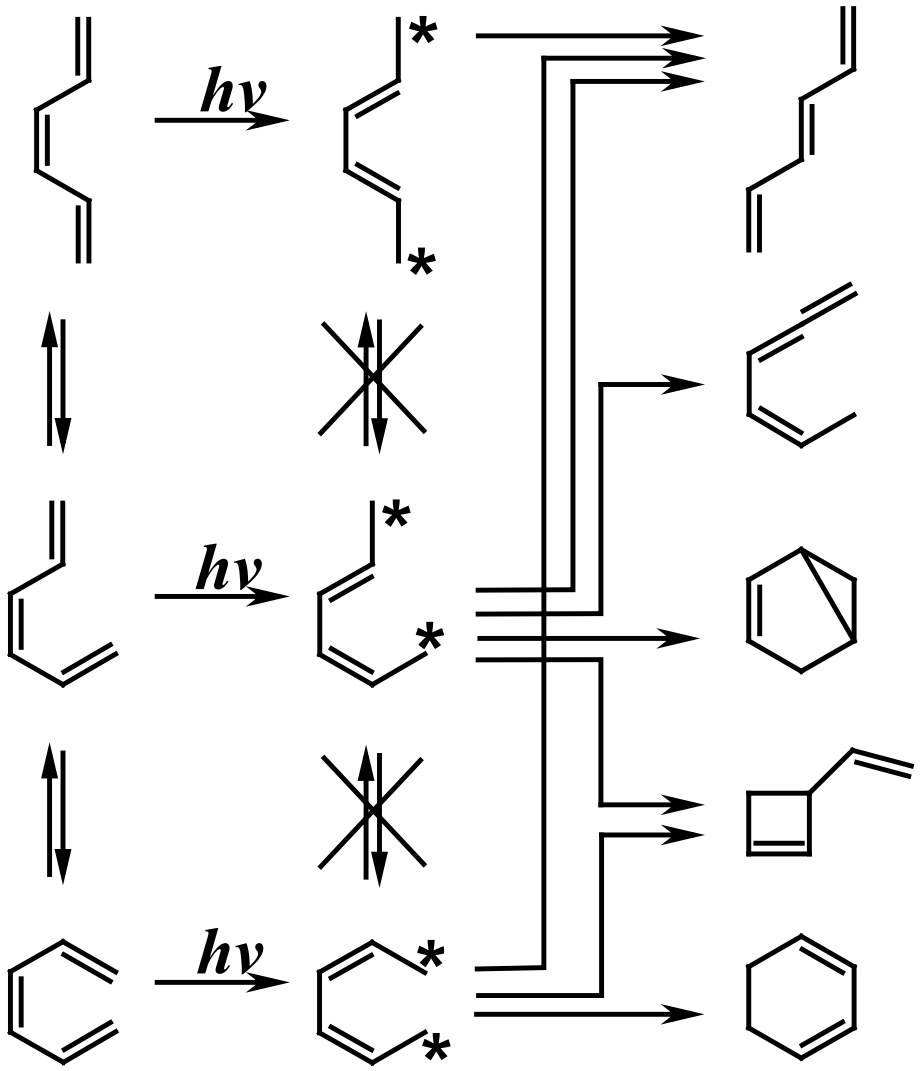
Rotation in the same direction leads to a bonding interaction (+ lobe on + lobe or - lobe on – lobe). The reaction passes through the same TS in both directions.



Rotation in opposite directions leads to a bonding interaction (+ lobe on + lobe or - lobe on – lobe).
The reaction passes through the same TS in both directions.

NEER PRINCIPLE

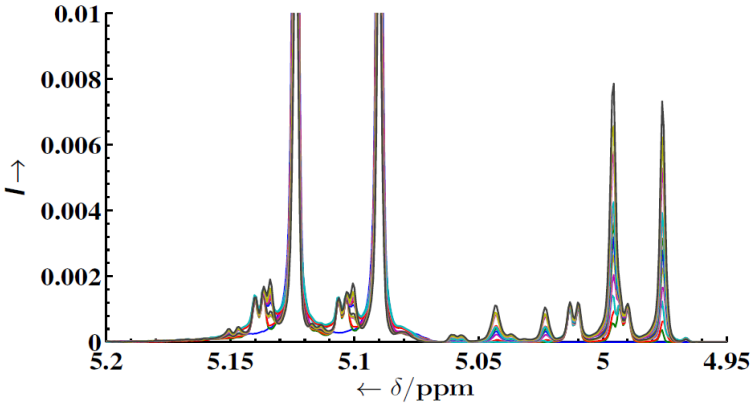
Egbert Havinga
1909-1988



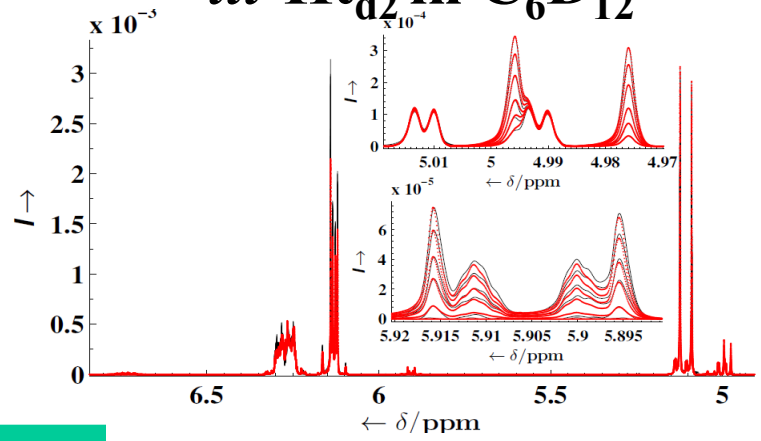
Havinga, *Tetrahedron*, 1973
$\phi_{ct} = 0.03, \phi_{tc} = 0.016$

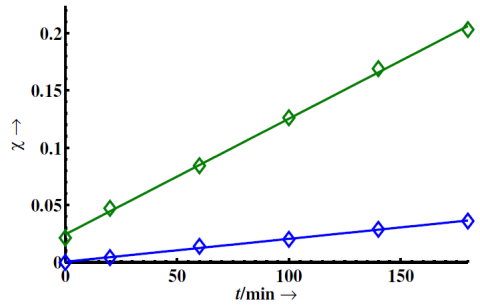
Havinga, E.; Schlatmann, J. L. M. A *Tetrahedron* 1961, *16*, 146-152.

1,6-Dideuteriohexatrienes



***ttt*-Ht$_{d2}$ in C_6D_{12}**

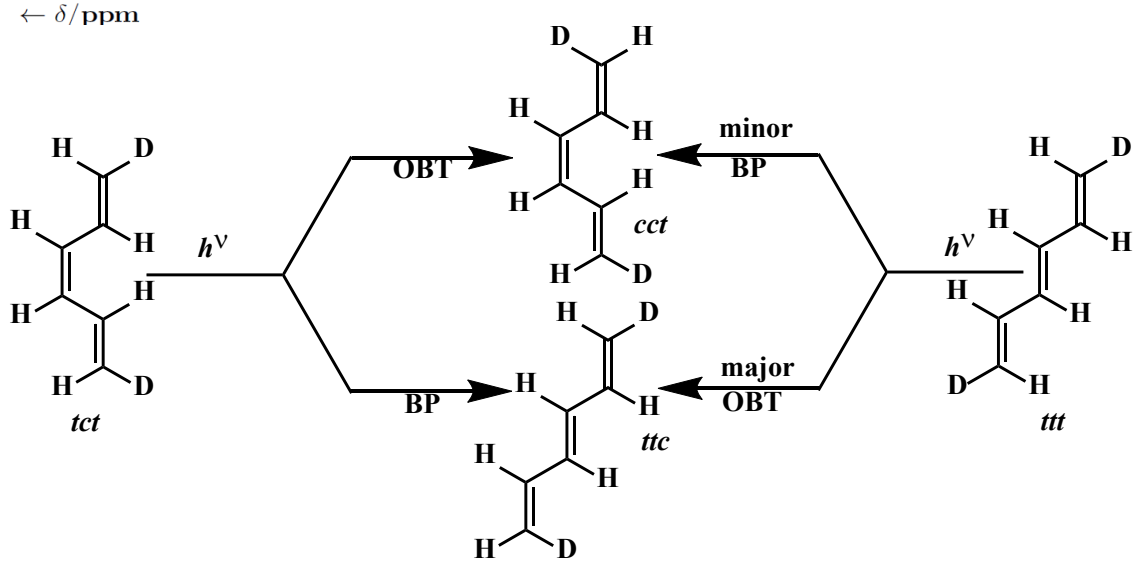




***ctt*-Ht**

***cct*-Ht**

	C_6D_{12}		CD_3CN	
x	$\phi_{ttt\rightarrow x}$	$\phi_{tct\rightarrow x}$	$\phi_{ttt\rightarrow x}$	$\phi_{tct\rightarrow x}$
ctt	0.44	0.24_5	0.54	0.24
cct	0.08_5	0.34	0.09_3	0.39
tct			0.01_4	
ttt		0.05_8		0.11



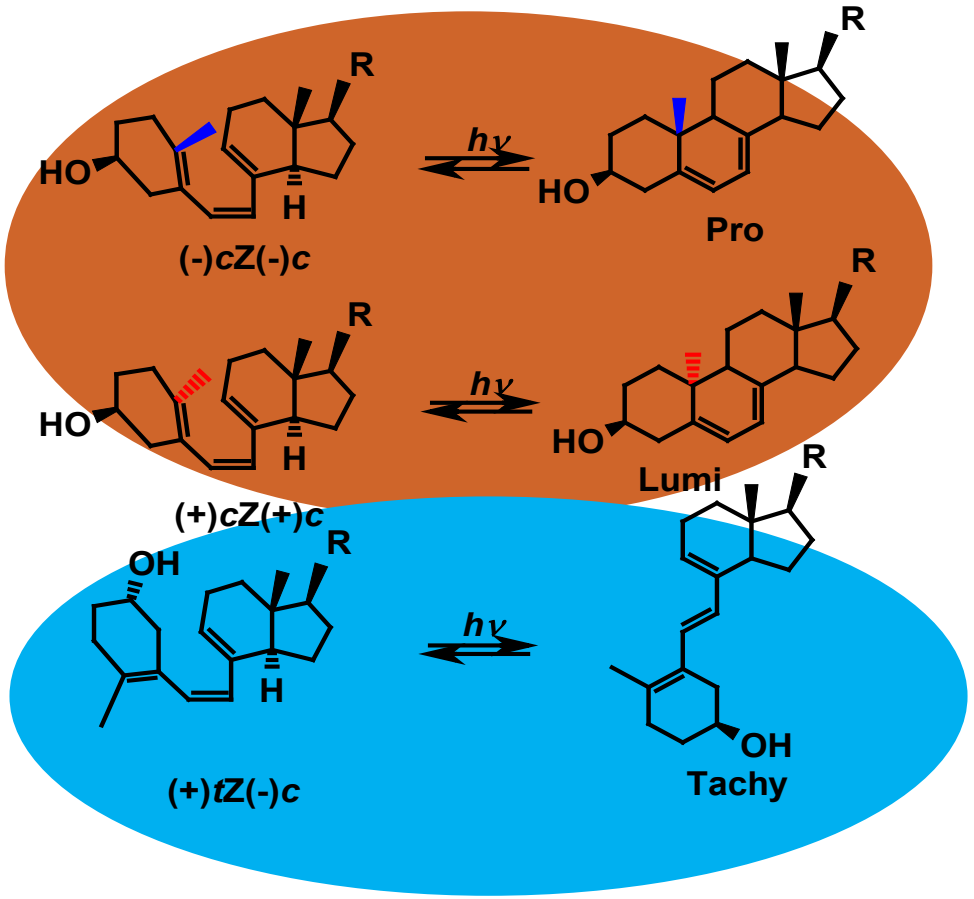
Saltiel, J.; Redwood, C. E.; Laohhasurayotin, K.; Samudrala, R. Photochemistry of the 1,6-Dideuterio-1,3,5-hexatrienes in Solution: *J. Phys. Chem. A* **2018**, *122*, 8477-8489.

