



Department of Chemistry **Florida State University**

Elementary Photophysical Transitions and Photochemical Reactions

NSF REU June 14, 2024

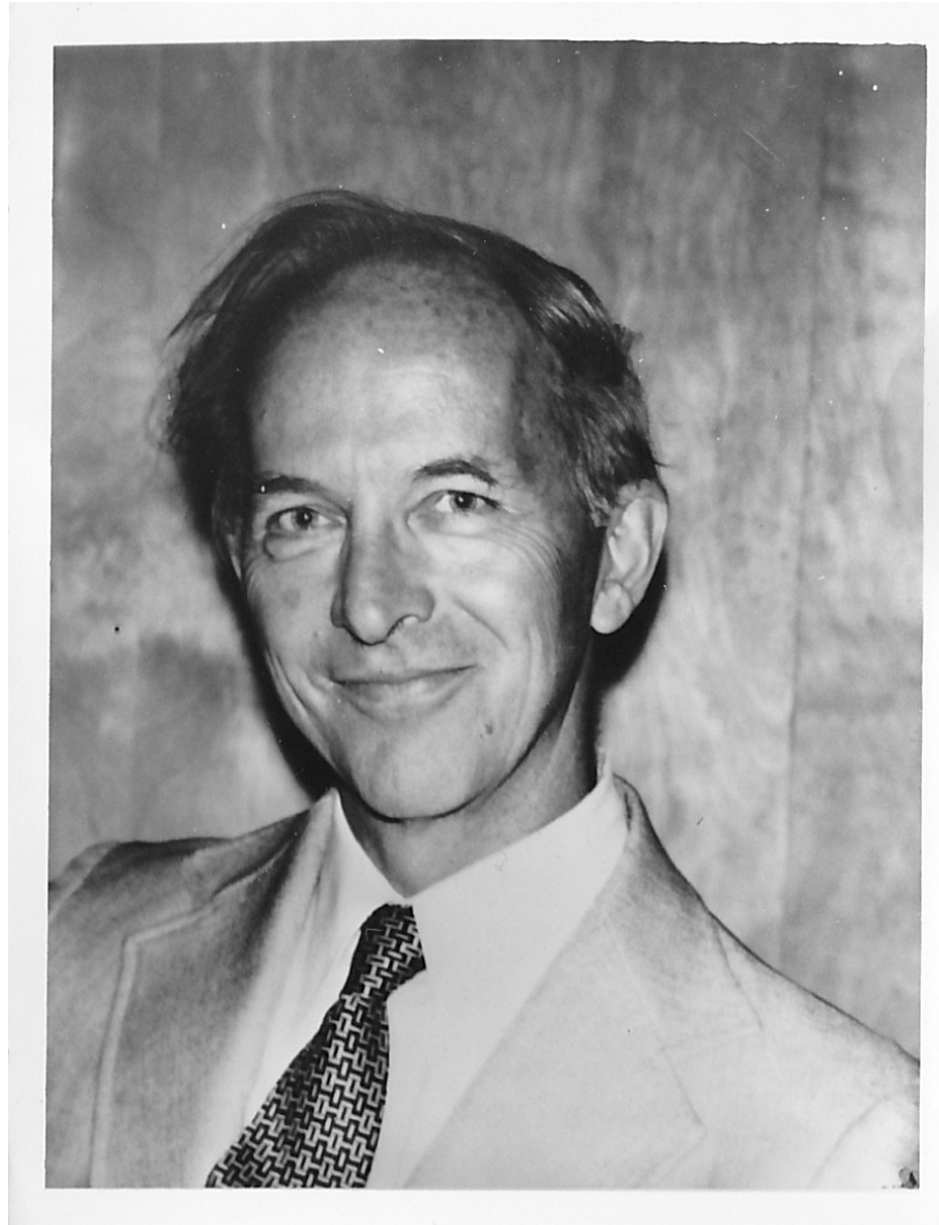
**Photochemistry's
Icons
Why I am here.**



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).

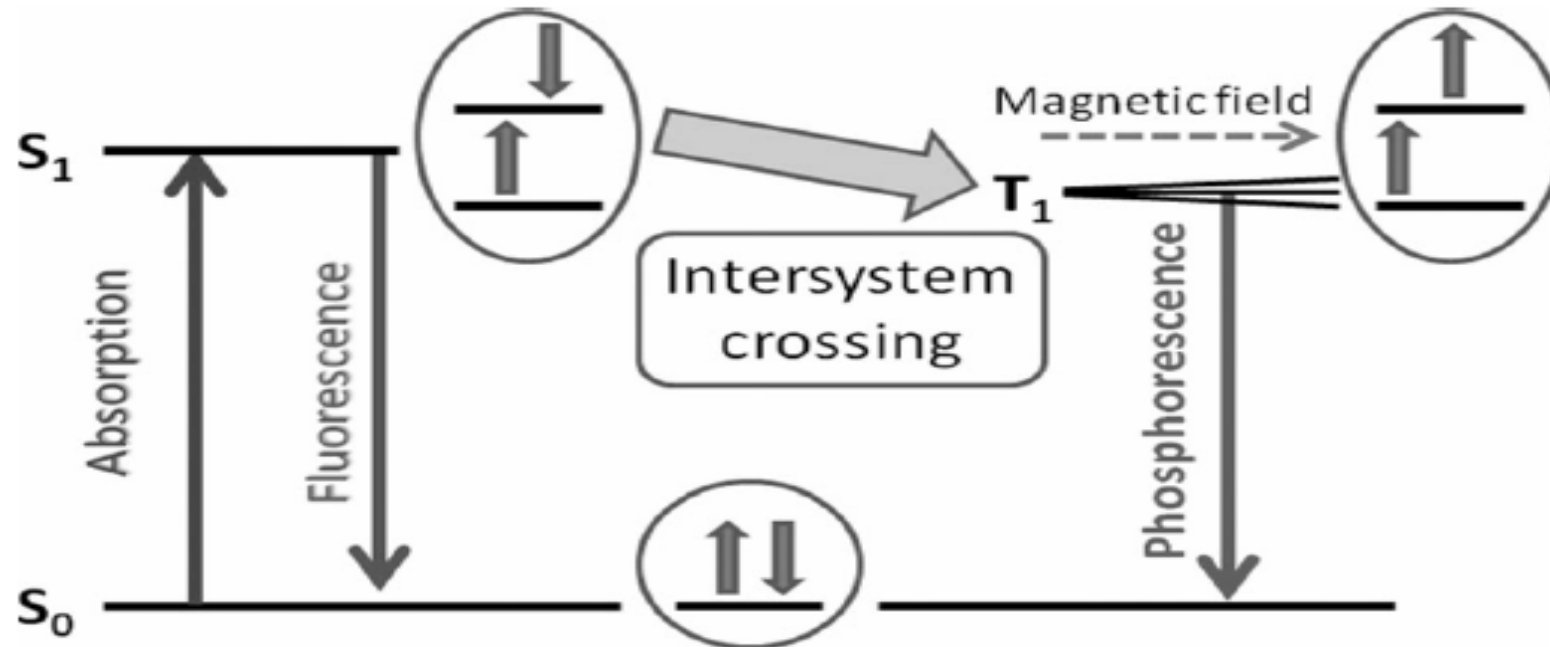
From Photochemistry of Organic Compounds by Peter Klán and Jakob Wirz, 2009

Photo by Lilli Kasha ca. 1970



1920 - 2013

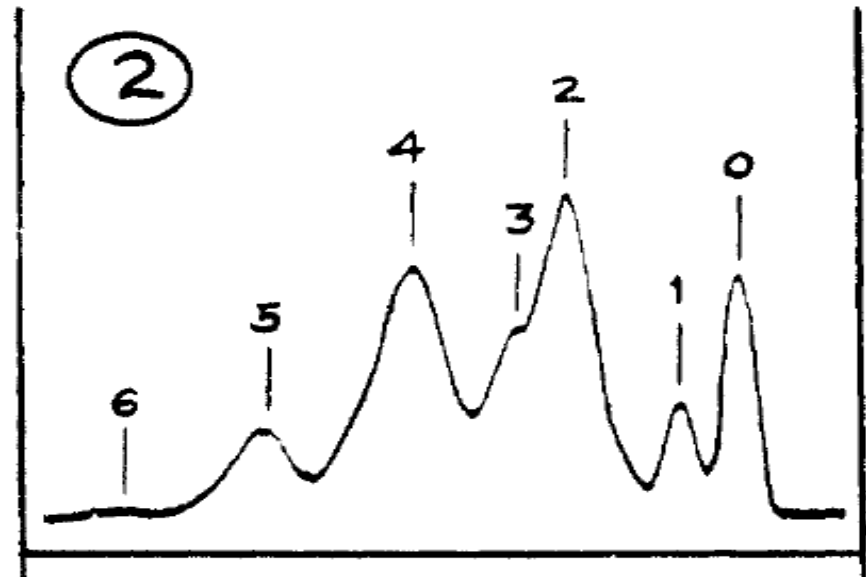
Intersystem Crossing



Demchenko, A. P. *et al.* Michael Kasha: From Photochemistry and Flowers to Spectroscopy and Music *Angew. Chem. Int. Ed.* 2014, 53, 14316-14323.

Phosphorescence and the Triplet State

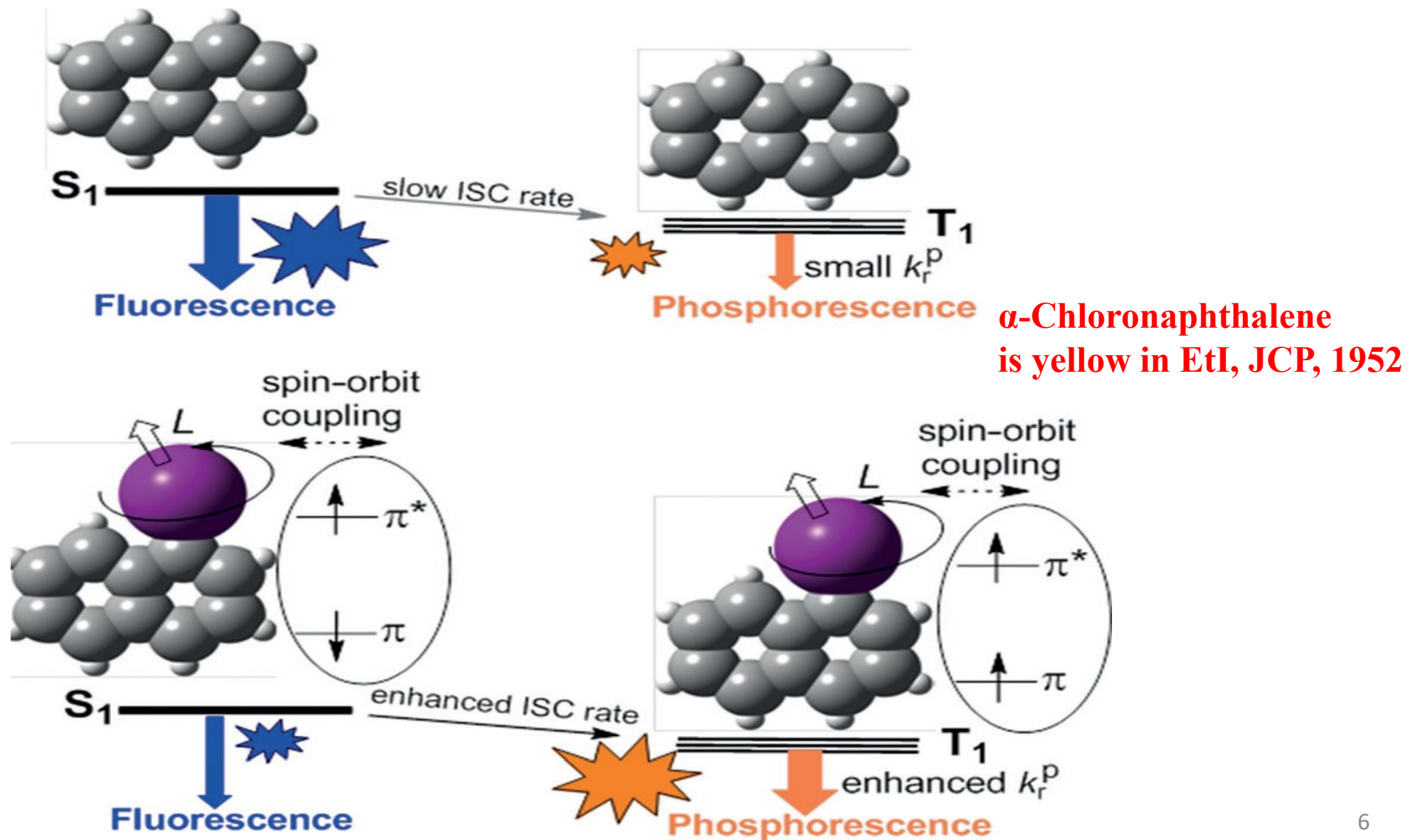
Gilbert N. Lewis , M. Kasha *J. Am. Chem. Soc.* 1944, 66, 2100-2116