Havinga's NEER Principle

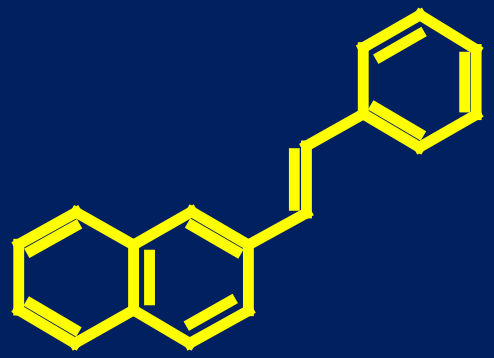
Egbert Havinga
1909-1988

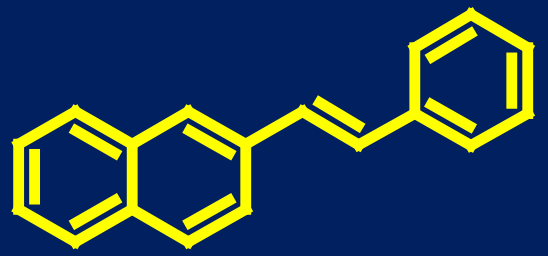
Photocyclization
Long λ

Photoisomerization
Short λ

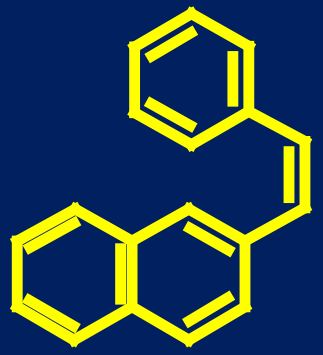


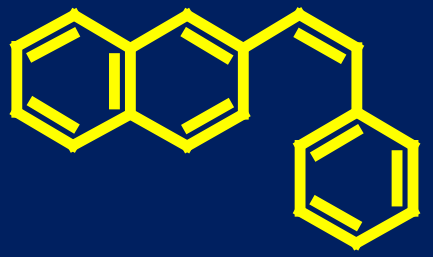
NPE Conformers





t-NPE$_A$ *t*-NPE$_B$

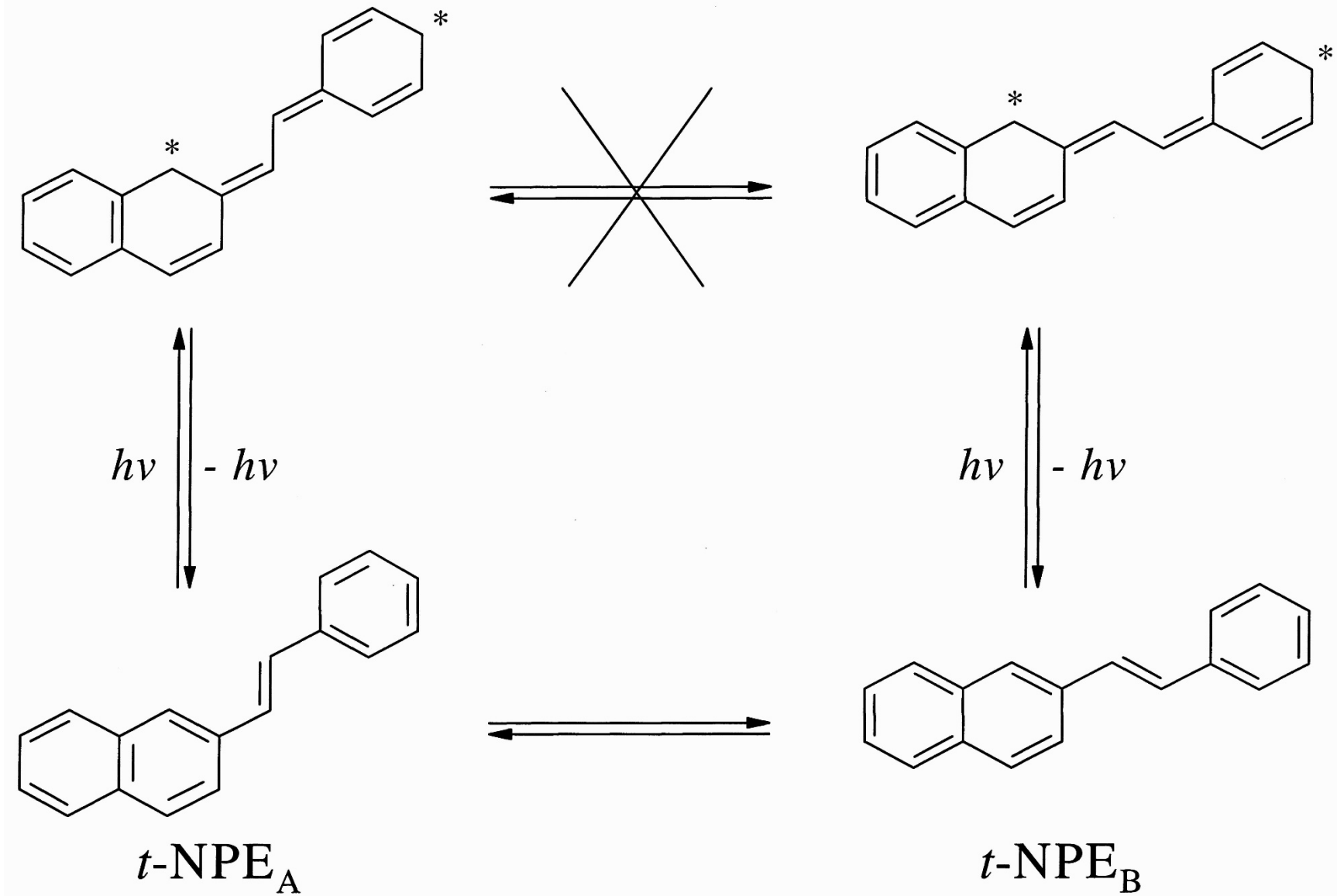




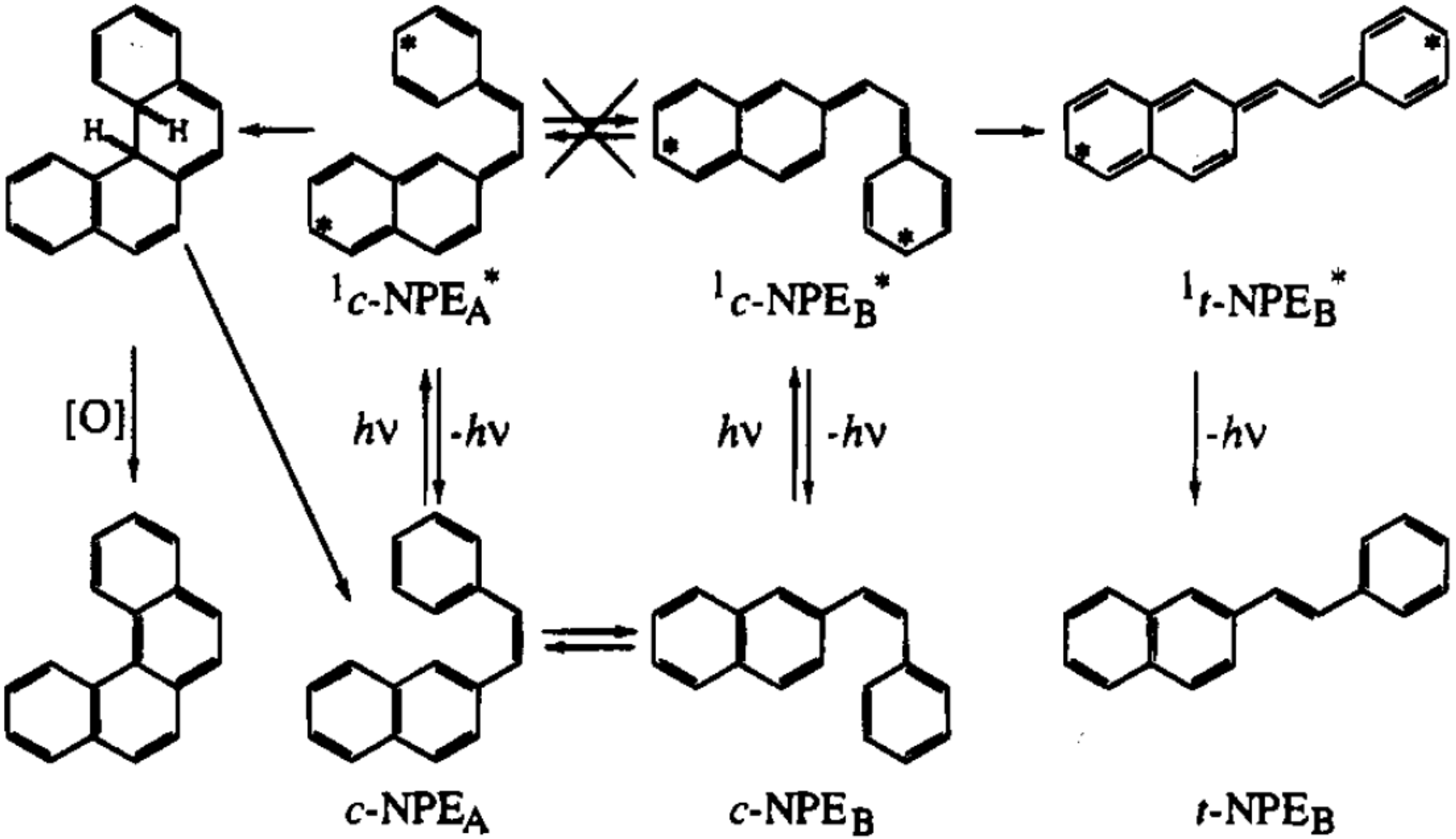
c-NPE$_A$ *c*-NPE$_B$

NPE conformers

trans-1-(2-Naphthyl)-2-phenylethene and the NEER Principle

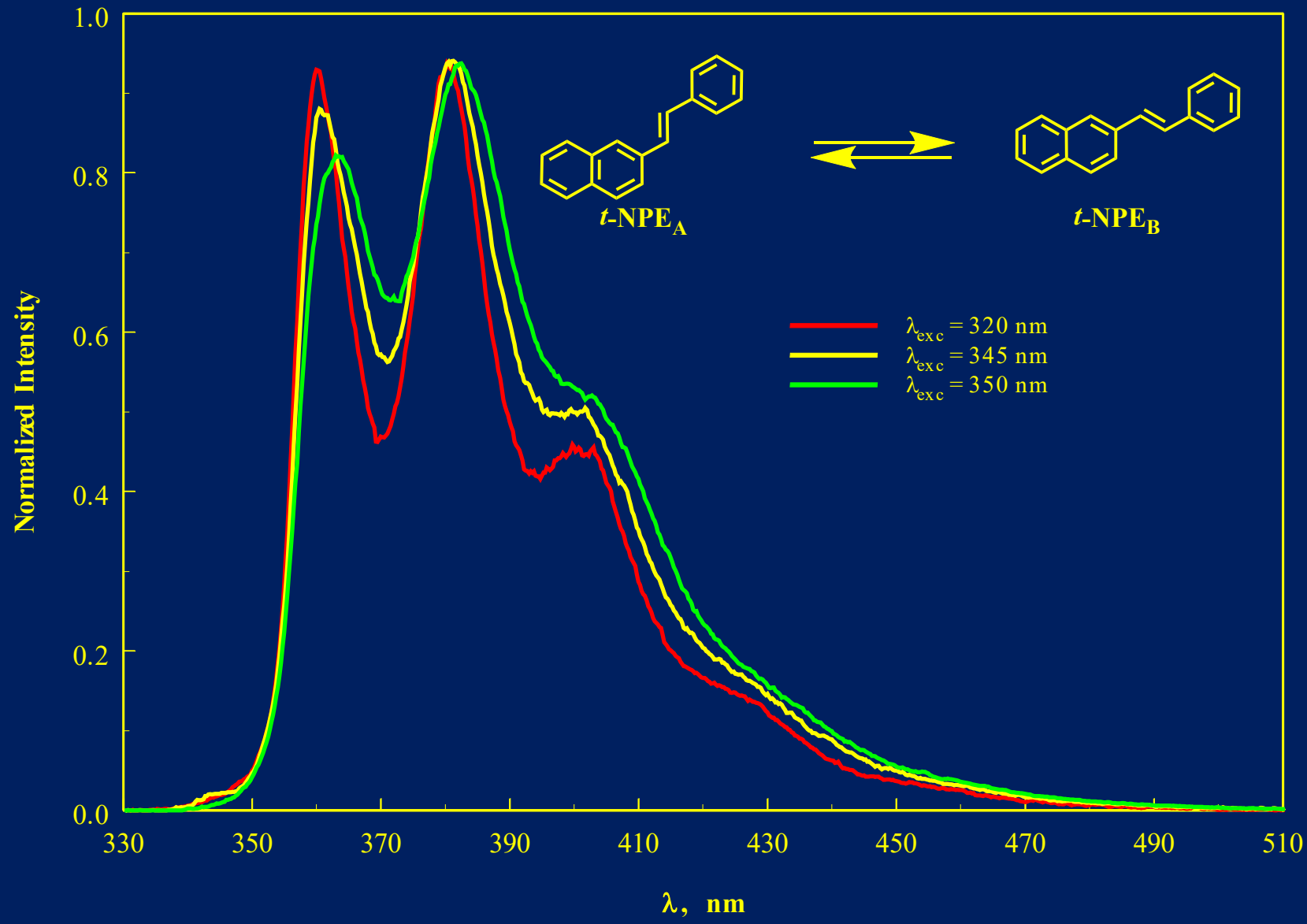


Conformer specific photochemistry in *c*- and *t*-NPE



t-NPE/Bz

Fluorescence Emission Spectra of *t*-NPE as a Function of λ_{exc} in Ar Outgassed Benzene at 20 °C