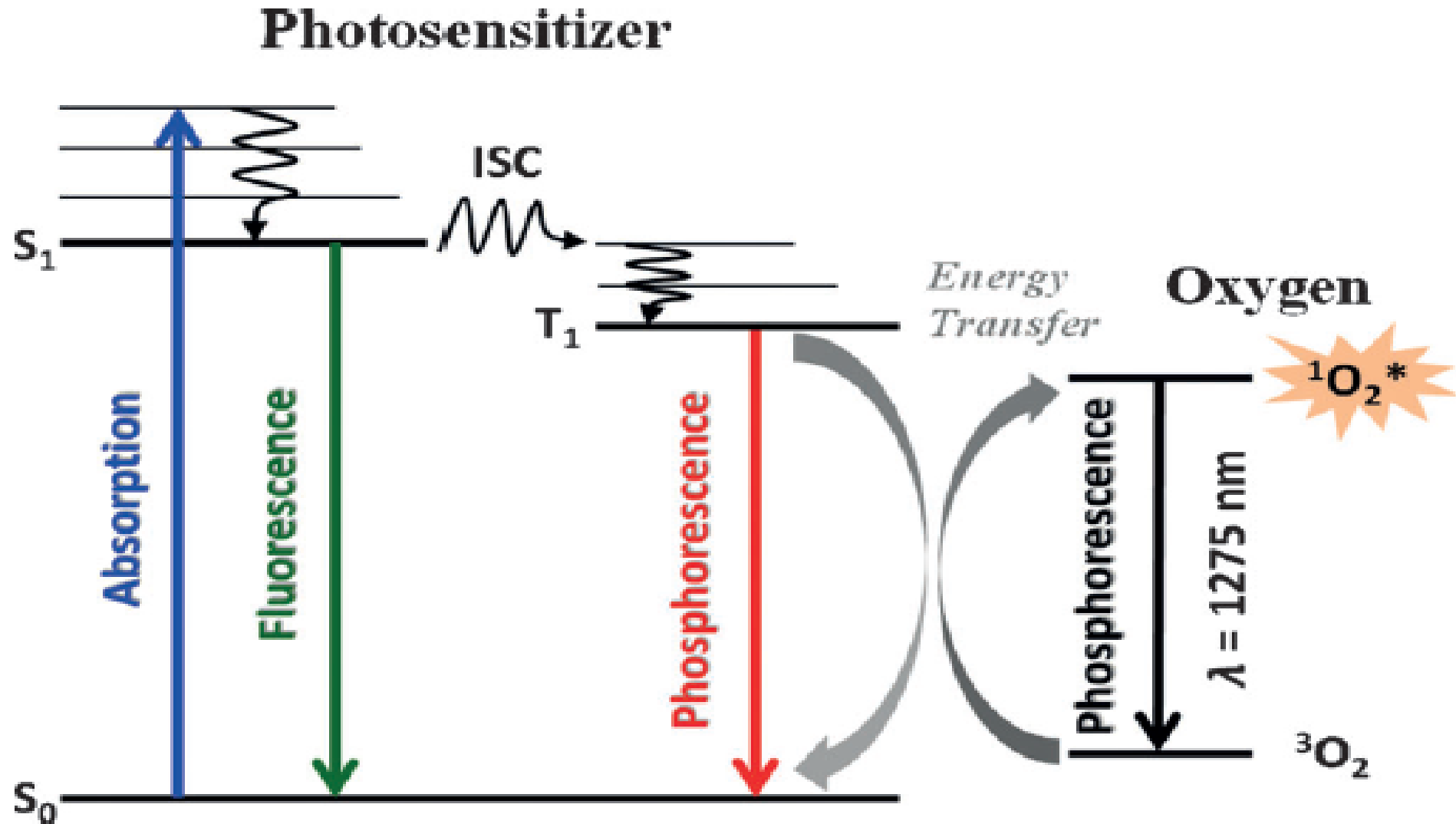
$$E_T = 2.86 \times 10^4 / \lambda(\text{nm}) \text{ in kcal/mol}$$

Naphthalene phosphorescence – triplet energies

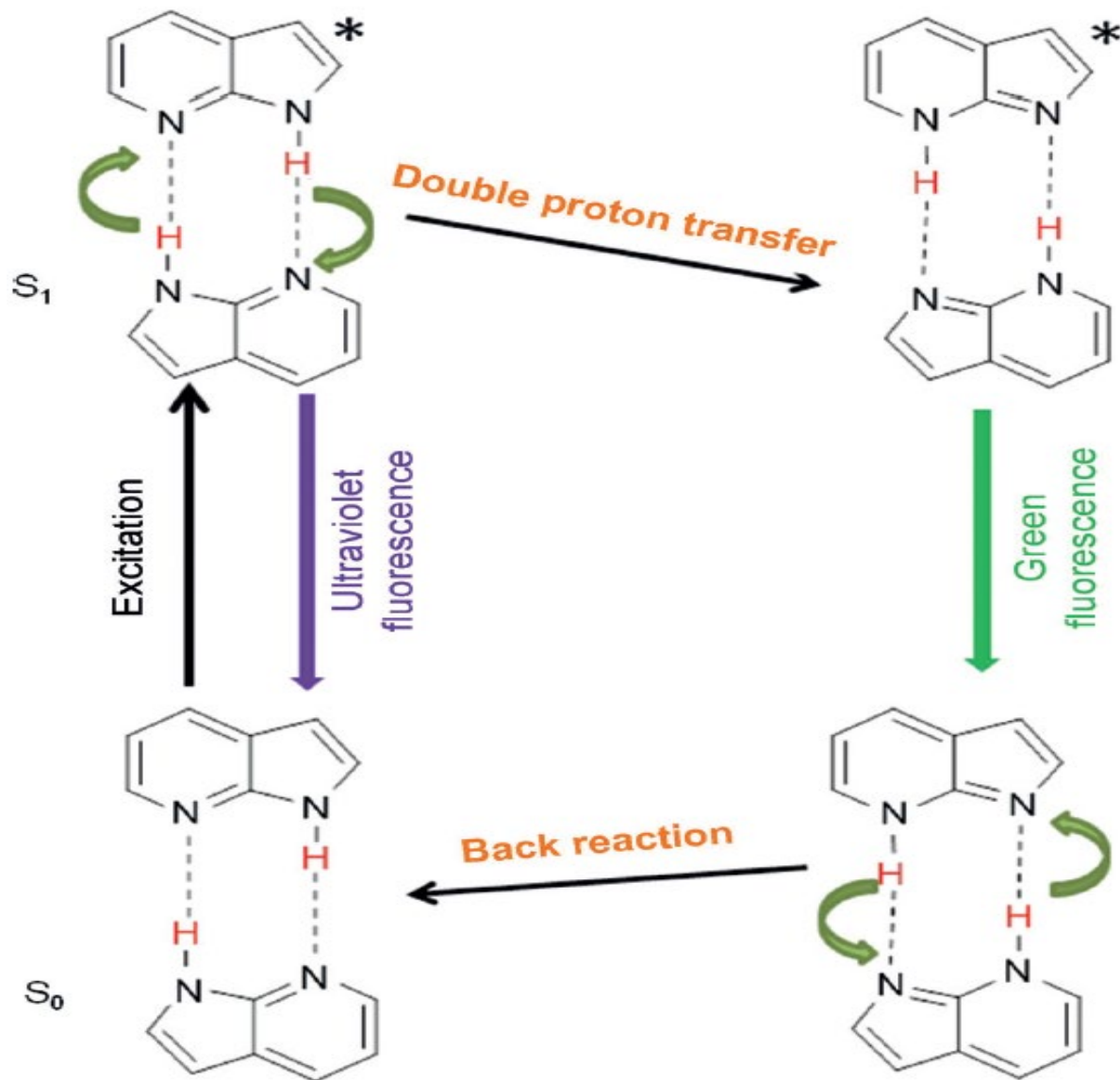
Internal and External Heavy Atom Effects



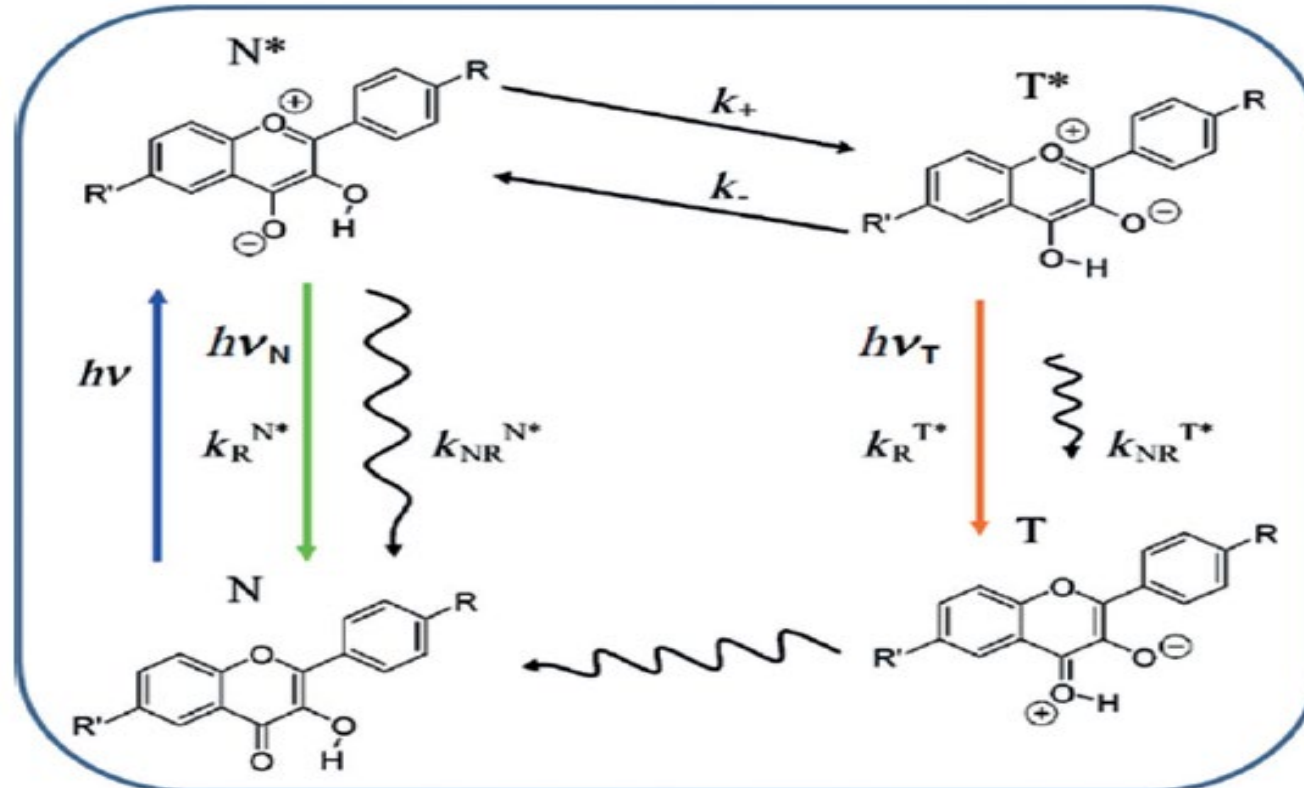
Singlet O₂ in Chemiluminescence and in Triplet Energy Transfer



Double Proton Transfer in 7-Azaindole Proton Transfer Spectroscopy



The Blue Daylily and Intramolecular S_1 Proton Transfer in Flavonoids

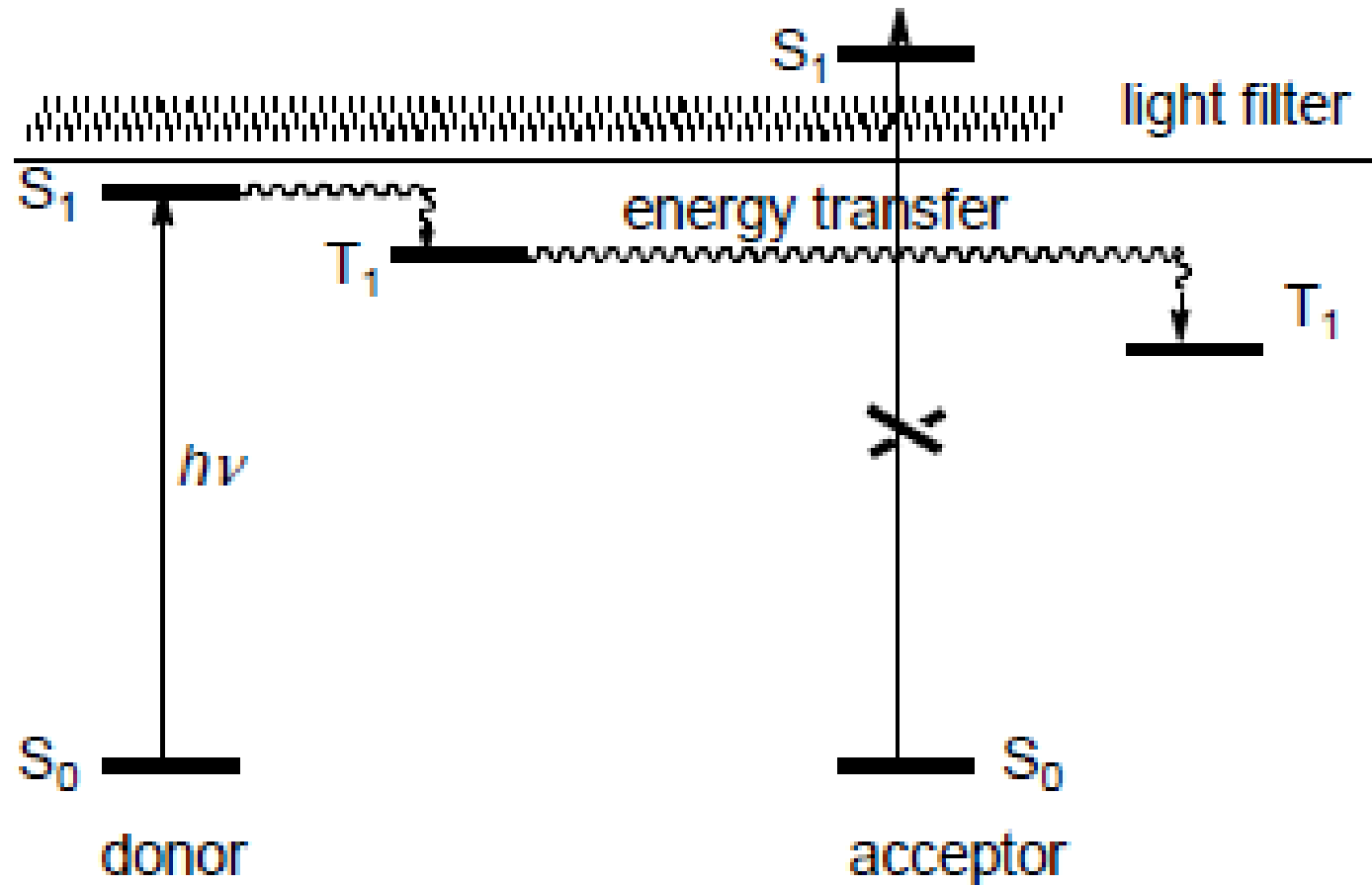


The Kasha Guitar

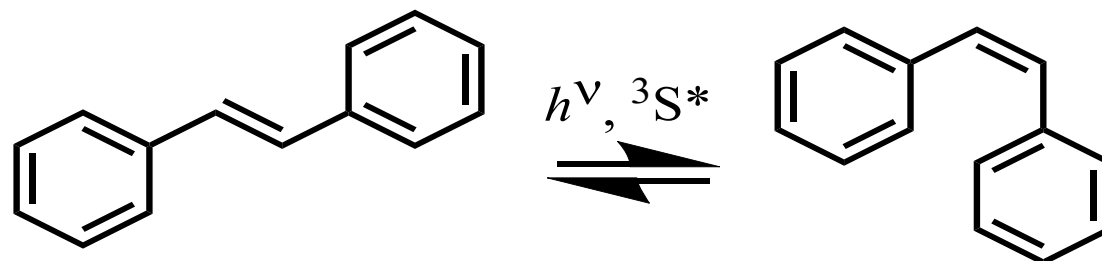
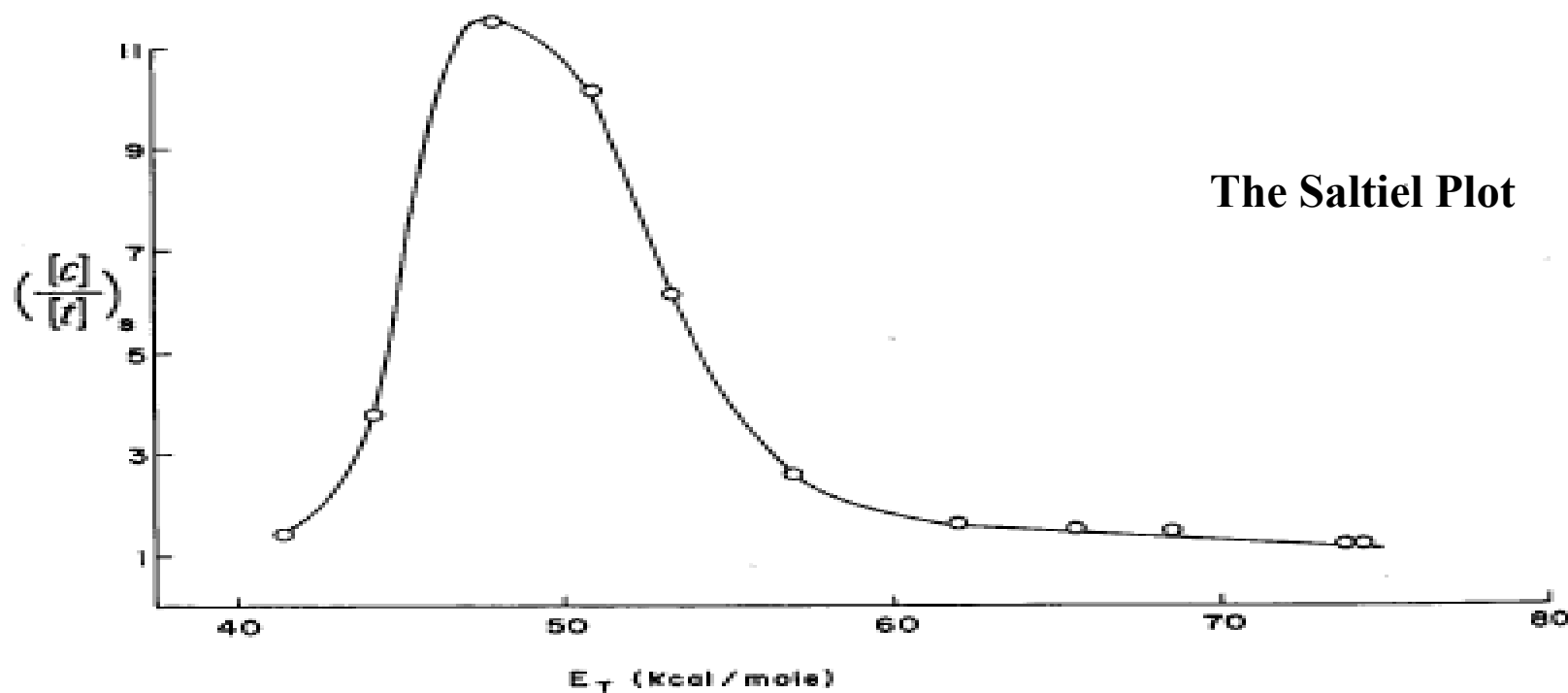


Kasha'schneider kasha model

Triplet Sensitization

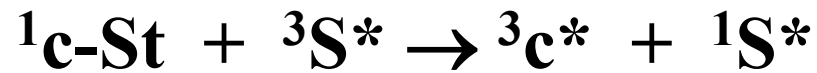
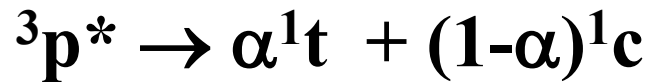
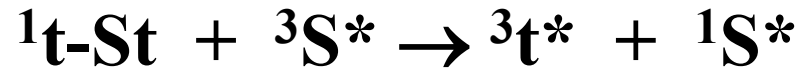


Triplet Sensitized Stilbene Photoisomerization



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

The Photostationary State



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

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

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

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

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

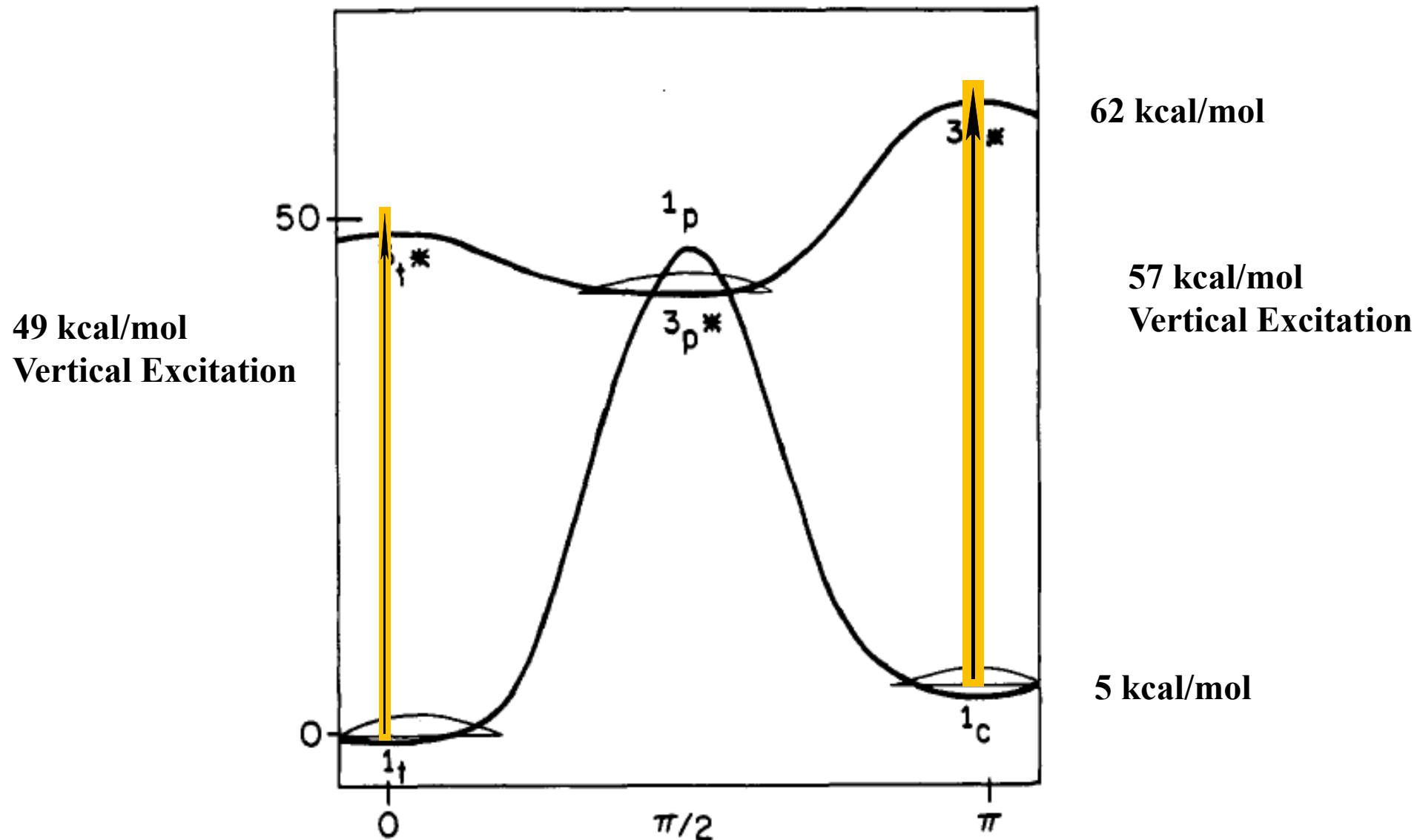


Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in S_0 and T_1 .

Nonvertical Triplet Energy Transfer

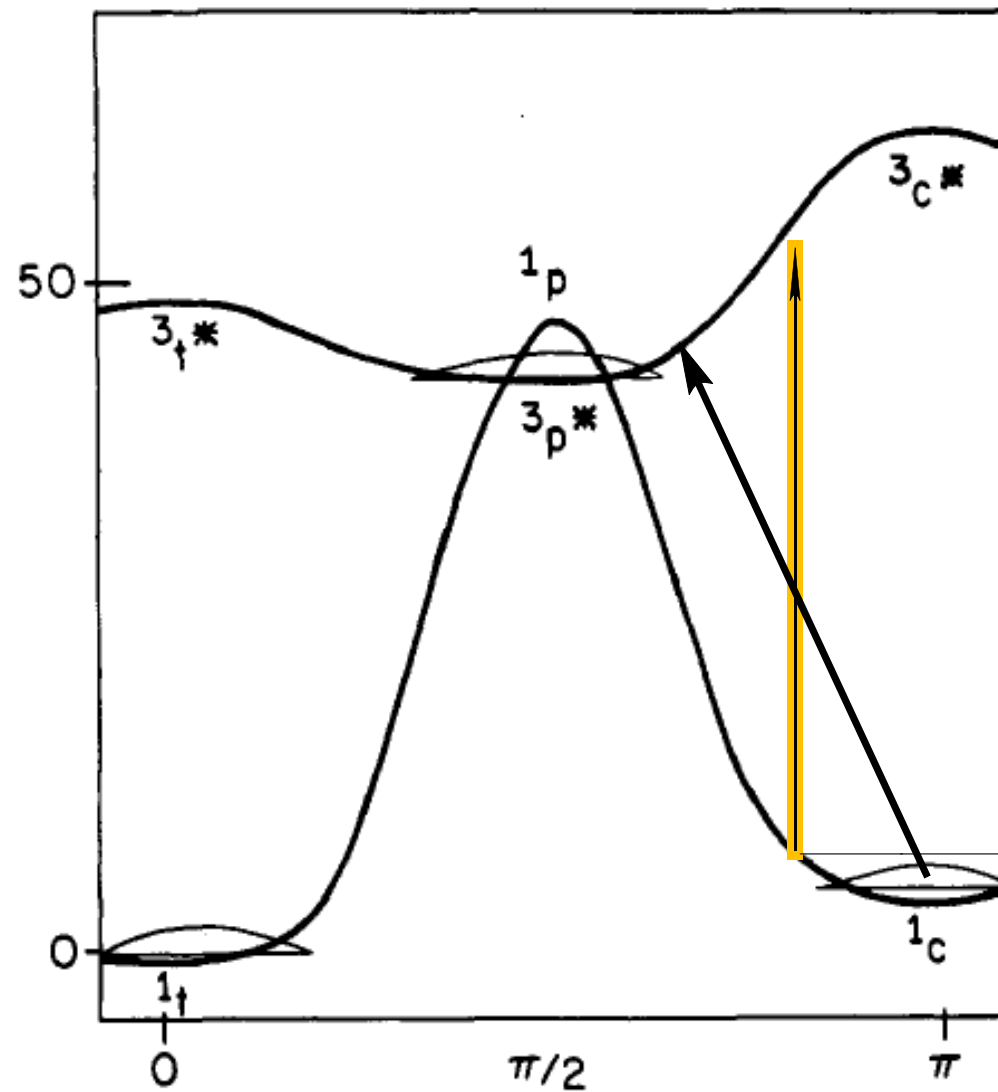
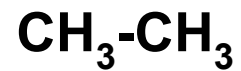
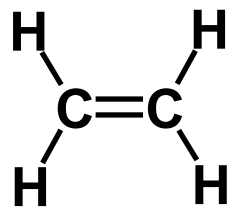


Figure 2. Proposed potential energy curves for twisting about the central bond of stilbene in S_0 and T_1 .