Summary of PCA-SM Mathematical Operations

Transposed Matrix x **Spectral Input Matrix** = **Covariance Matrix**

⇓

Diagonalized Matrix ⇐ **Eigenvalues** ⇐ **Number of Components**

Eigenvector Matrix ⇐ **Eigenvectors**

$$\alpha_i = V_\alpha \cdot S_i,\ \beta_i = V_\beta \cdot S_i$$
$$S_i = \alpha_i V_\alpha + \beta_i V_\beta$$

Pure Component Spectra

$$S^A = \alpha^A V_\alpha + \beta^A V_\beta$$
$$S^B = \alpha^B V_\alpha + \beta^B V_\beta$$

Pure Component Coefficients

α^A, β^A and α^B, β^B

Experimental Spectra

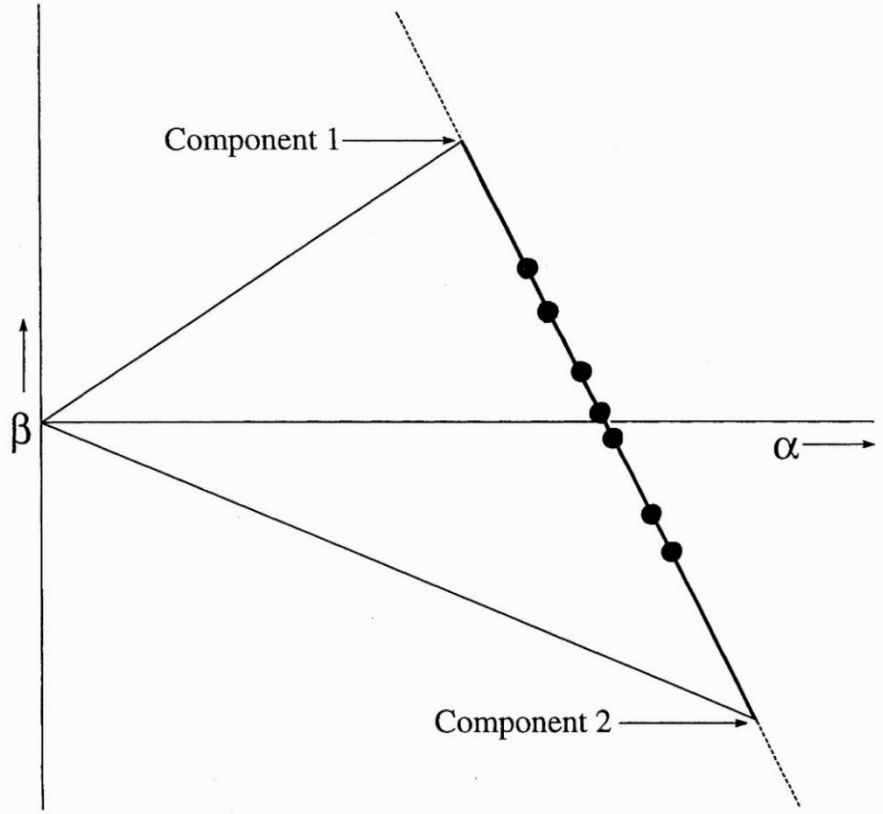
$$S_i = \alpha_i V_\alpha + \beta_i V_\beta$$

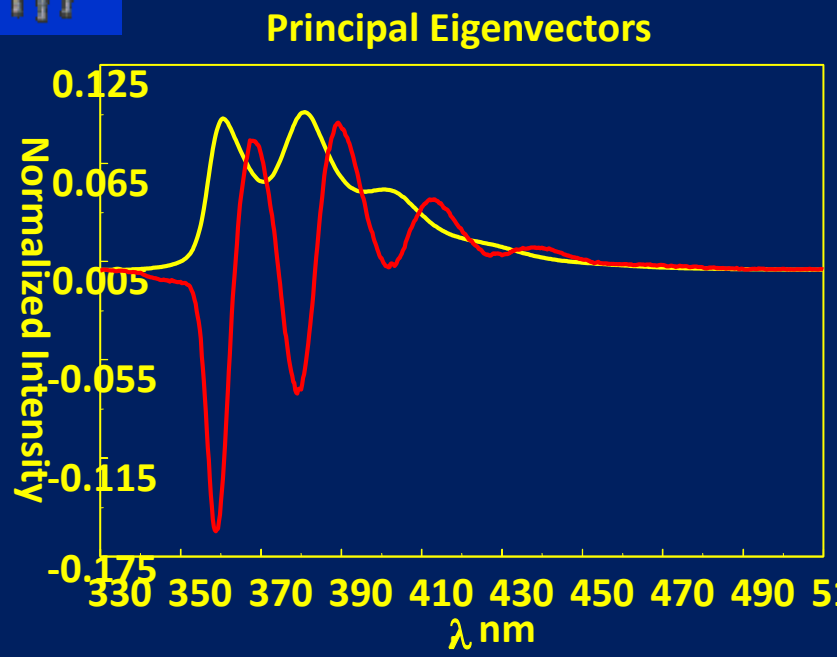
TWO COMPONENTS

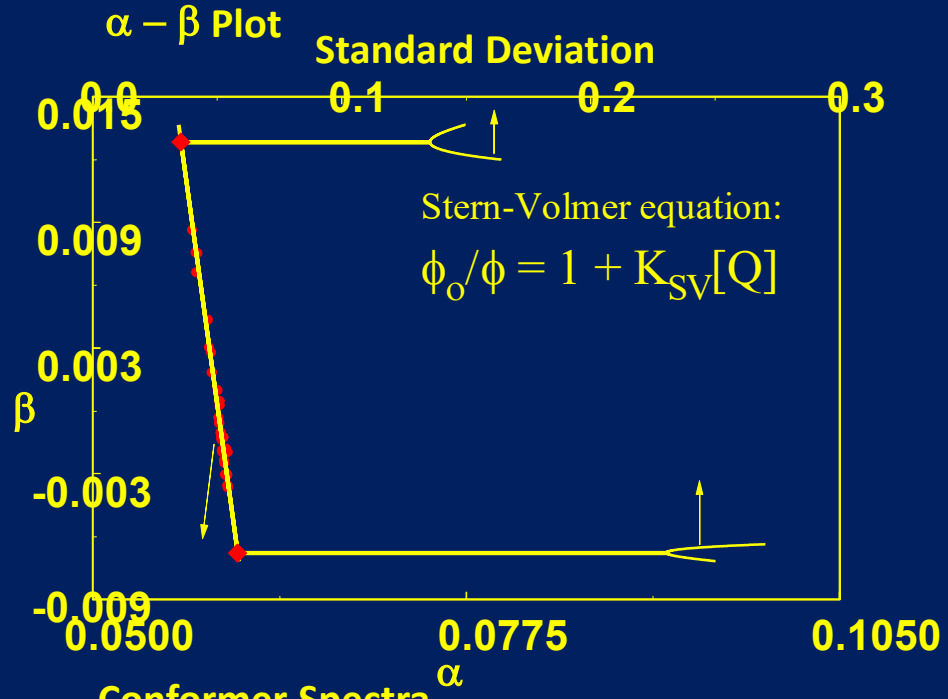
$$S_i = \alpha_i V_\alpha + \beta_i V_\beta$$

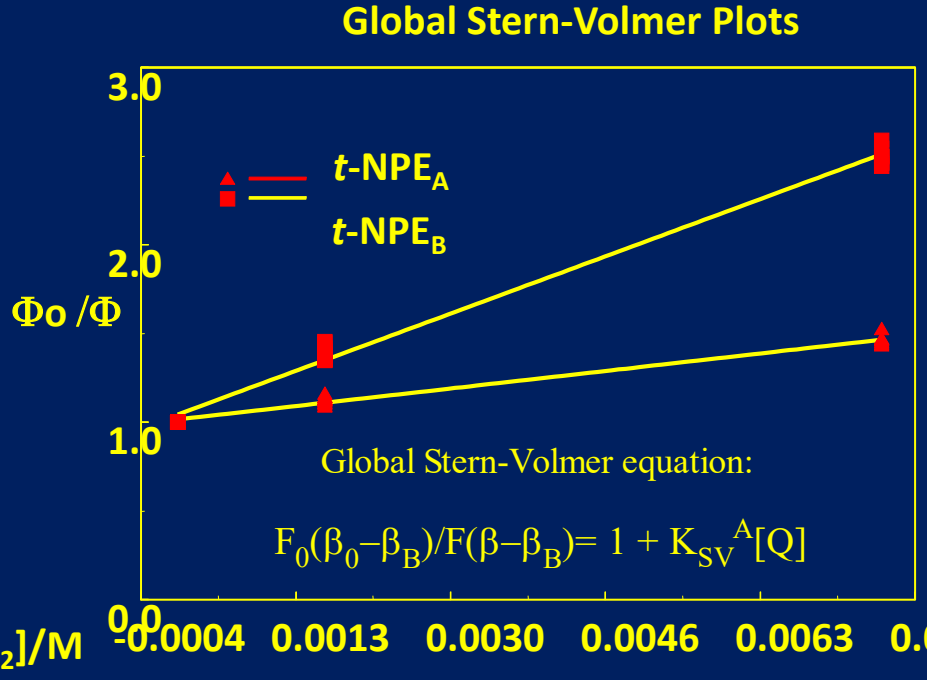
$$\alpha \Sigma V_{\alpha i} + \beta \Sigma V_{\beta k} = 1$$

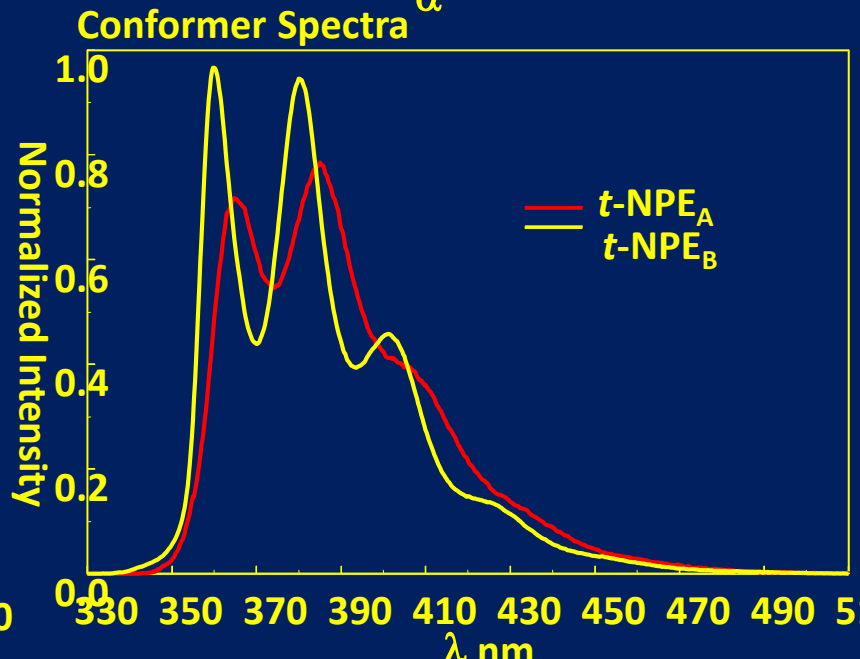
$$\alpha V_{\alpha k} + \beta V_{\beta k} \geq 0$$




Principal Eigenvectors
Normalized Intensity
0.125
0.065
0.005
-0.055
-0.115
-0.175
330 350 370 390 410 430 450 470 490 510
λ nm


α – β Plot
Standard Deviation
0.0
0.1
0.2
0.3
0.015
0.009
0.003
-0.003
-0.009
β
Stern-Volmer equation:
$\phi_o/\phi = 1 + K_{SV}[Q]$
0.0500
0.0775
0.1050
α


Global Stern-Volmer Plots
3.0
2.0
1.0
0.0
Φo /Φ
t-NPE_A
t-NPE_B
Global Stern-Volmer equation:
$F_0(\beta_0-\beta_B)/F(\beta-\beta_B)= 1 + K_{SV}^{A}[Q]$
-0.0004 0.0013 0.0030 0.0046 0.0063 0.0080
[O2]/M


Conformer Spectra
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Intensity
t-NPE_A
t-NPE_B
330 350 370 390 410 430 450 470 490 510
λ nm

t-NPE/PCA-SM

Stern-Volmer Quenching

Equation	Rate
$^1A + h\nu_{exc} \rightarrow {}^1A^*$	I_a
$^1A^* \rightarrow {}^1A + h\nu_f$	$k_f[^1A^*]$
$^1A^* \rightarrow {}^3A^*$	$k_{is}[^1A^*]$
$^1A^* \rightarrow P$	$k_p[^1A^*]$
$^1A^* + Q \rightarrow {}^1A + Q^*$	$k_q[Q][^1A^*]$