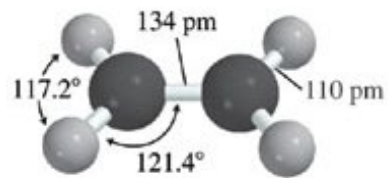
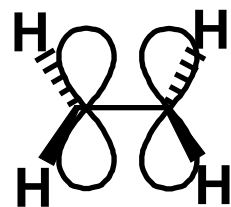


Average bond energies

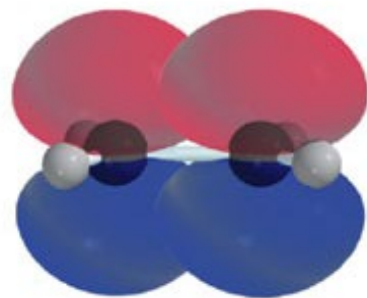
C-C 83 kcal/mol

C=C 146 kcal/mol

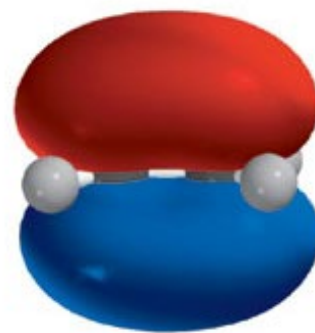
π bond ~ 63 kcal/mol



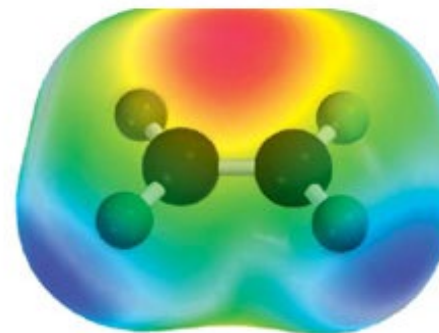
(a)



(b)



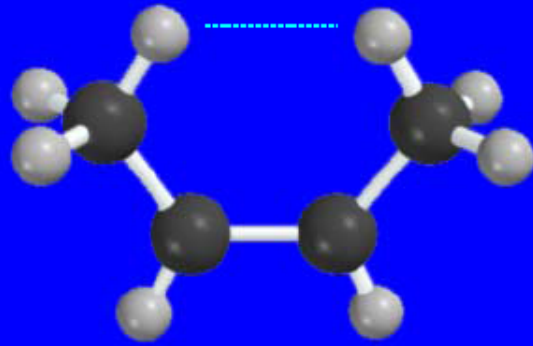
(c)



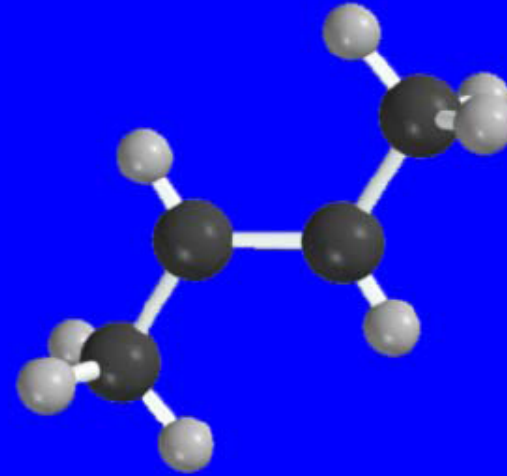
(d)

cis and trans-2-Butene

van der Waals strain
due to crowding of
cis-methyl groups

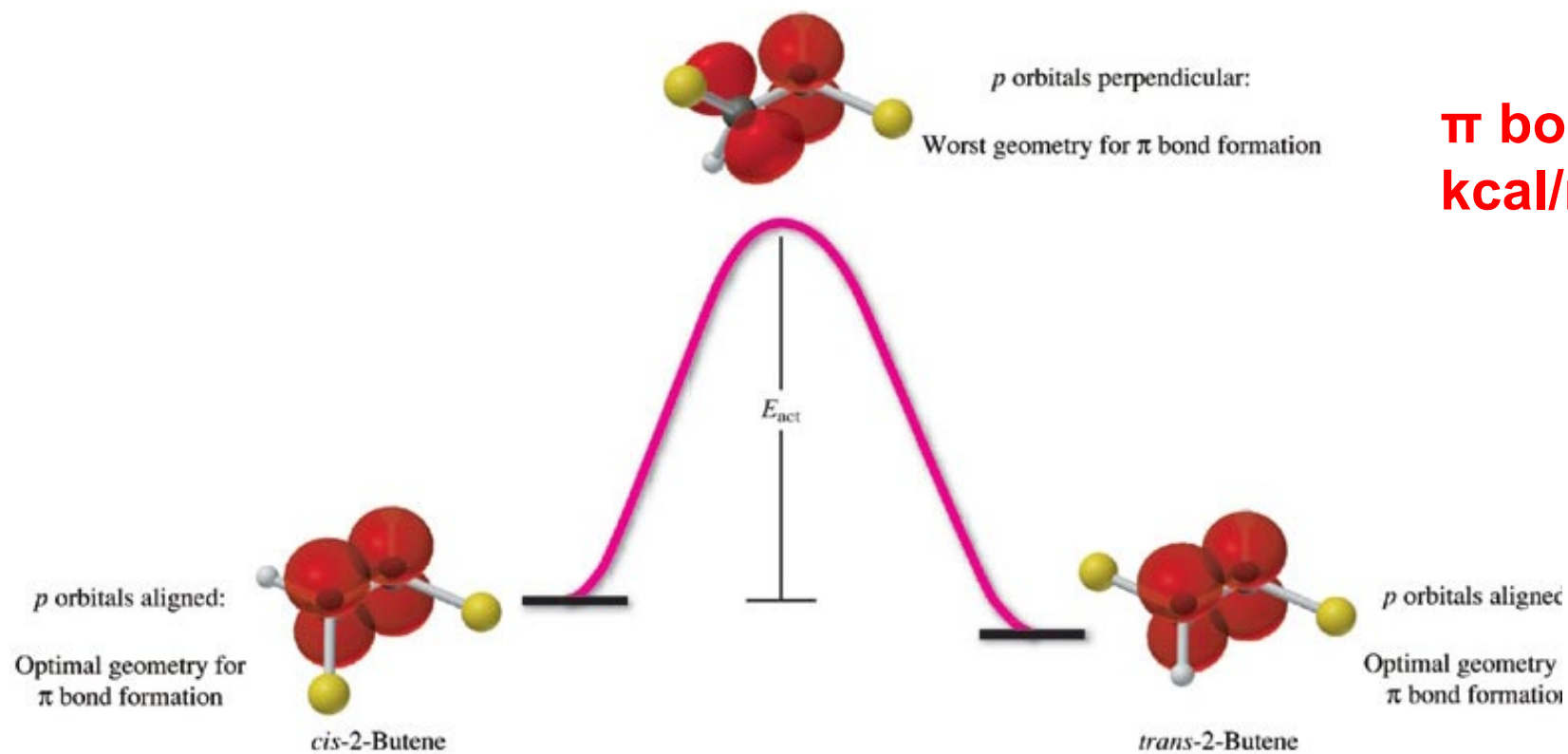


cis-2-butene

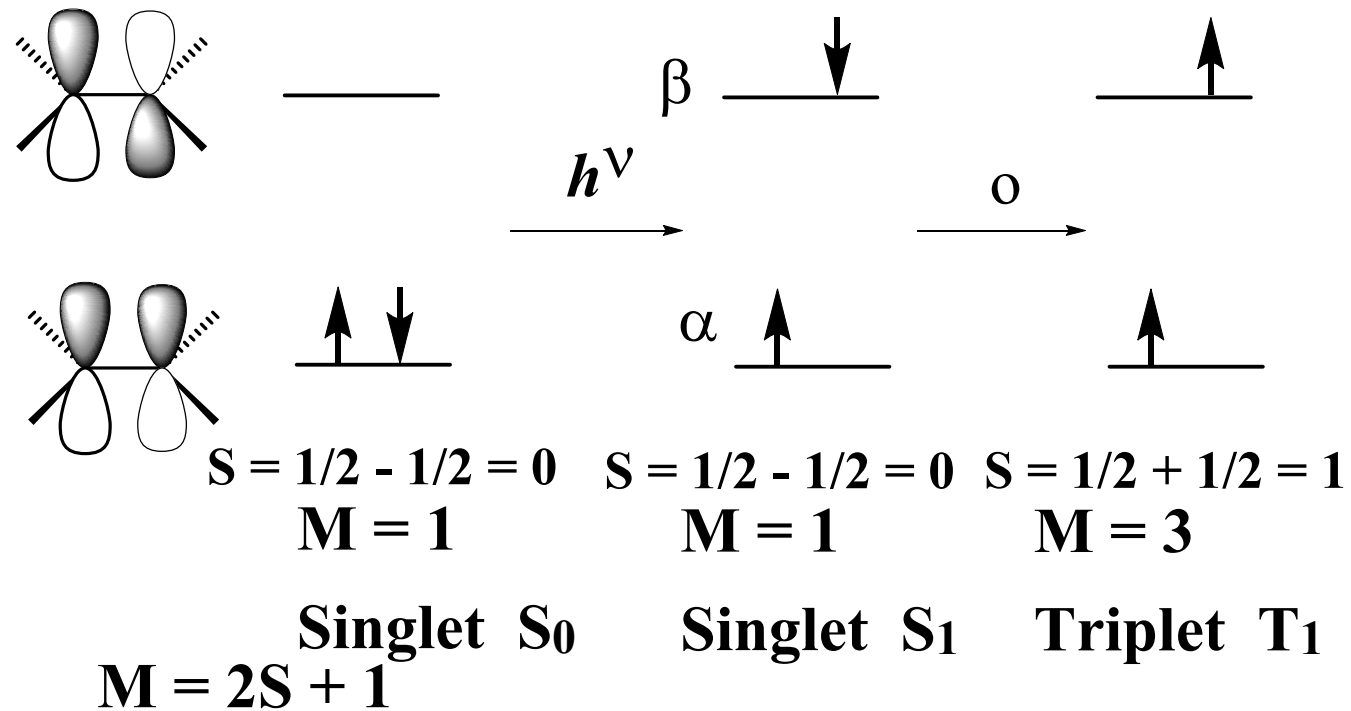


trans-2-butene

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.

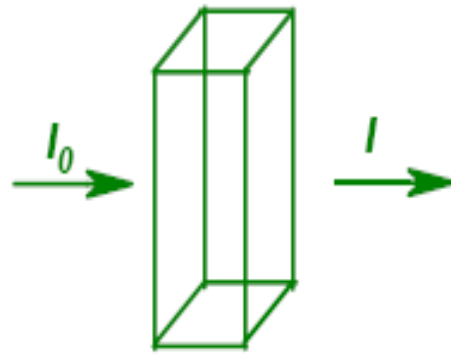


π bond $\sim E_{act} = 62.4$
kcal/mol



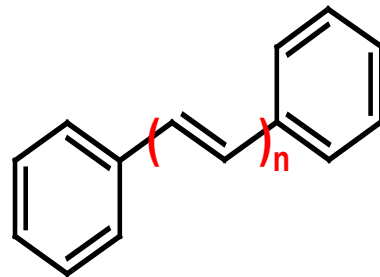
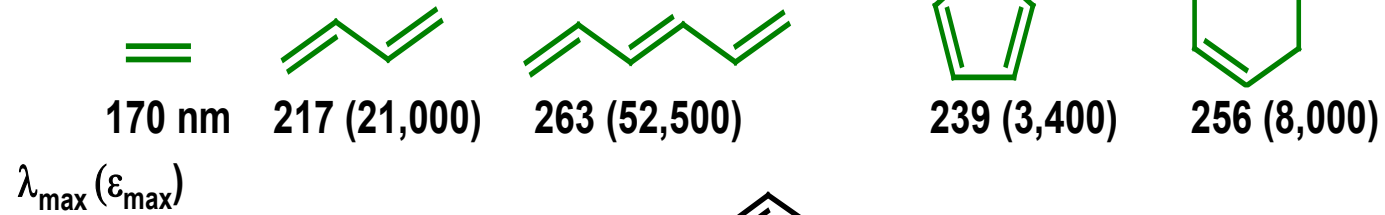
Spin States $\alpha\alpha$, $\beta\beta$, $\sqrt{1/2}(\alpha\beta + \beta\alpha)$, $\sqrt{1/2}(\alpha\beta - \beta\alpha)$

T **T** **T** **S**



Absorbance

$$A = \log(I_0/I) = \epsilon cl$$



n	λ_{\max} , nm	$\epsilon_{\max} \times 10^{-3}$, $M^{-1}cm^{-1}$
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)



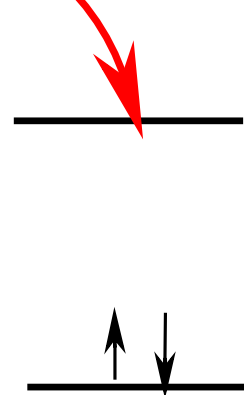
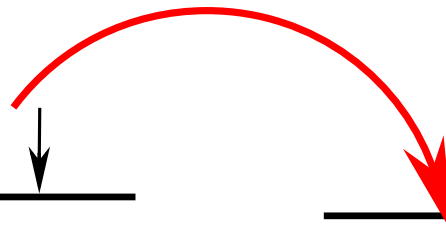
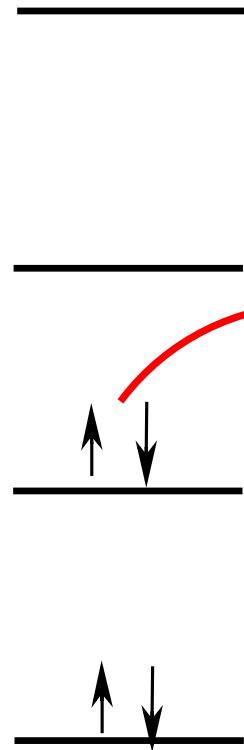
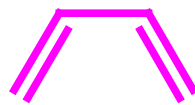
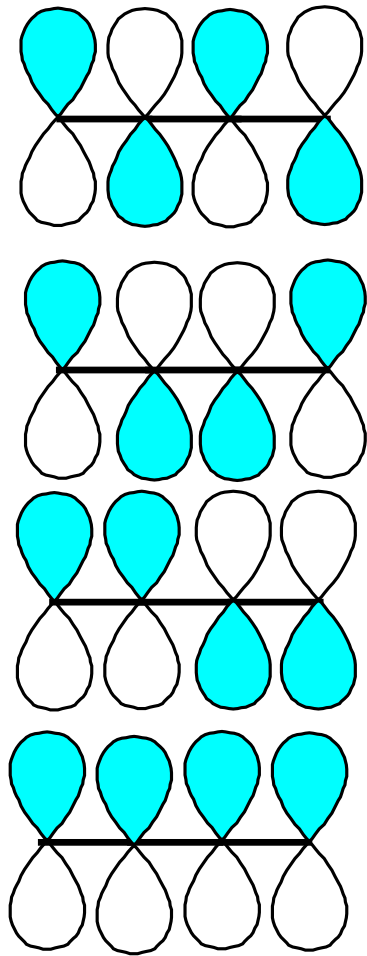
1965