The Stern-Volmer Plot

$$\frac{d[h\nu_f]}{dt} = k_f[^1A^*]$$

$$\phi_f^o = \frac{1}{I_a}\frac{d[h\nu_f]}{dt} = \frac{k_f}{k_f + k_{is} + k_p} = k_f\tau$$

$$\frac{d[^1A^*]}{dt} = I_a - (k_f + k_{is} + k_p)[^1A^*] = 0$$

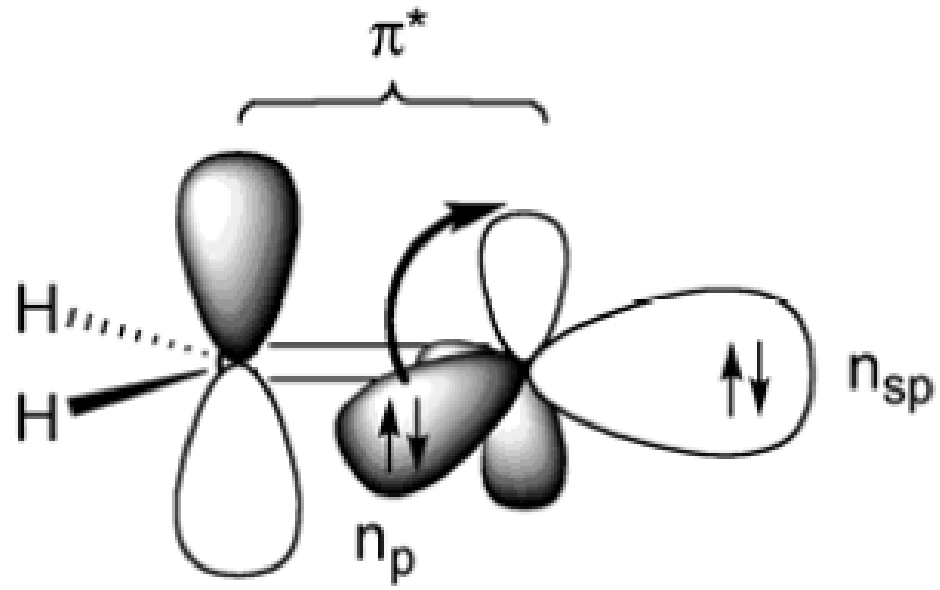
where I_a is the rate of light absorption

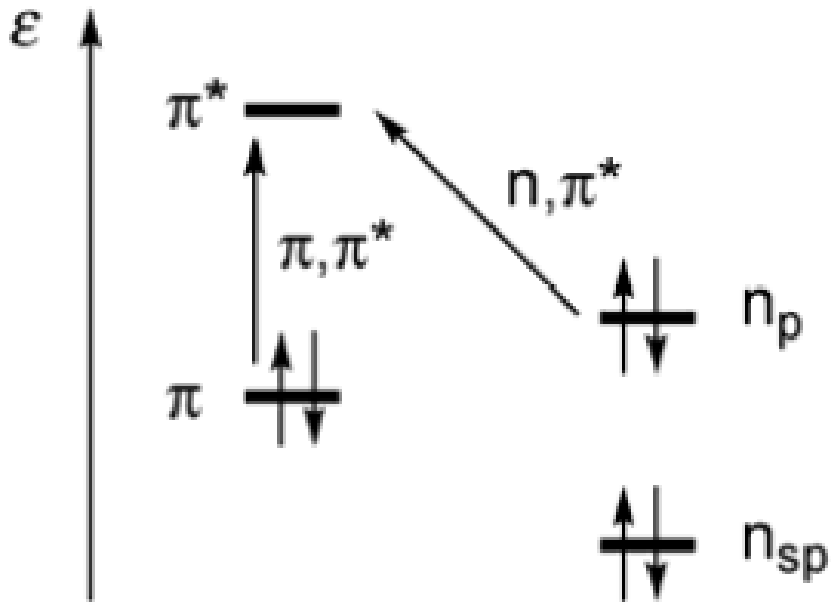
$$[^1A^*] = \frac{I_a}{k_f + k_{is} + k_p}$$

$$\phi_f = \frac{k_f}{k_f + k_{is} + k_p + k_q[Q]} = \frac{k_f\tau}{1 + k_q\tau[Q]}$$

$$\frac{d[h\nu_f]}{dt} = \frac{k_f I_a}{k_f + k_{is} + k_p}$$

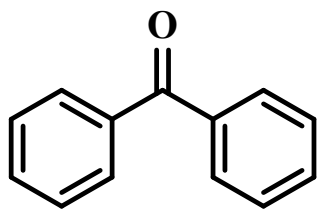
$$\left(\phi_f^o / \phi_f\right) = 1 + k_q\tau[Q] = 1 + K_{SV}[Q]$$

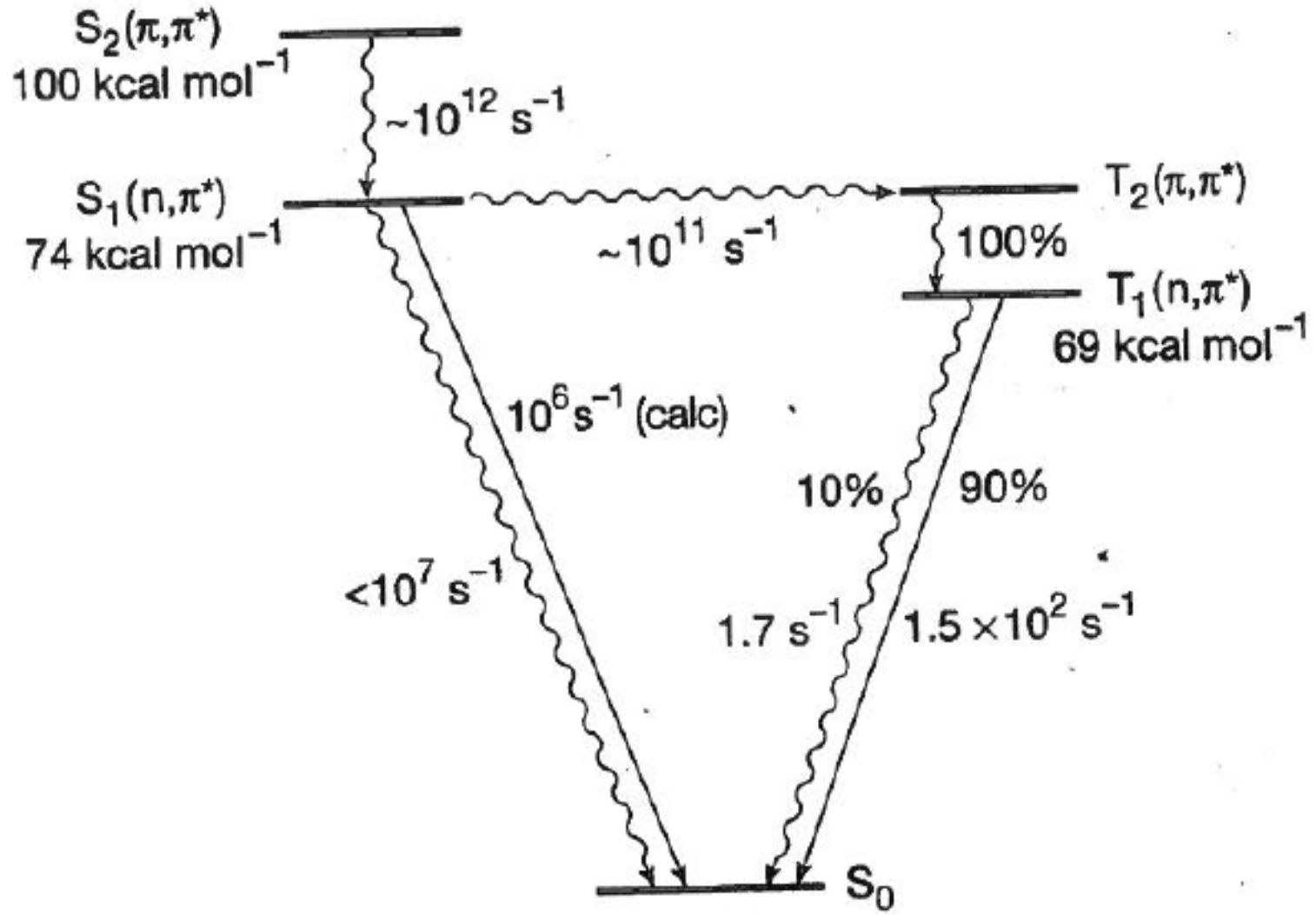




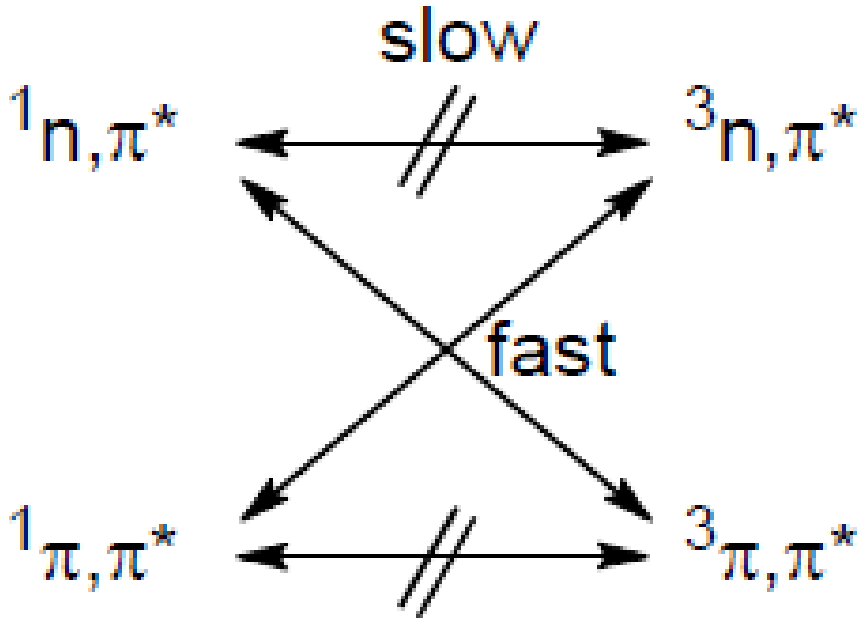
The n,π*-transition of formaldehyde.

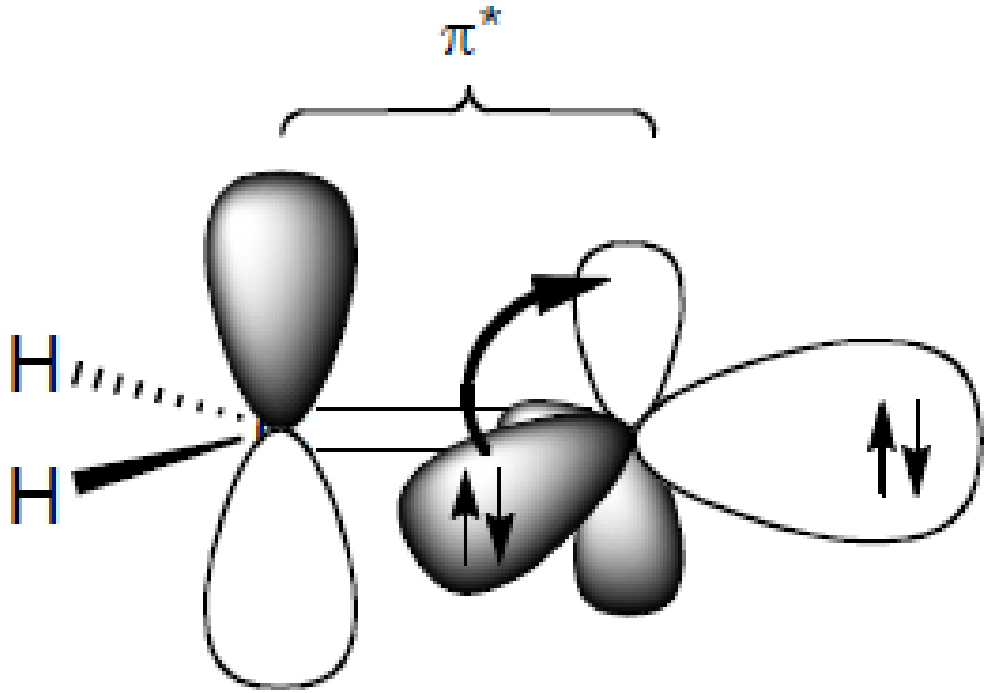
Benzophenone State Diagram





El-Sayed's Rules for Intersystem Crossing





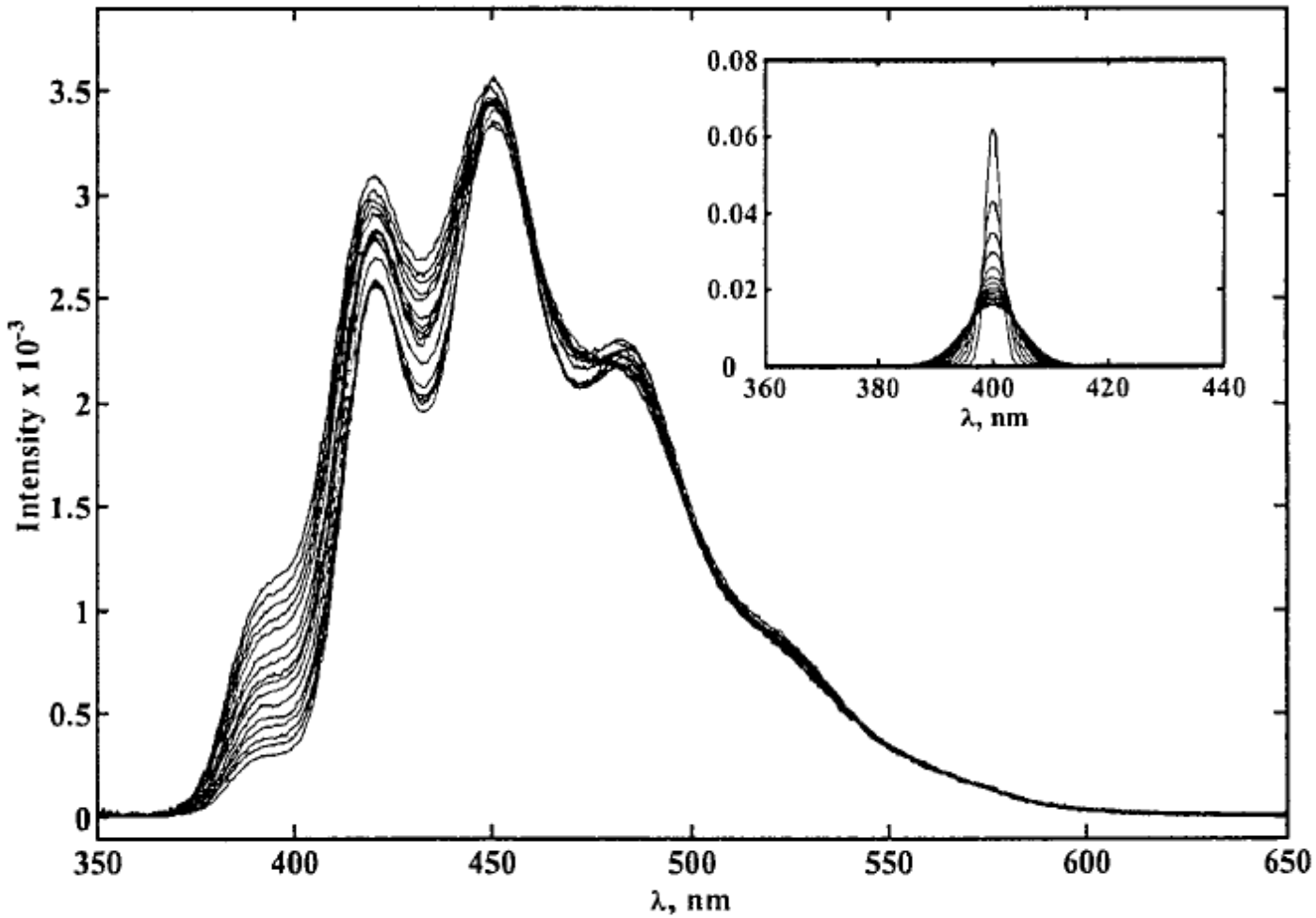


Figure 1. Benzophenone luminescence spectra (self-absorption-corrected, instrumental-response-uncorrected) at different temperatures (Table 1) from the degassed CCl_4 solution. The inset shows the set of Gaussian functions used to compensate the spectra for thermal broadening.

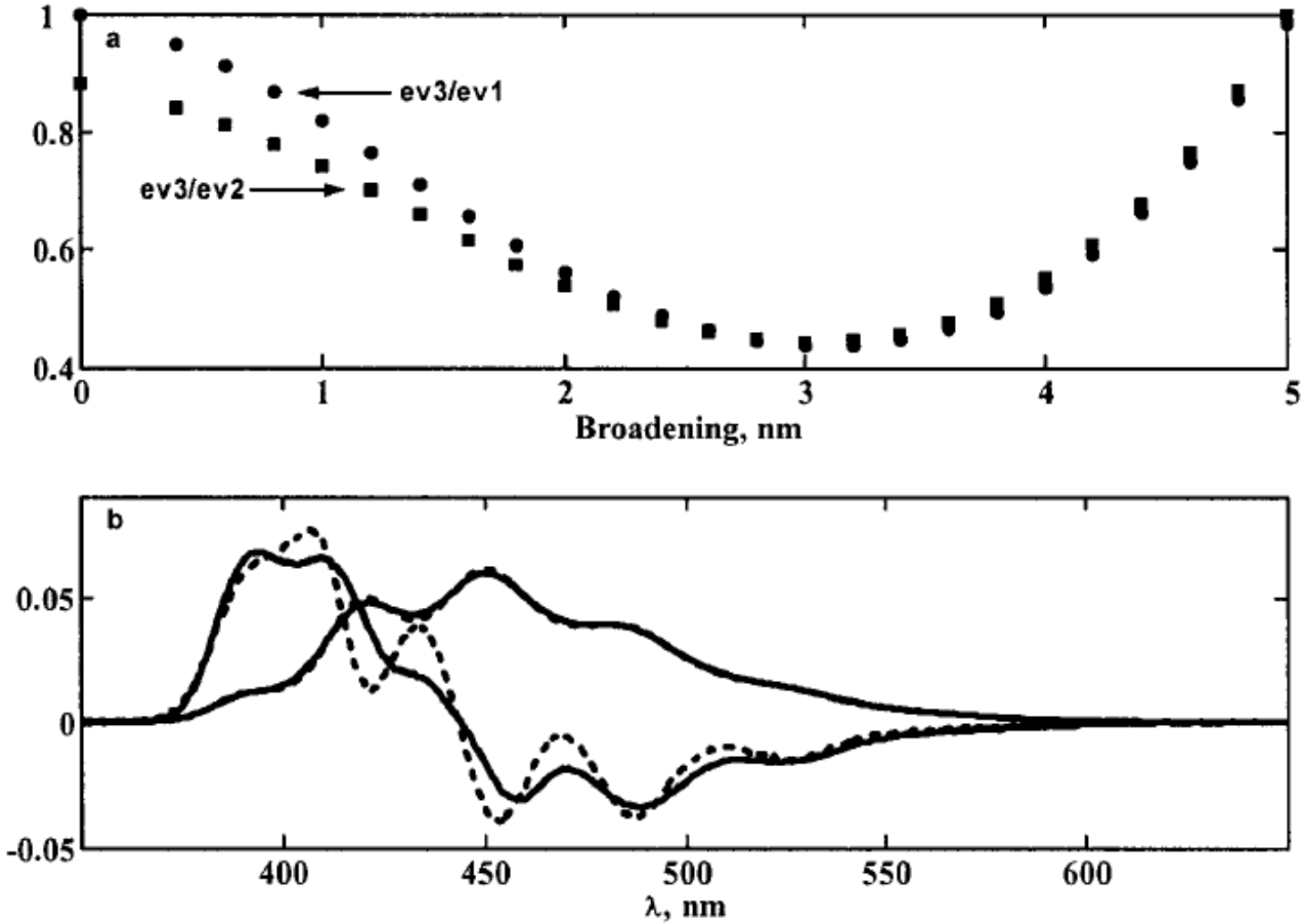


Figure 3. (a) Ratios of the third to the first eigenvalue (circles) and the third to the second eigenvalue (squares) as a function of the compensating broadening parameter *k*. (b) First and second eigenvectors before the compensation for thermal broadening (dashed lines) and after the compensation

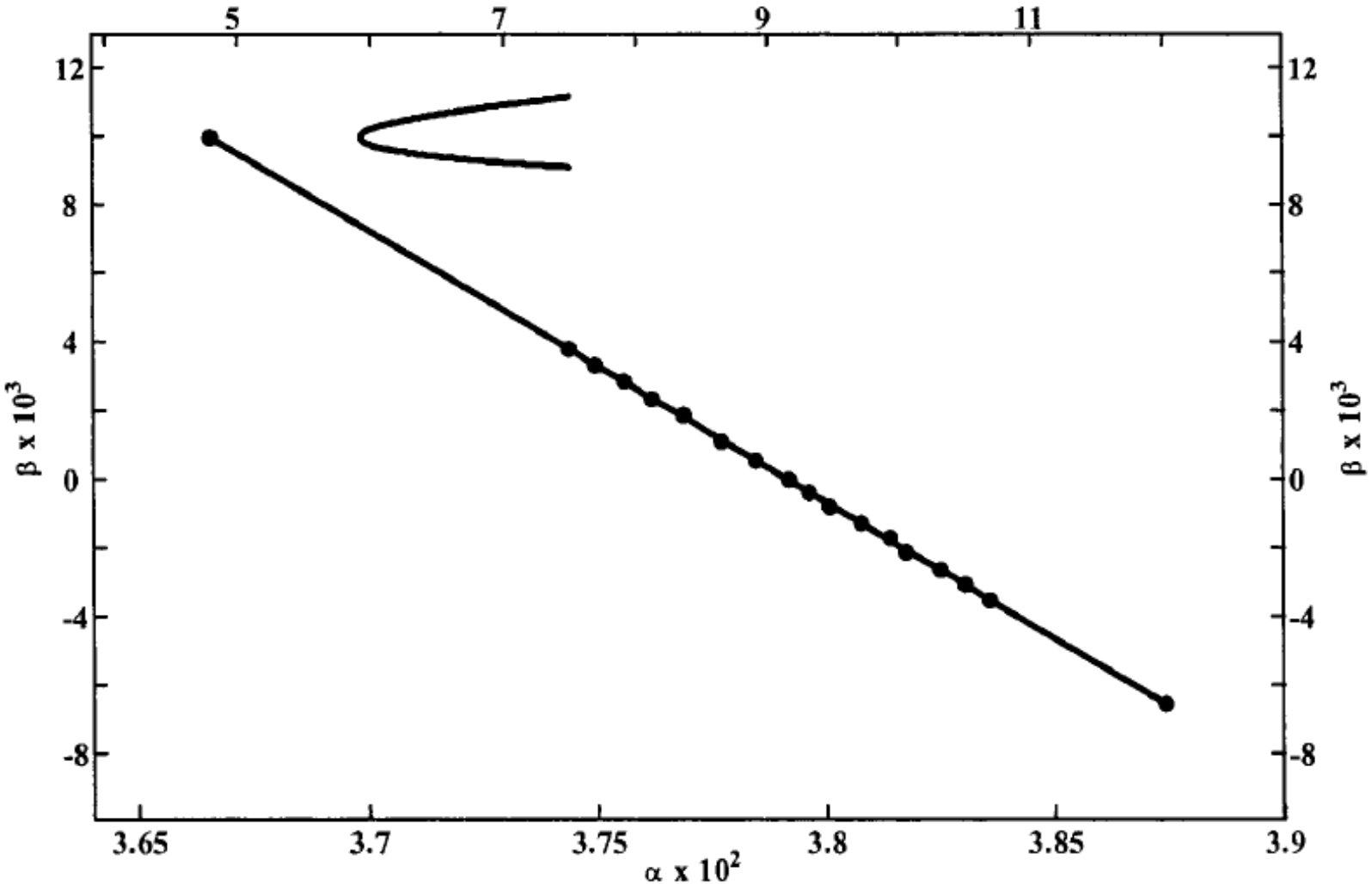


Figure 5. α,β normalization line for the benzophenone luminescence system. The standard deviation for the van't Hoff plot as a function of β is also shown. The minimum determines the β_{DF} value corresponding to the spectrum of the pure delayed benzophenone fluorescence.