1981

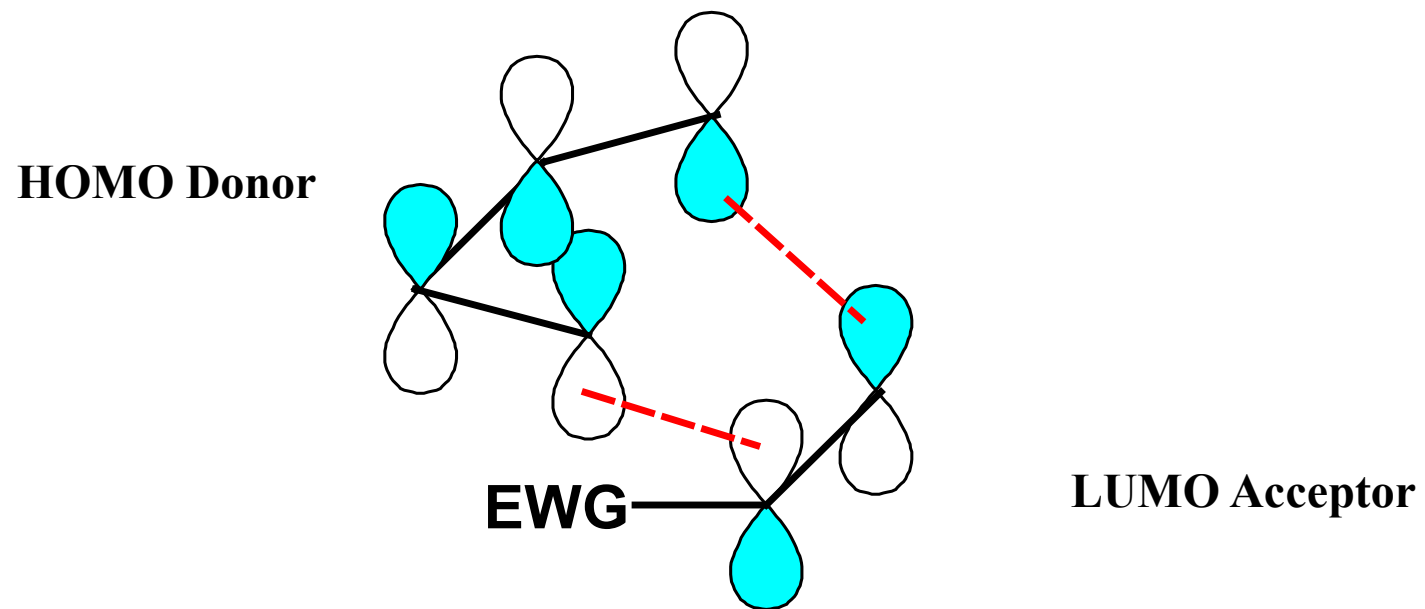


HOMO

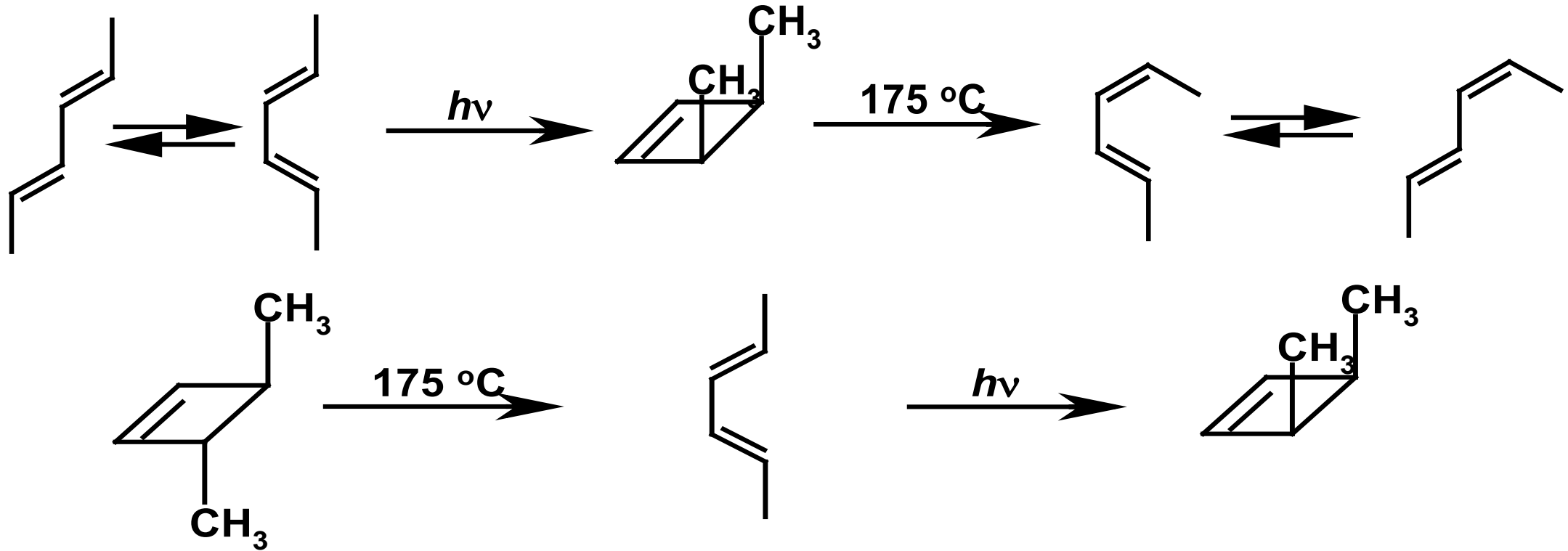


LUMO

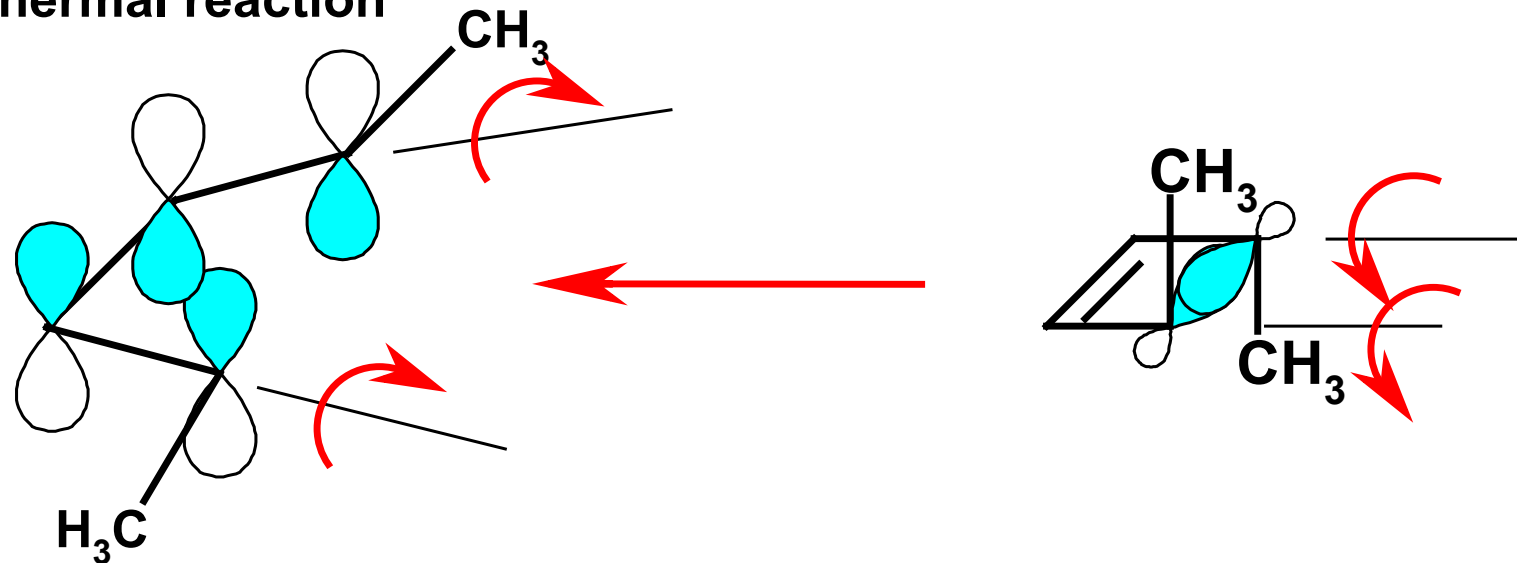
Frontier Orbital Control of Diels-Alder Reaction



Electrocyclic reactions are stereospecific

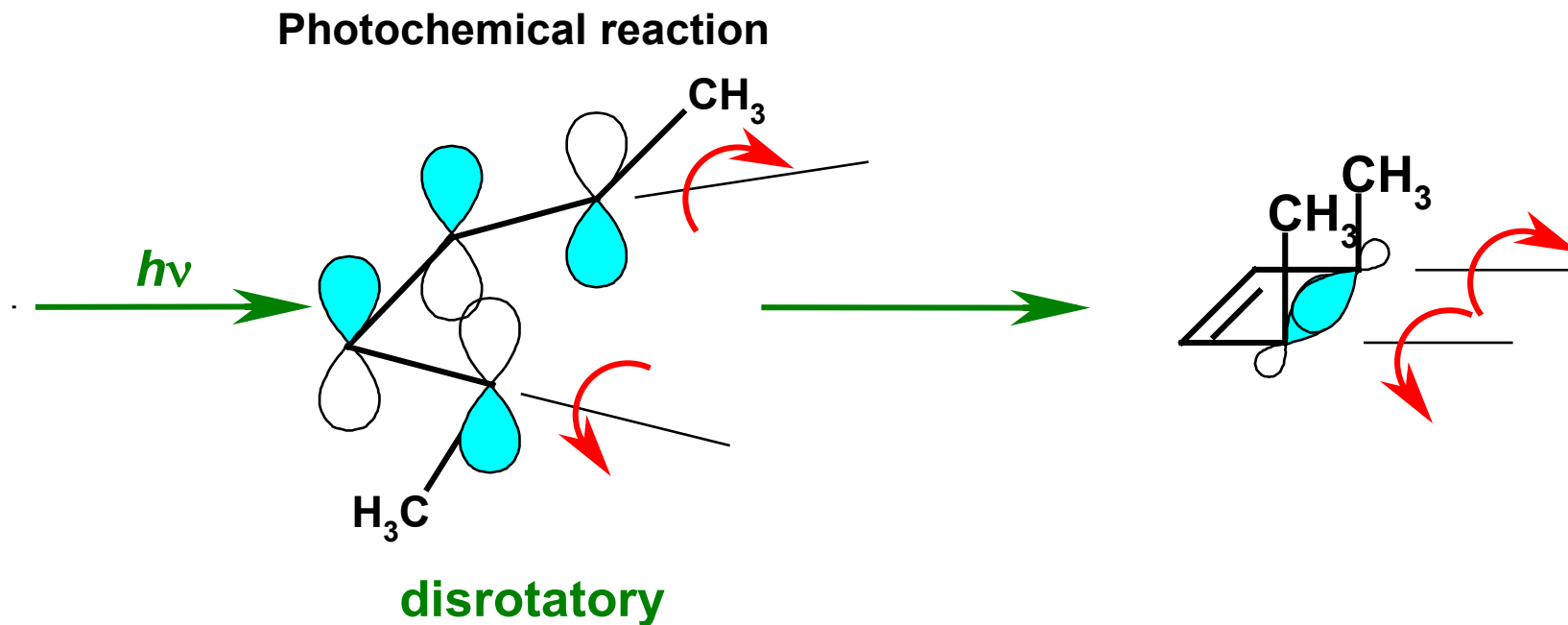


Thermal reaction



conrotatory

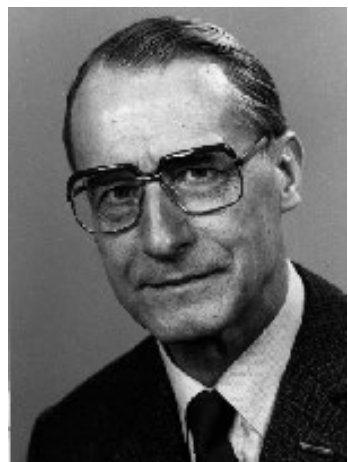
Rotation in the **same direction** leads to a bonding interaction (+ lobe on + lobe or - lobe on - lobe). The reaction passes through the same TS in both directions.