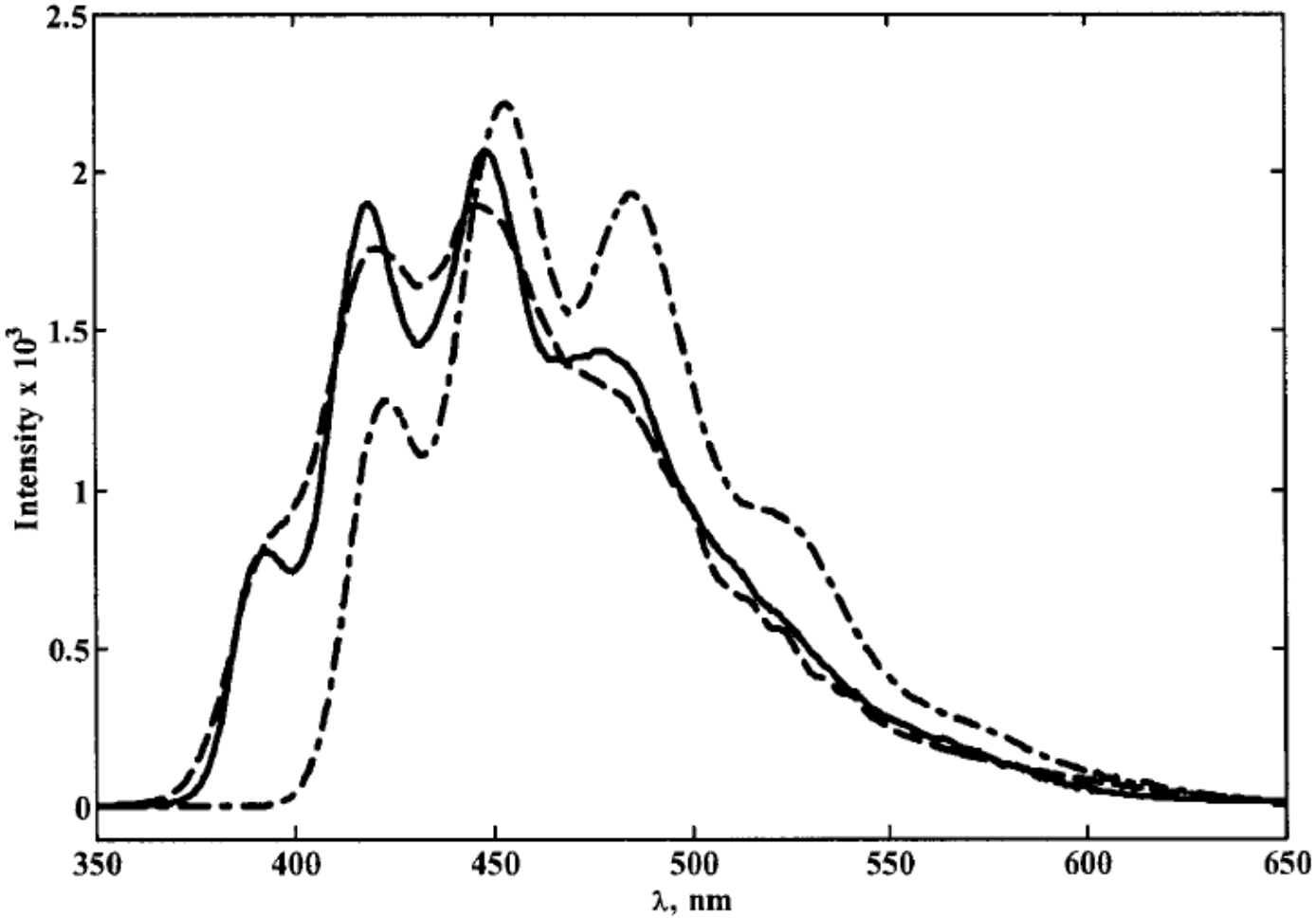
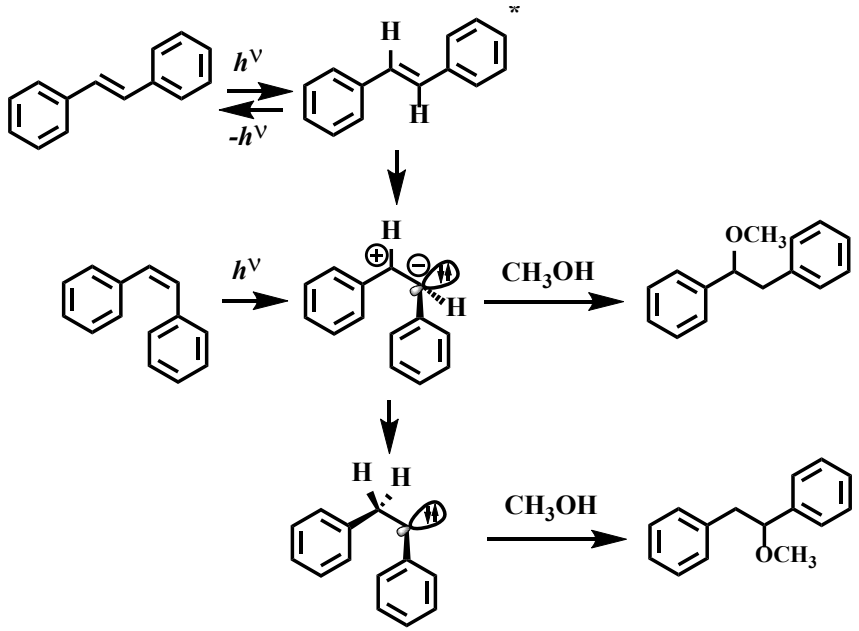
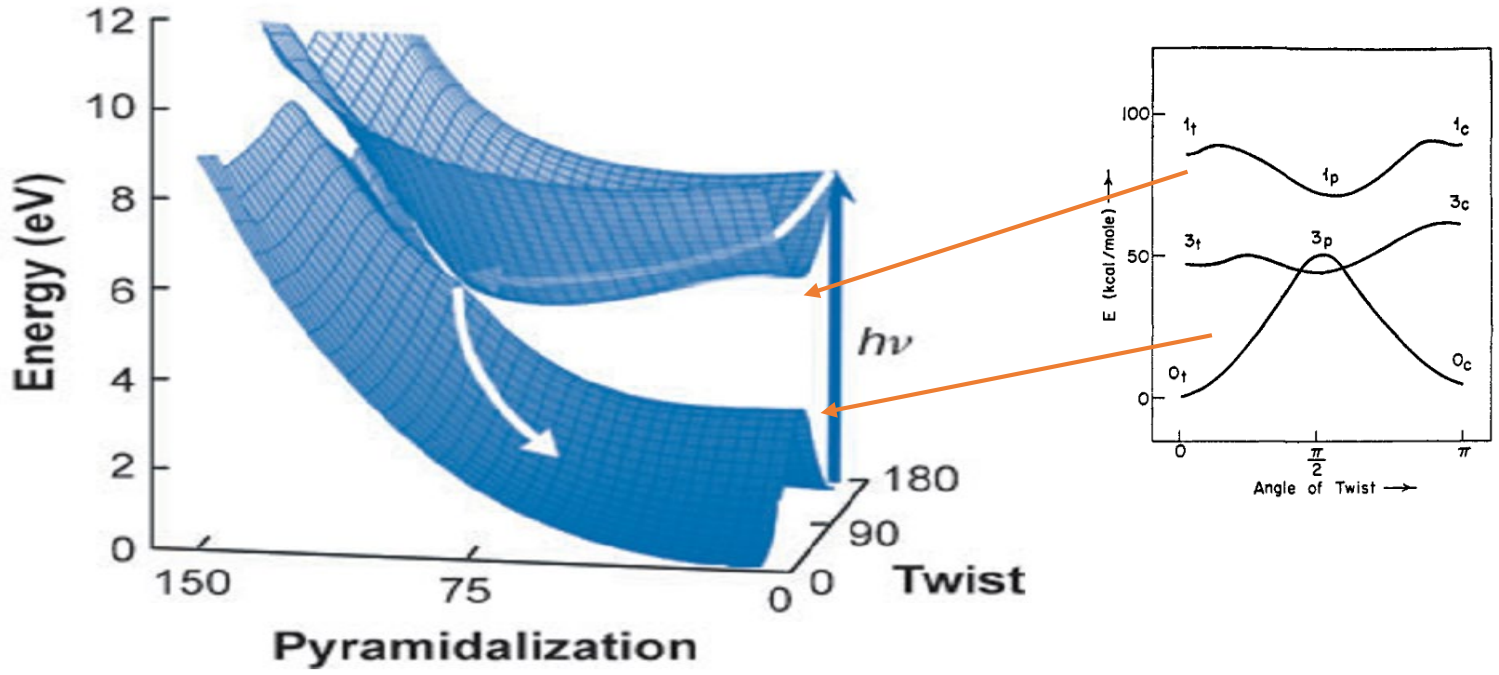


Figure 9. Emission spectra of benzophenone in CCl_4 corrected for nonlinearity in instrumental response and normalized to unit area: phosphorescence (dashed−dotted line), delayed fluorescence (solid line), and prompt fluorescence (dashed line). The first two spectra are obtained by extrapolation of the α, β coefficients of the pure component spectra to 23.5 °C, and the prompt fluorescence is an average of 40 spectra measured at room temperature (ca. 22.0 °C) for $\lambda_{exc} = 326$ nm.

Multidimensional Isomerization – Conical Intersections – Trapping Twisted Intermediates

$$\vec{h}_{S_0S_1} = (E_1 - E_0)^{-1} \left\langle \psi_{S_0}^{el} \left| \frac{\partial \hat{H}}{\partial R} \right| \psi_{S_1}^{el} \right\rangle$$





Saltiel, J.; Gupta, S. Photochemistry of the Stilbenes in Methanol. Trapping the Common Phantom Singlet State. *J. Phys. Chem. A* **2018**, *122*, 6089-6099.

B. G. Levine, T. J. Martínez. *Annu. Rev. Phys. Chem.* **2007**, *58*, 613-34.


Levi's

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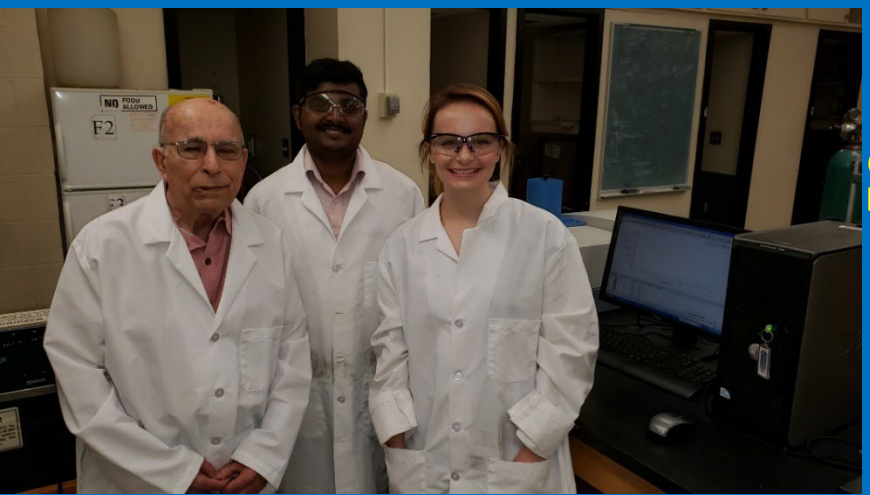
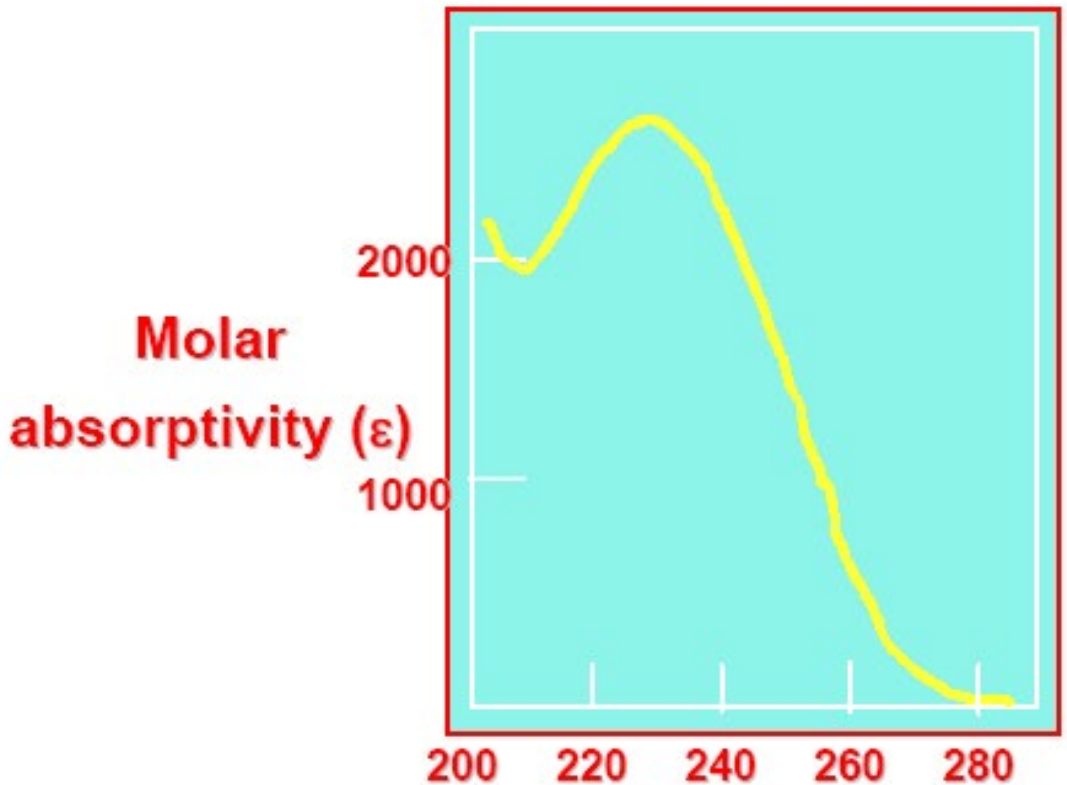