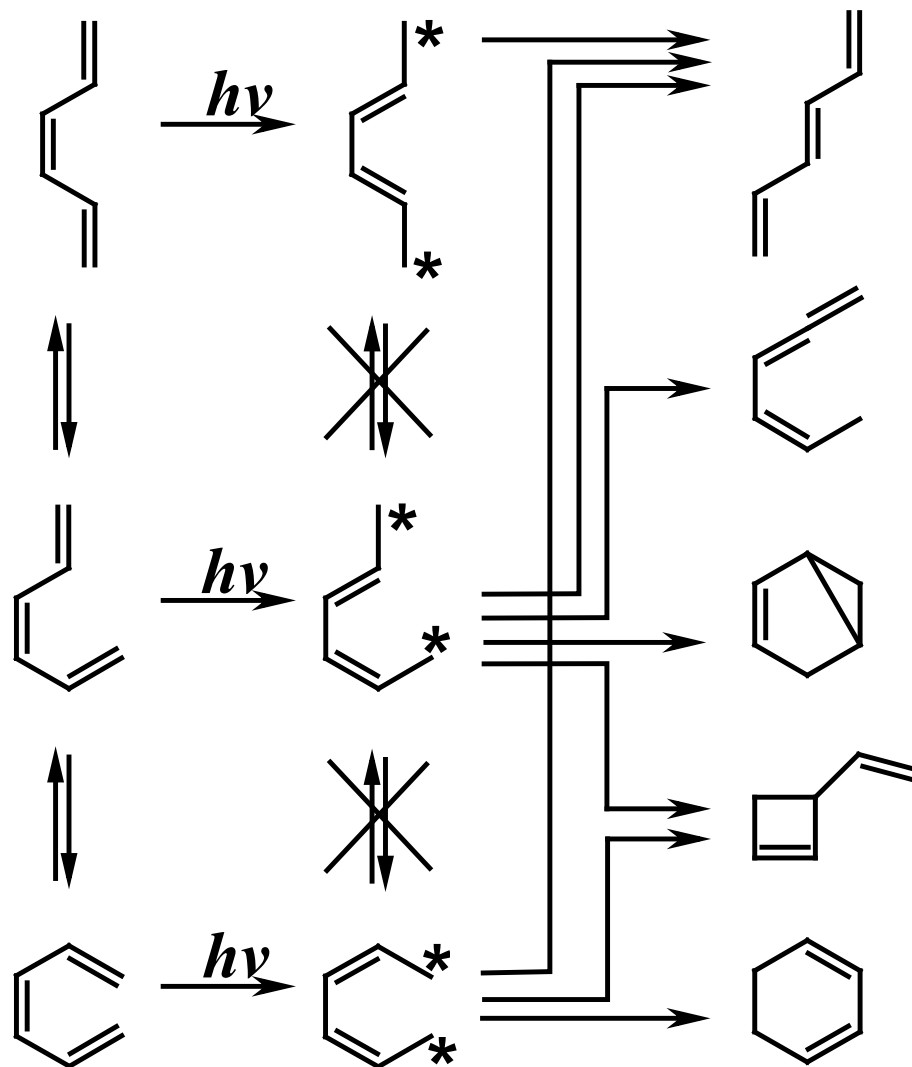
Rotation in **opposite directions** leads to a bonding interaction (+ lobe on + lobe or - lobe on - lobe).

The reaction passes through the same TS in both directions.

NEER PRINCIPLE



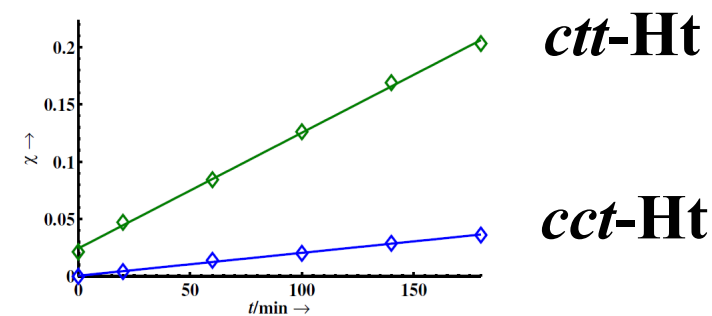
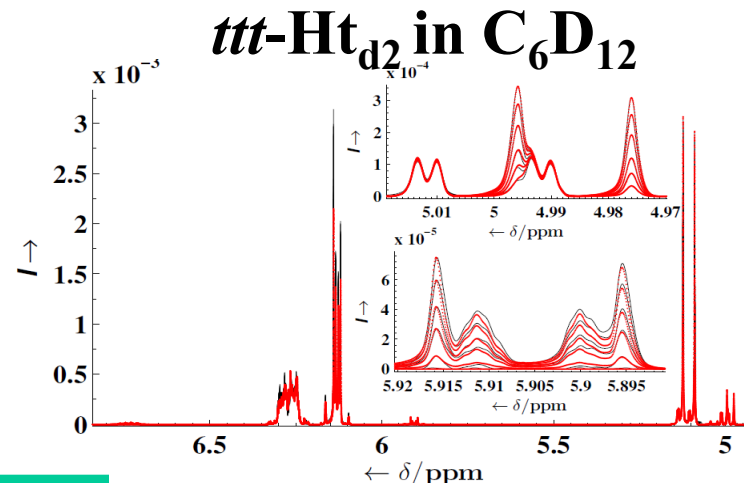
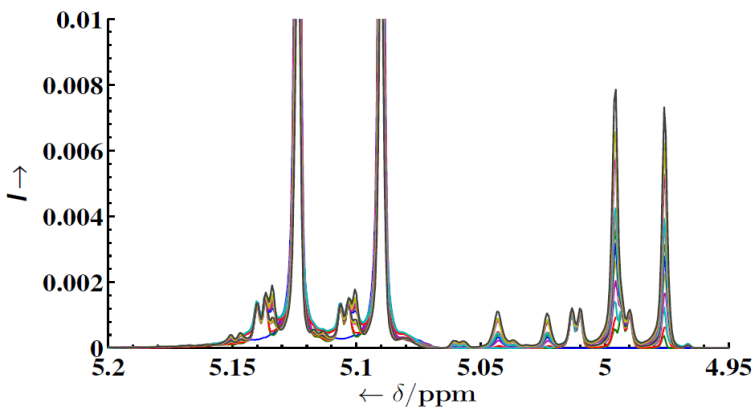
Egbert Havinga
1909-1988



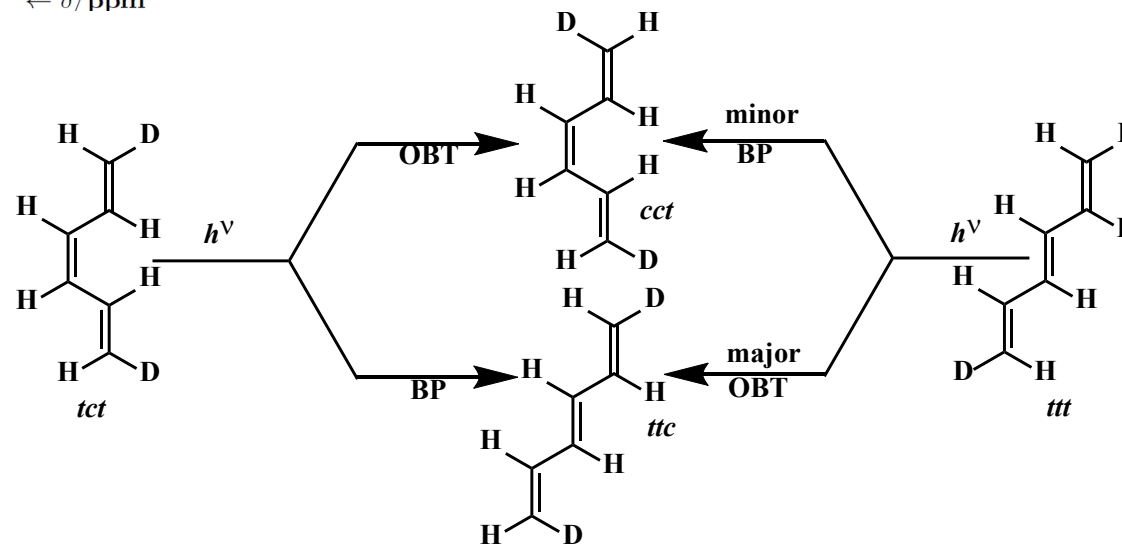
Havinga, *Tetrahedron*, 1973

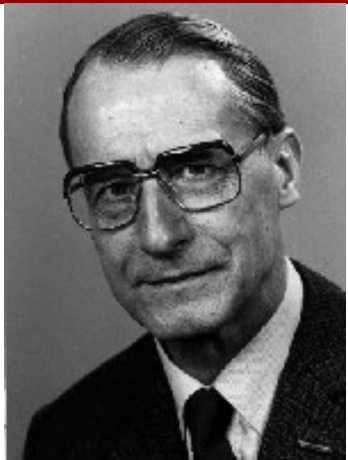
$$\phi_{ct} = 0.03, \phi_{tc} = 0.016$$

1,6-Dideuteriohexatrienes



	C ₆ D ₁₂		CD ₃ CN	
X	$\phi_{ttt \rightarrow X}$	$\phi_{tct \rightarrow X}$	$\phi_{ttt \rightarrow X}$	$\phi_{tct \rightarrow X}$
ctt	0.44	0.24₅	0.54	0.24
cct	0.08₅	0.34	0.09₃	0.39
tct			0.01₄	
ttt		0.05₈		0.11



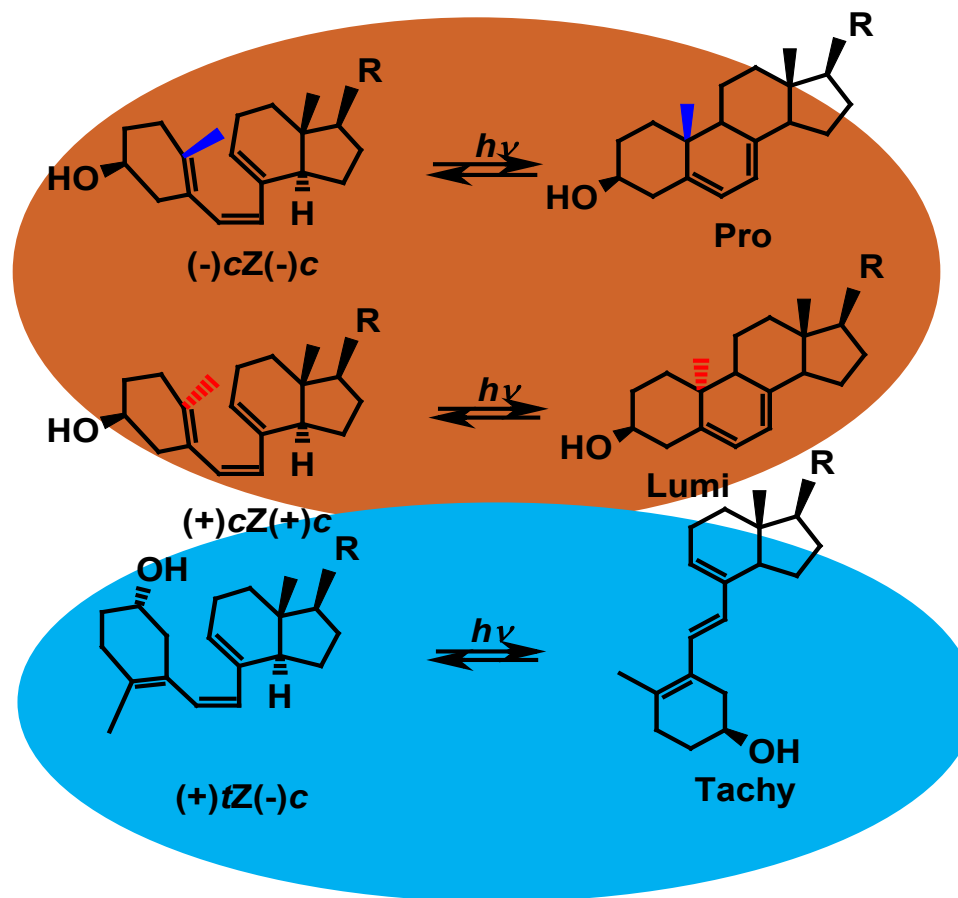


Havinga's NEER Principle

Egbert Havinga
1909-1988

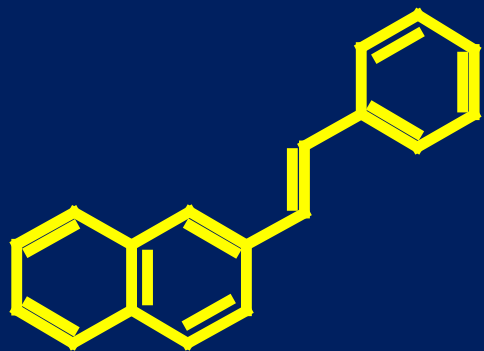
Photocyclization
Long λ

Photoisomerization
Short λ

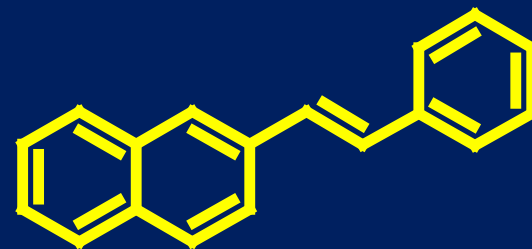




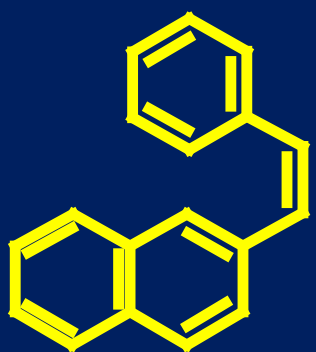
NPE Conformers



***t*-NPE_A**



***t*-NPE_B**



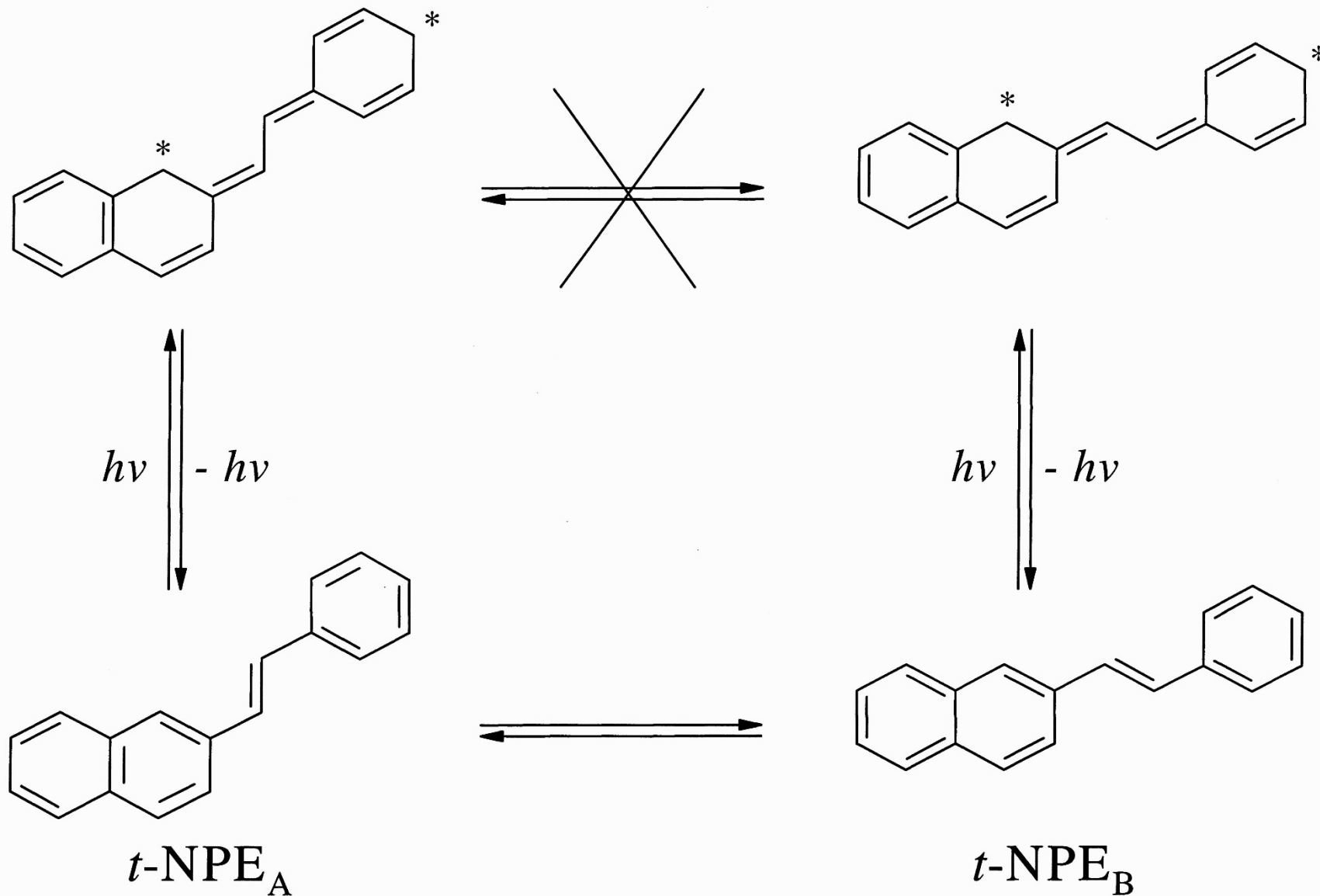
***c*-NPE_A**



***c*-NPE_B**

NPE
conformers

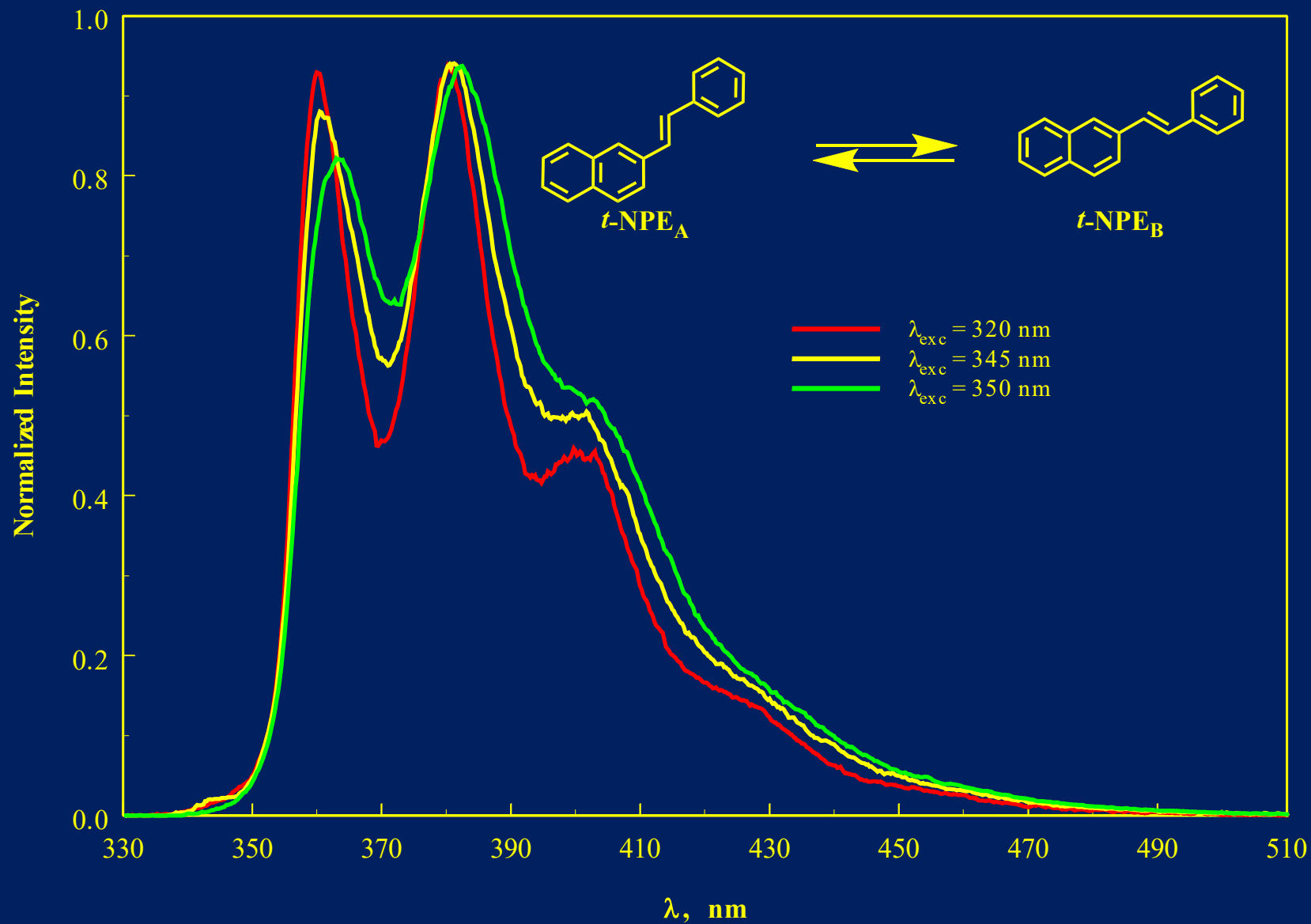
trans-1-(2-Naphthyl)-2-phenylethene and the NEER Principle





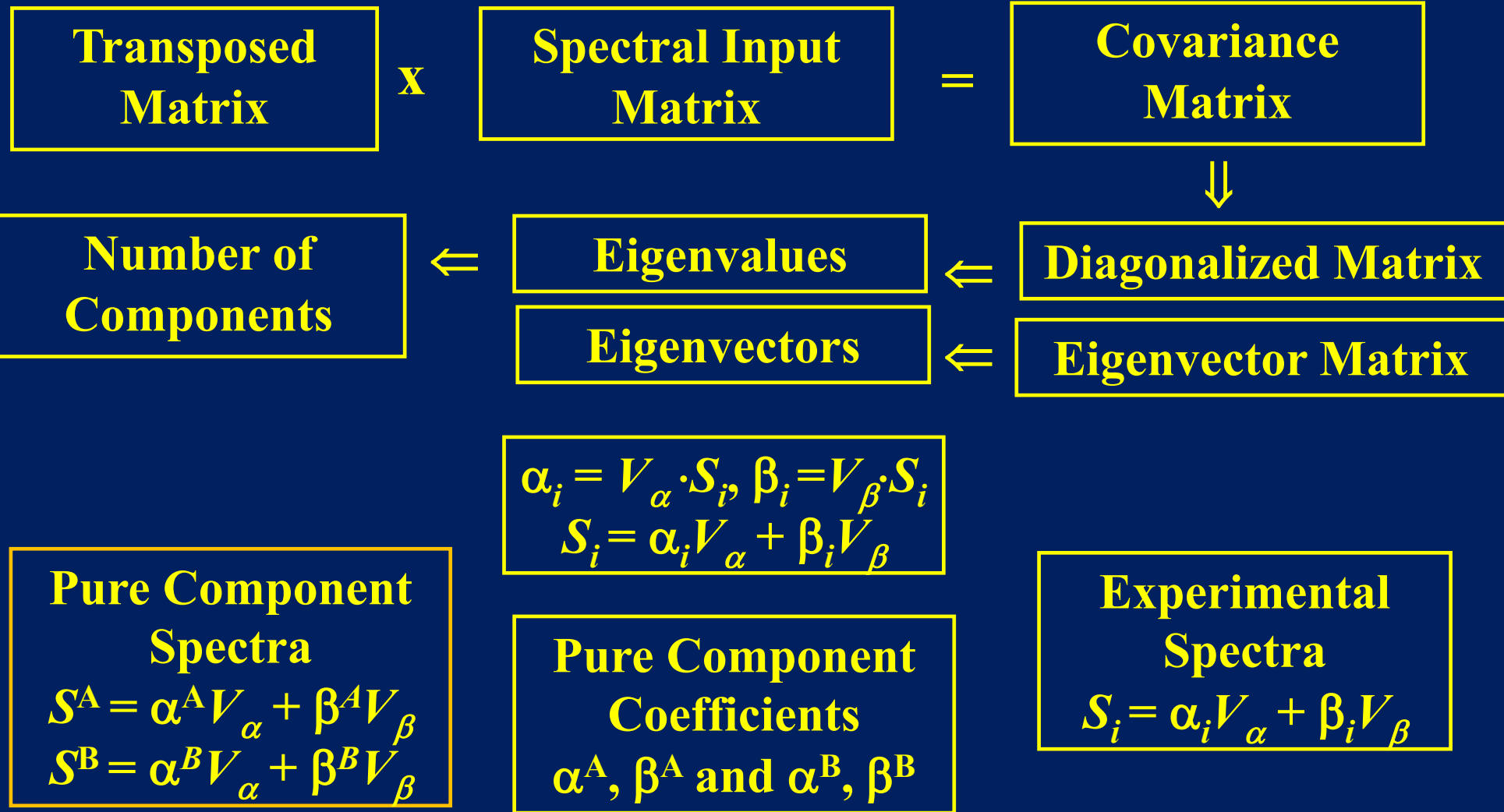
Fluorescence Emission Spectra of *t*-NPE as a Function of λ_{exc} in Ar Outgassed Benzene at 20 °C

t-NPE/Bz





Summary of PCA-SM Mathematical Operations



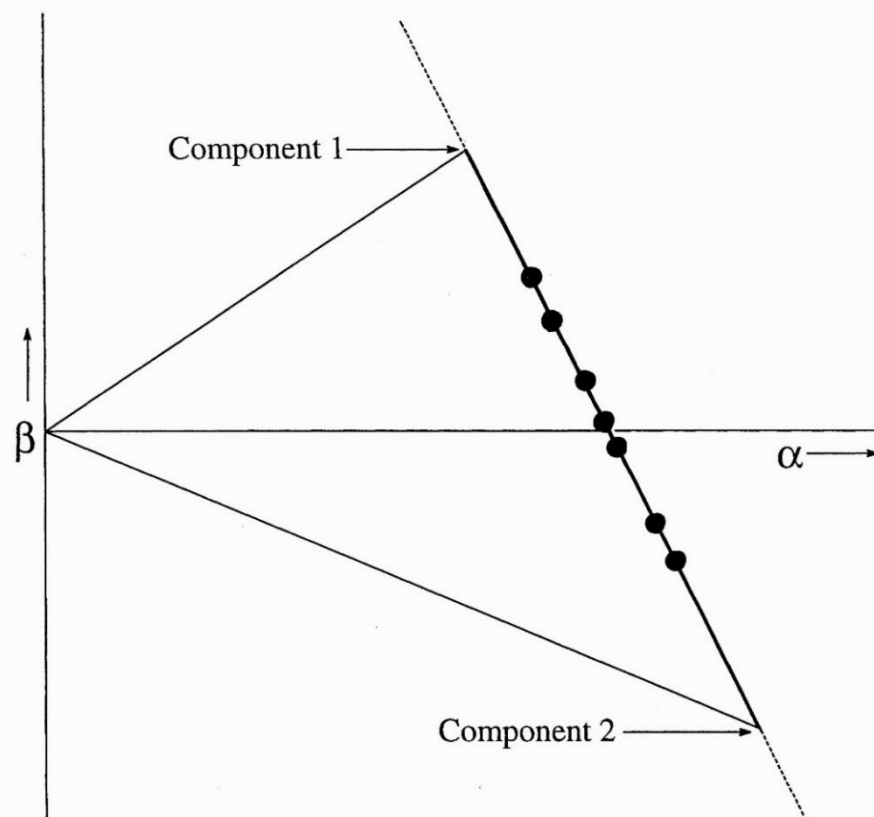


TWO COMPONENTS

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

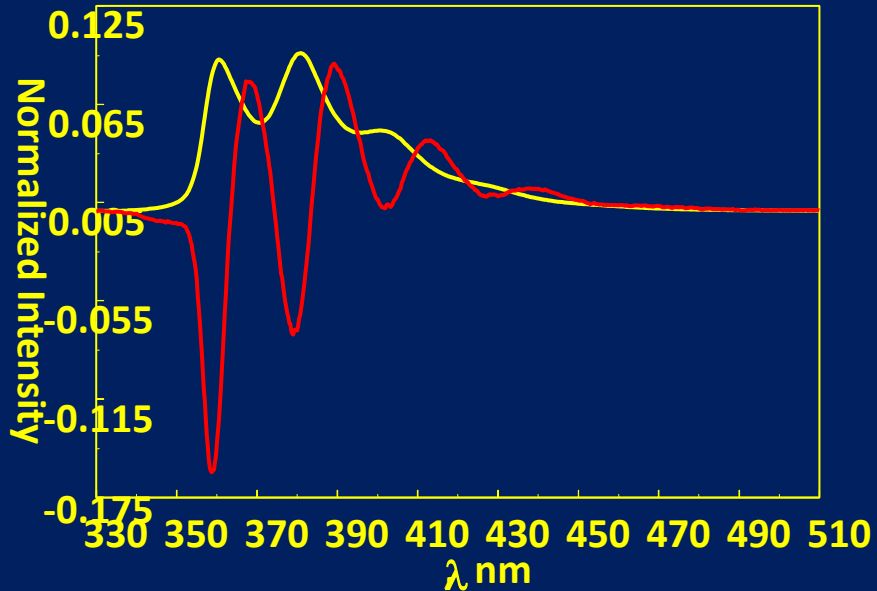
$$\alpha \Sigma V_{\alpha i} + \beta \Sigma V_{\beta k} = 1$$