UV Spectrum of cis,trans-1,3-cyclooctadiene



λ_{max} 230 nm

ε_{max} 2630

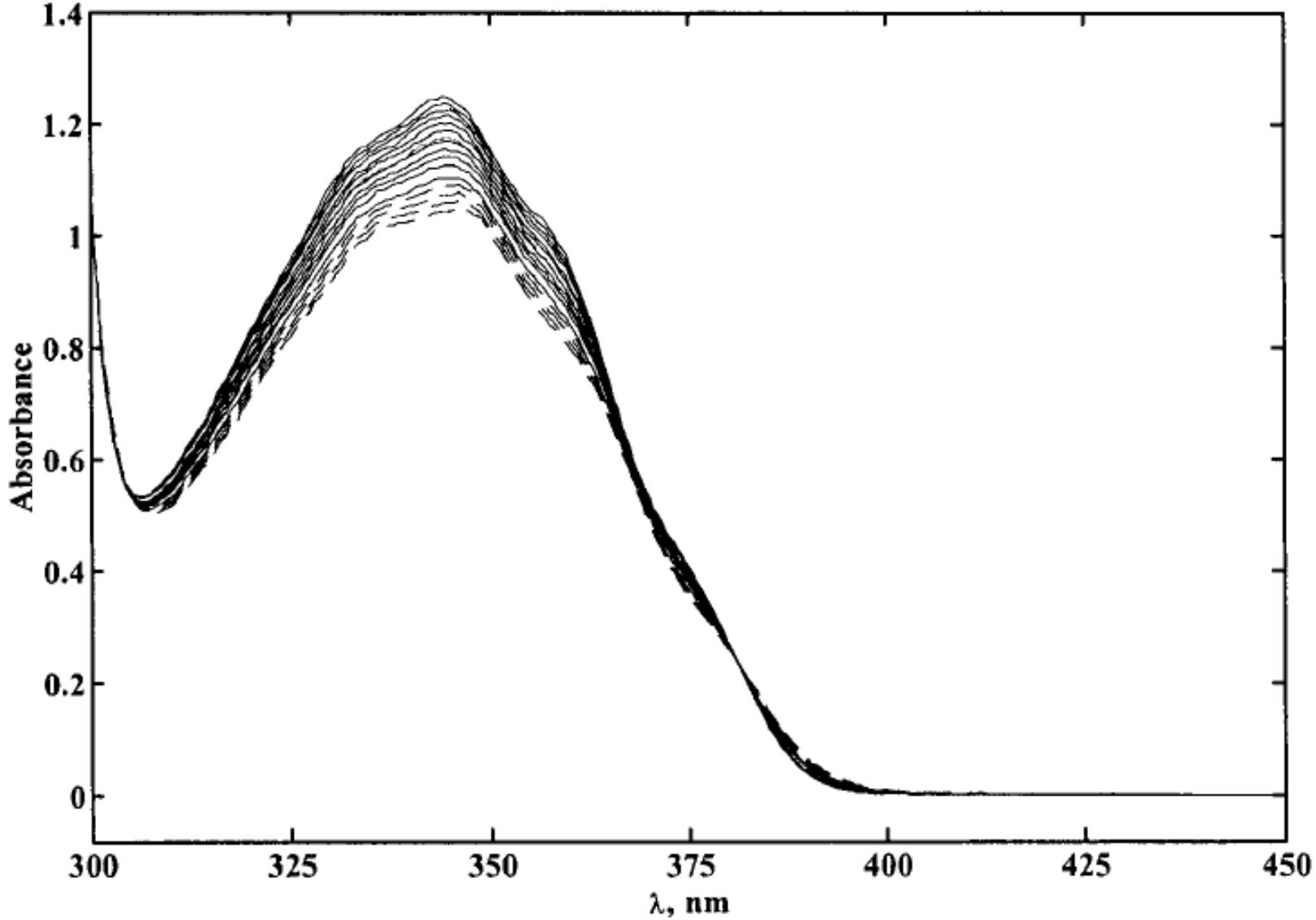
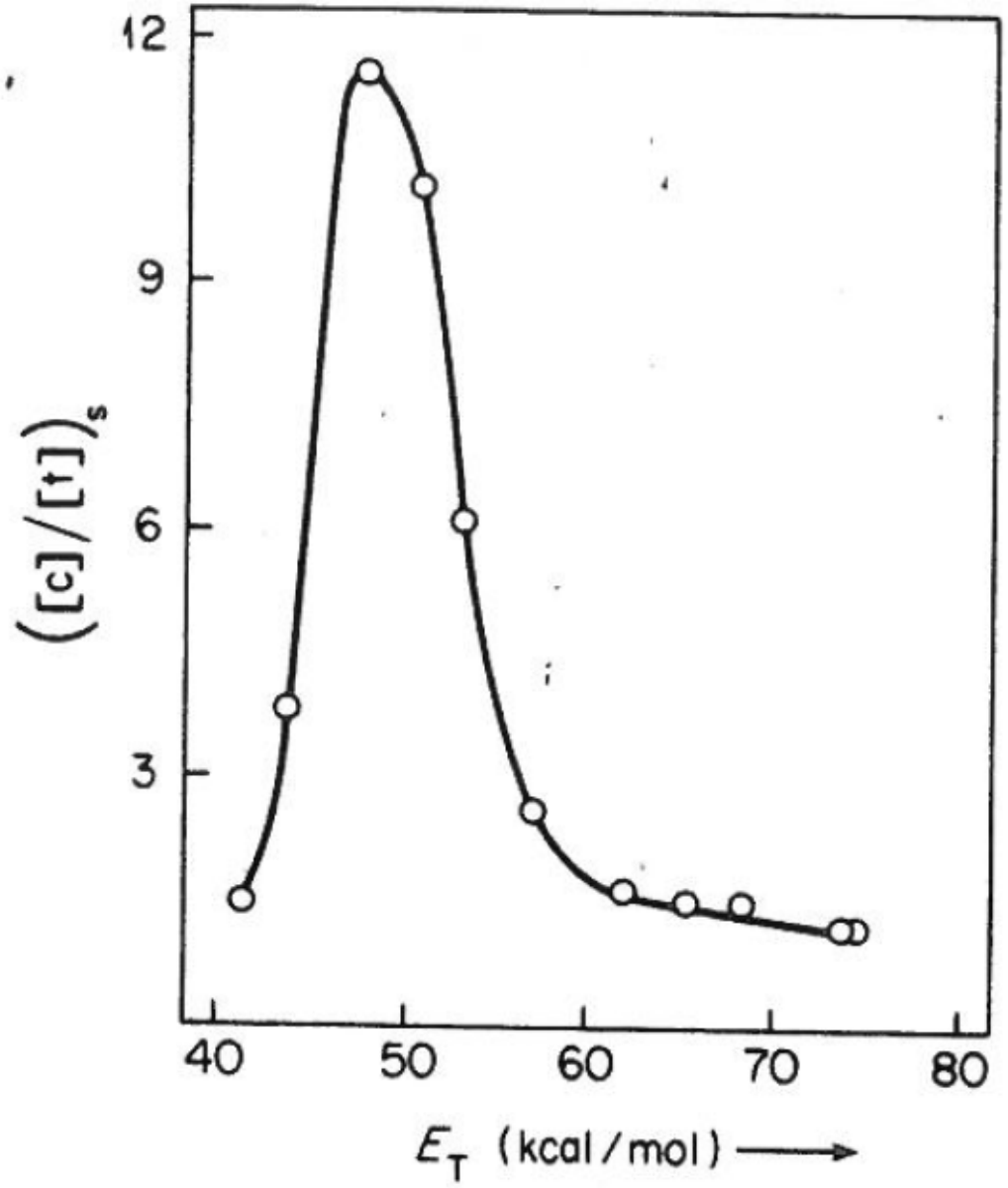


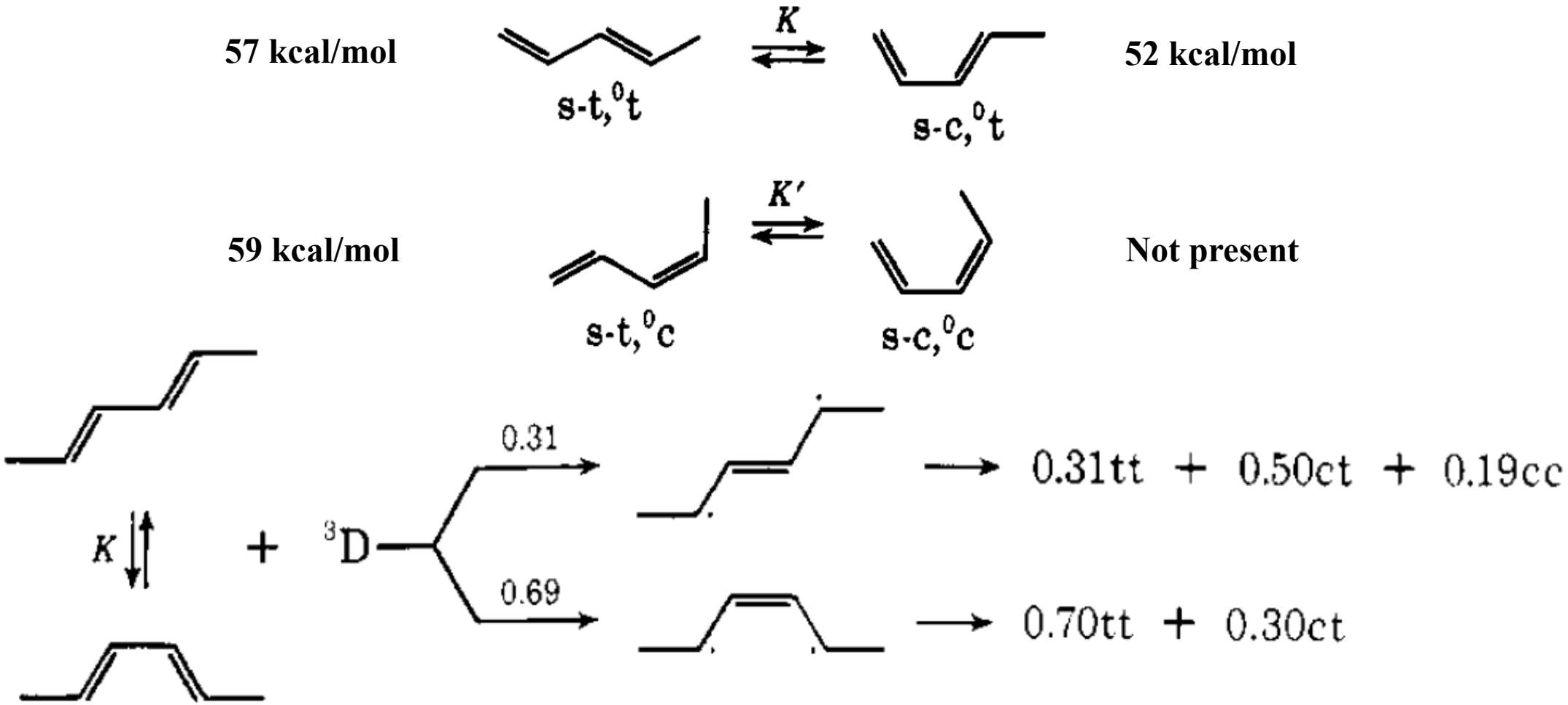
Figure 2. Temperature dependence of the n, π^* absorption spectrum of a 0.0093 M benzophenone solution in CCl_4: experimental spectra (14.7−68.1 °C), solid lines; extrapolated spectra (73.5−88.5 °C), dashed lines (see the Supporting Information).

The Saltiel Plot for Stilbene Triplet Photoisomerization



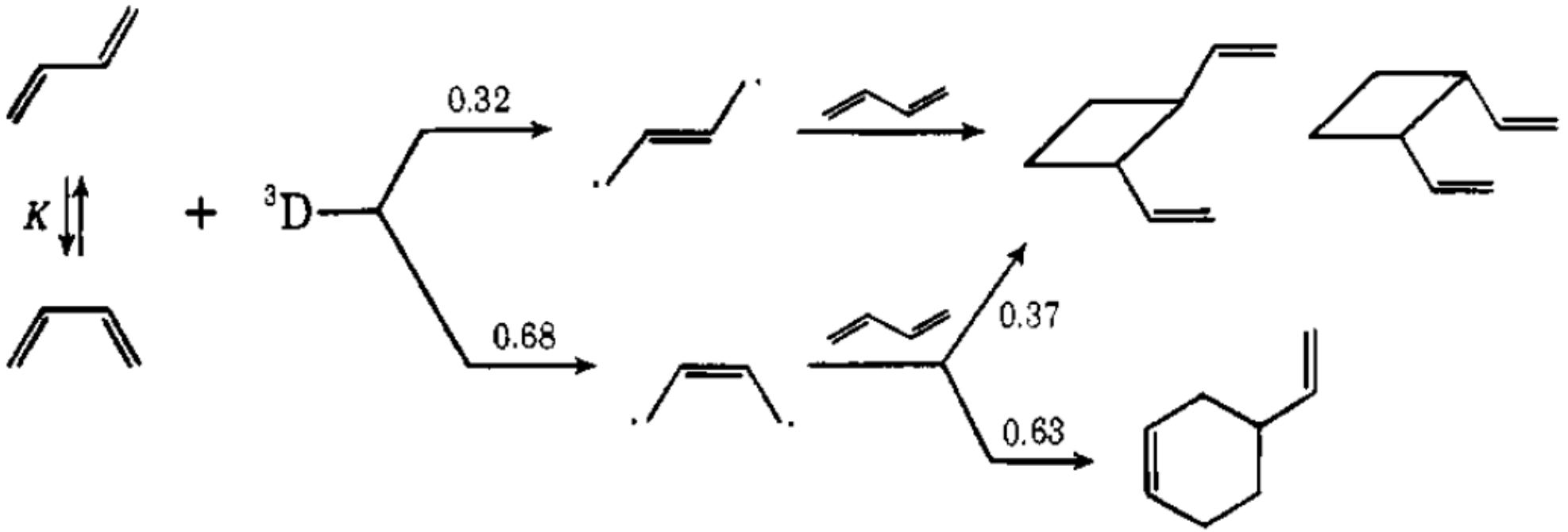
1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized photoisomerization

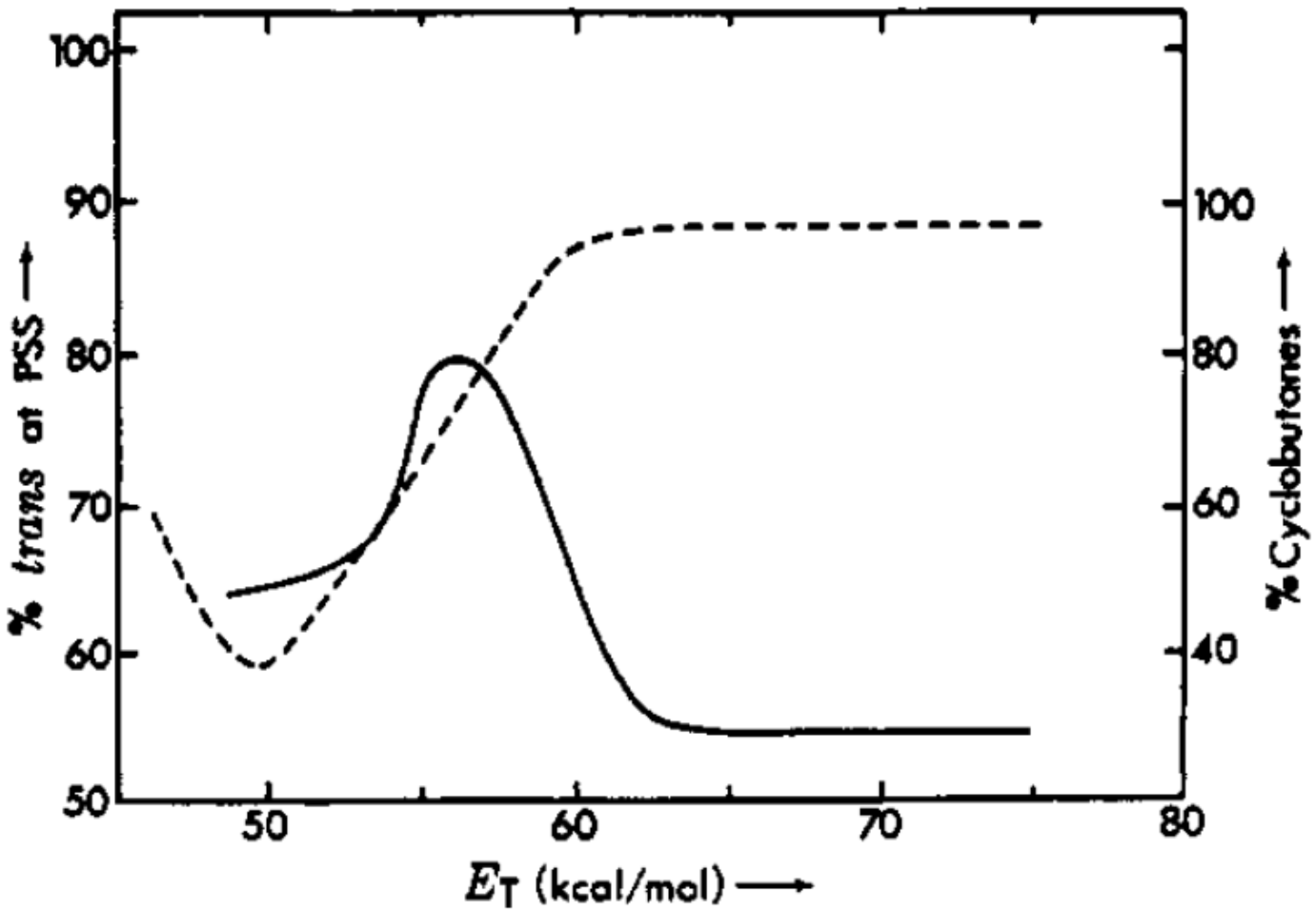


1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized dimerization



Saltiel Plots



1,3-butadiene dimerization
dashes
1,3-pentadiene *E,Z* isomerization
solid line

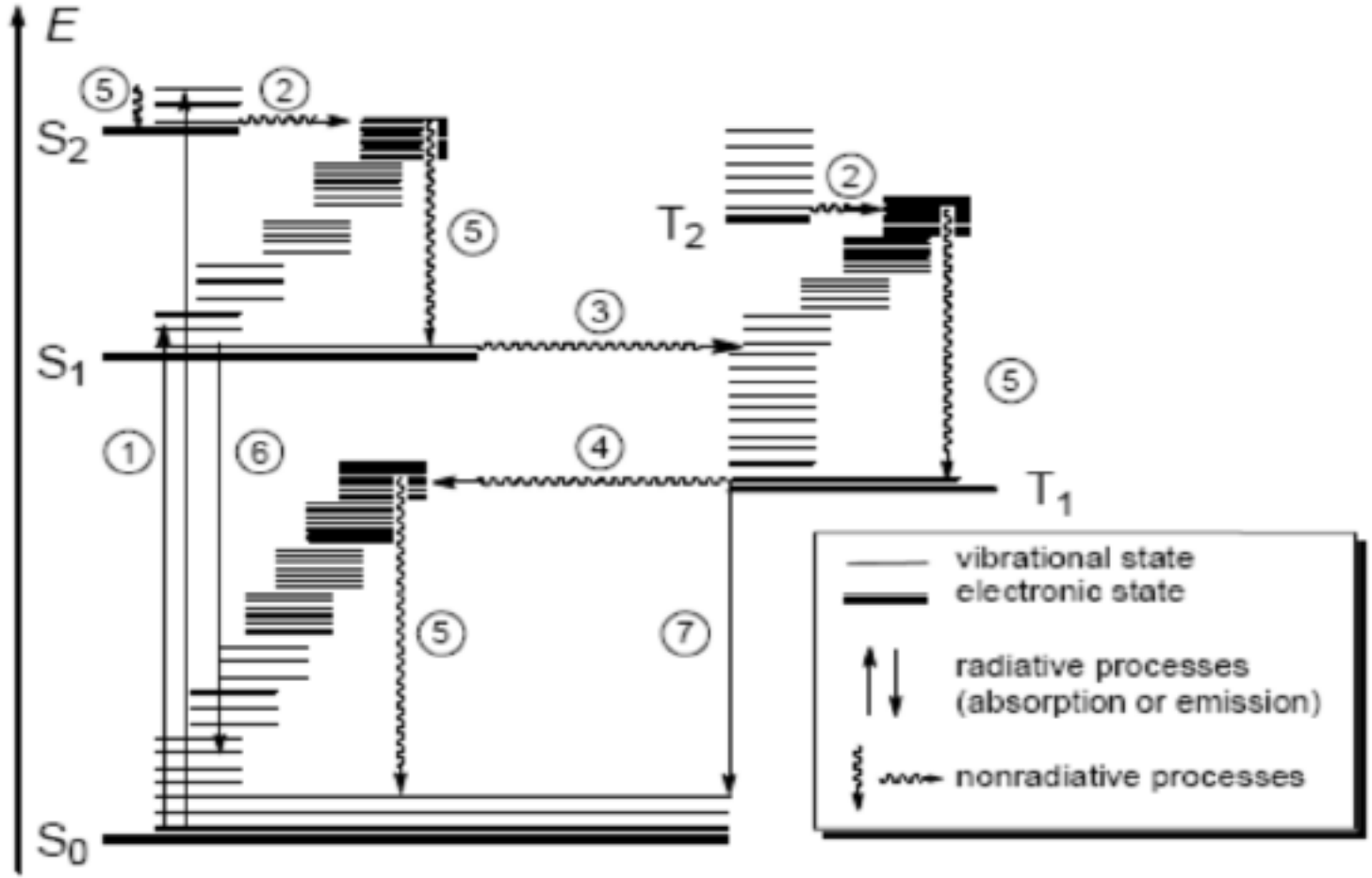
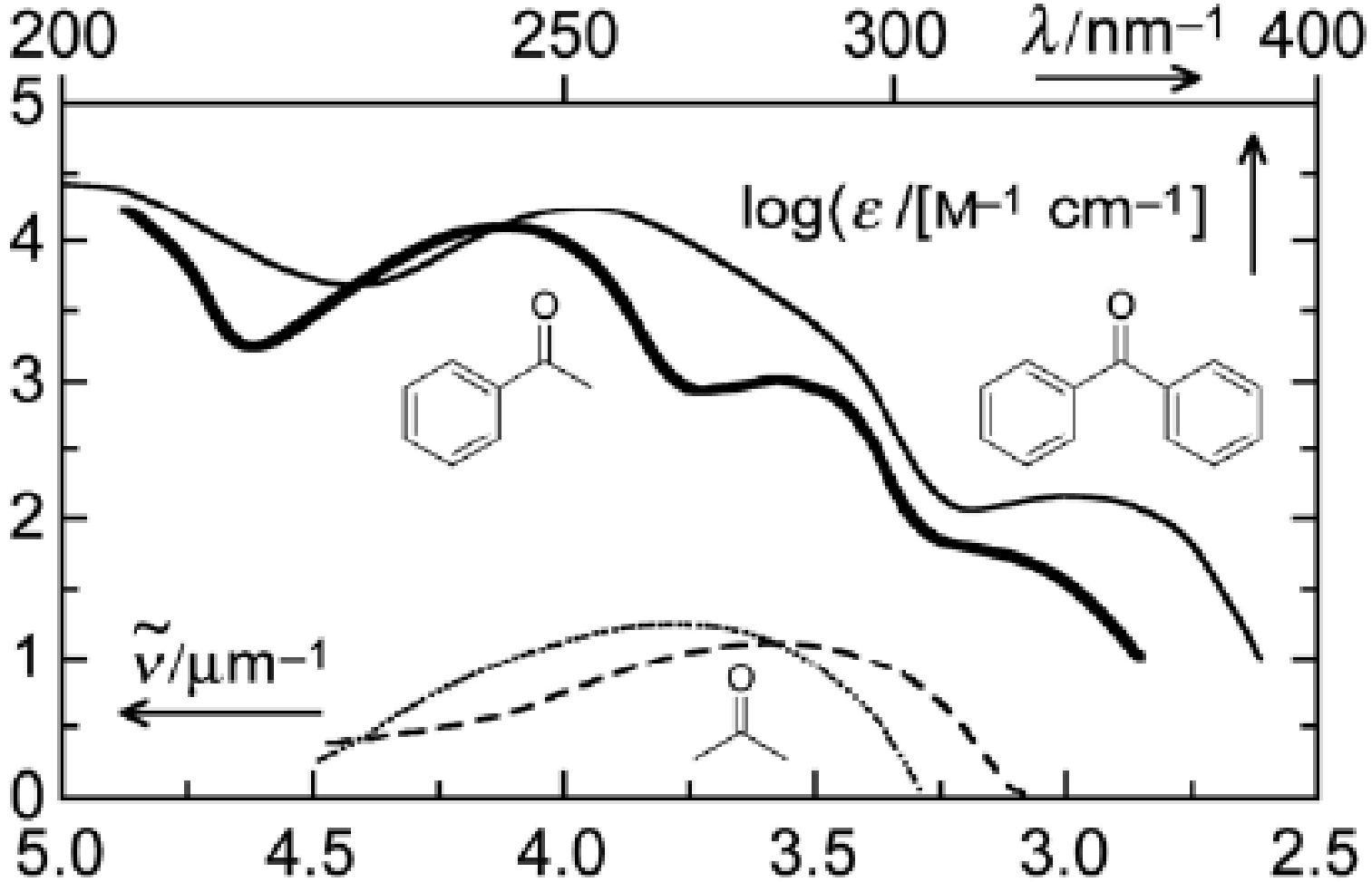


Figure 2-1. State diagram (commonly called Jablonski diagram) depicting molecular states and photophysical processes. The vertical position of thick horizontal lines represents the electronic energy minimum. Vibrational energy levels are shown as thin lines. The width of the horizontal lines and their position along the abscissa are chosen merely to avoid congestion in the graphical diagram and have no physical connotation.



Heptane - - -
Water