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

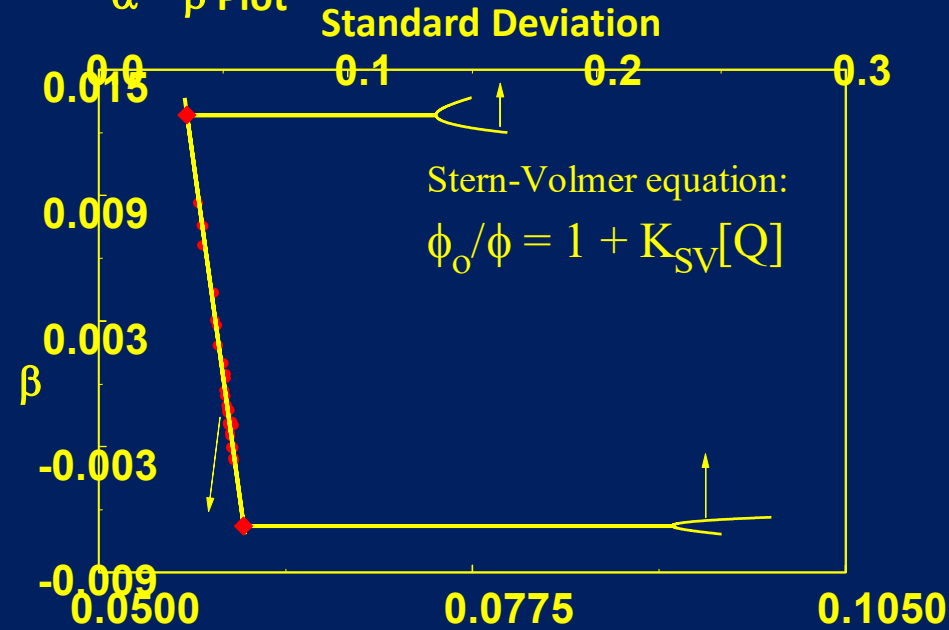




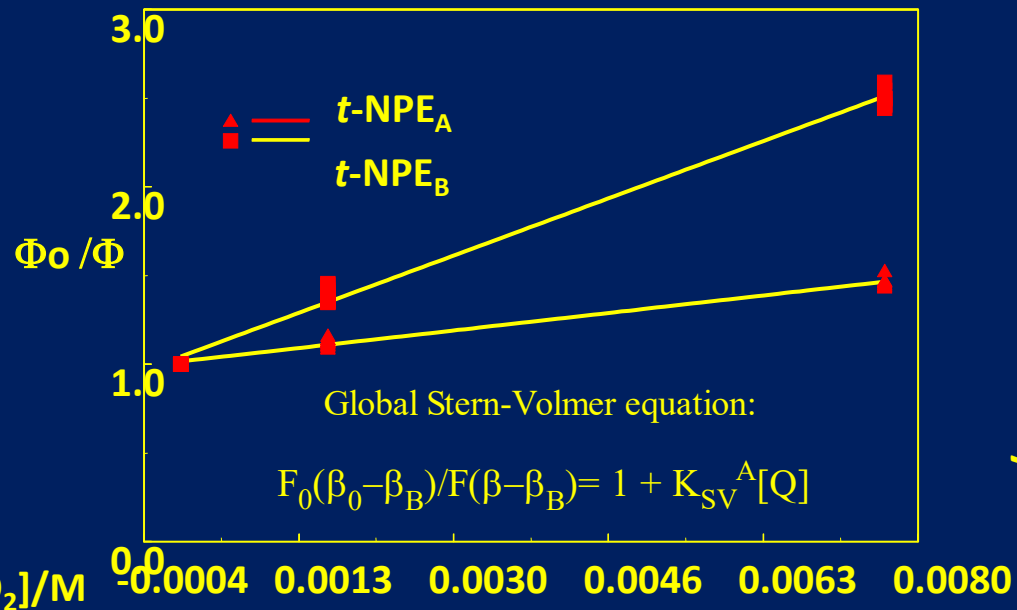
Principal Eigenvectors



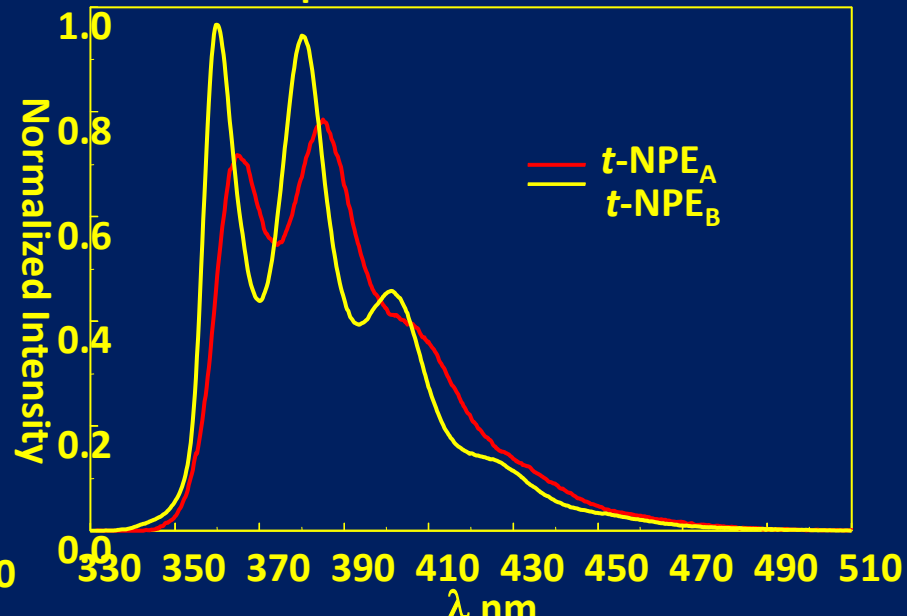
$\alpha - \beta$ Plot



Global Stern-Volmer Plots



Conformer Spectra



t-NPE/PCA-SM

Stern-Volmer Quenching

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



The Stern-Volmer Plot

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

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

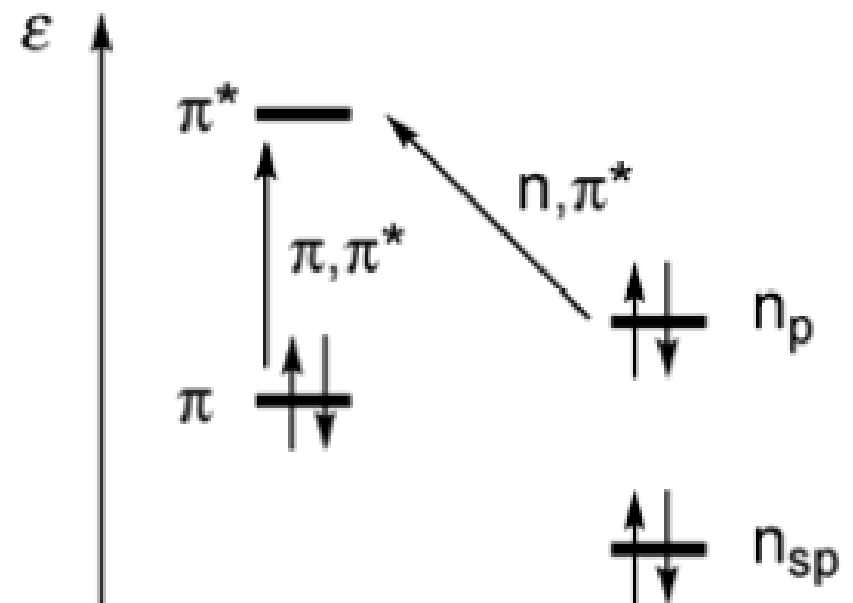
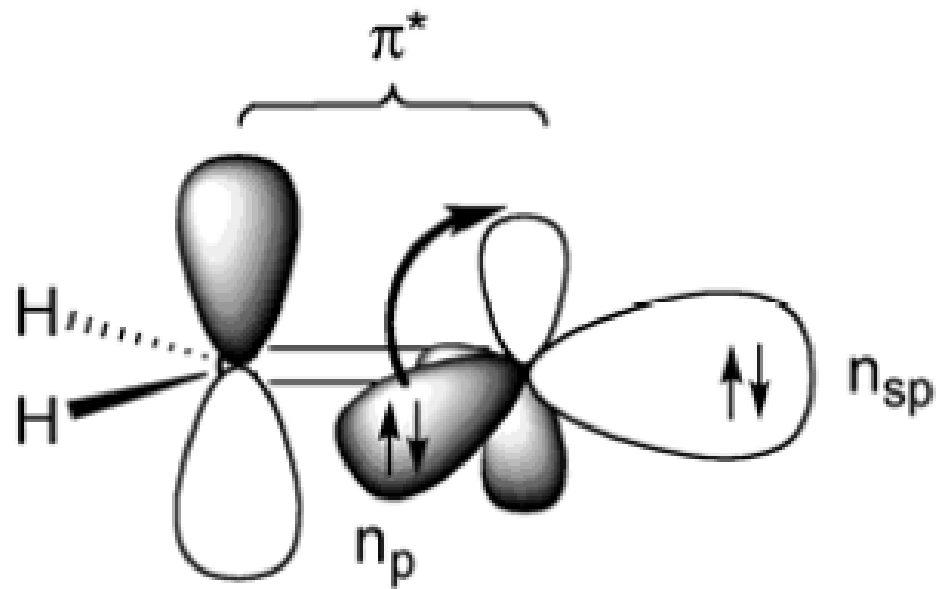
$$\frac{d[^1A^*]}{dt} = I_a - (k_f + k_{is} + k_p)[^1A^*] = 0 \quad \text{where } I_a \text{ is the rate of light absorption}$$

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

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

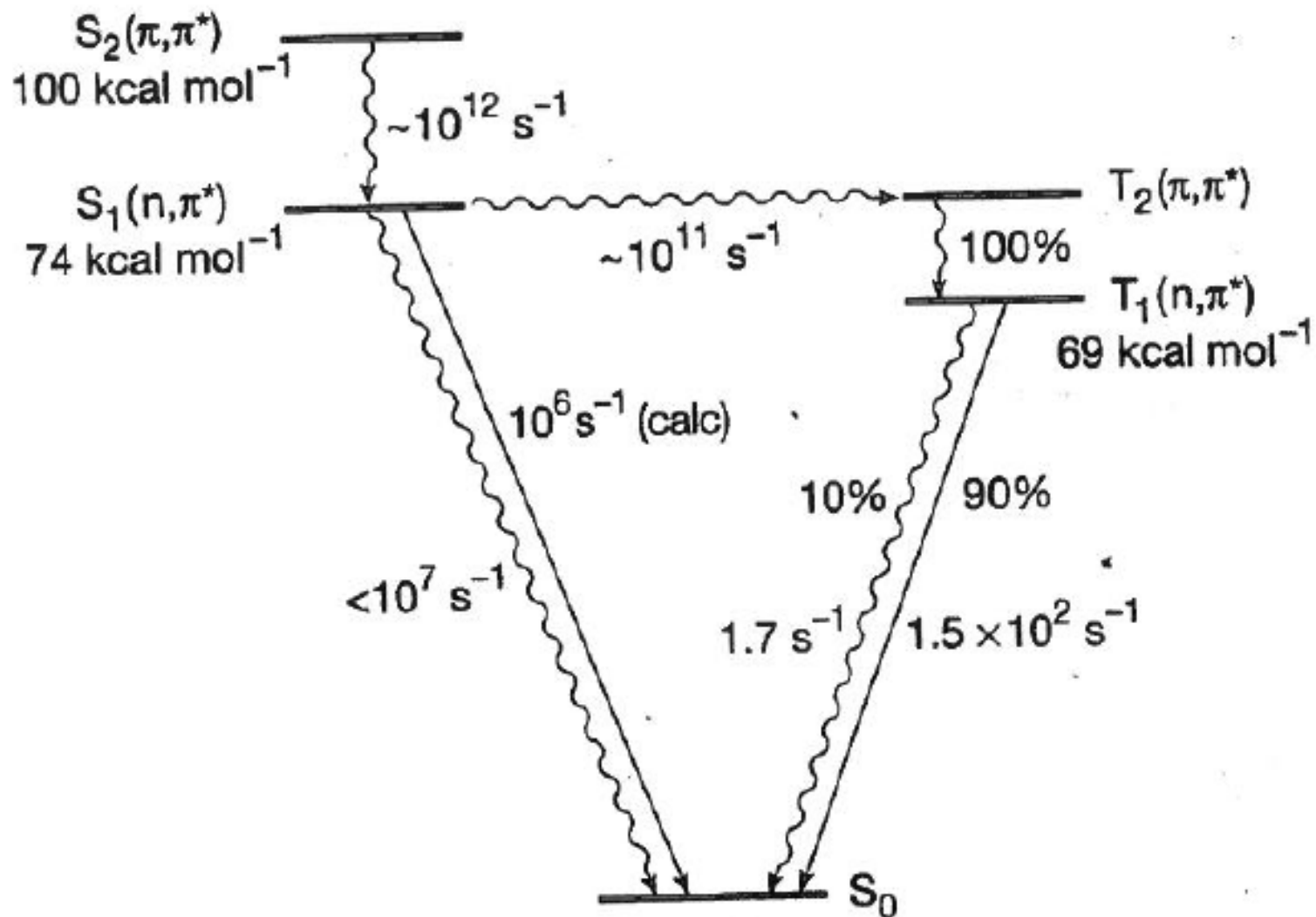
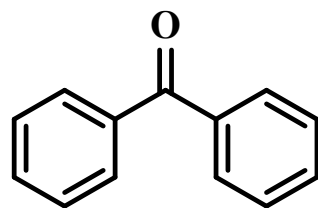
$$\frac{d[h\nu_f]}{dt} = \frac{k_f I_a}{k_f + k_{is} + k_p}$$

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

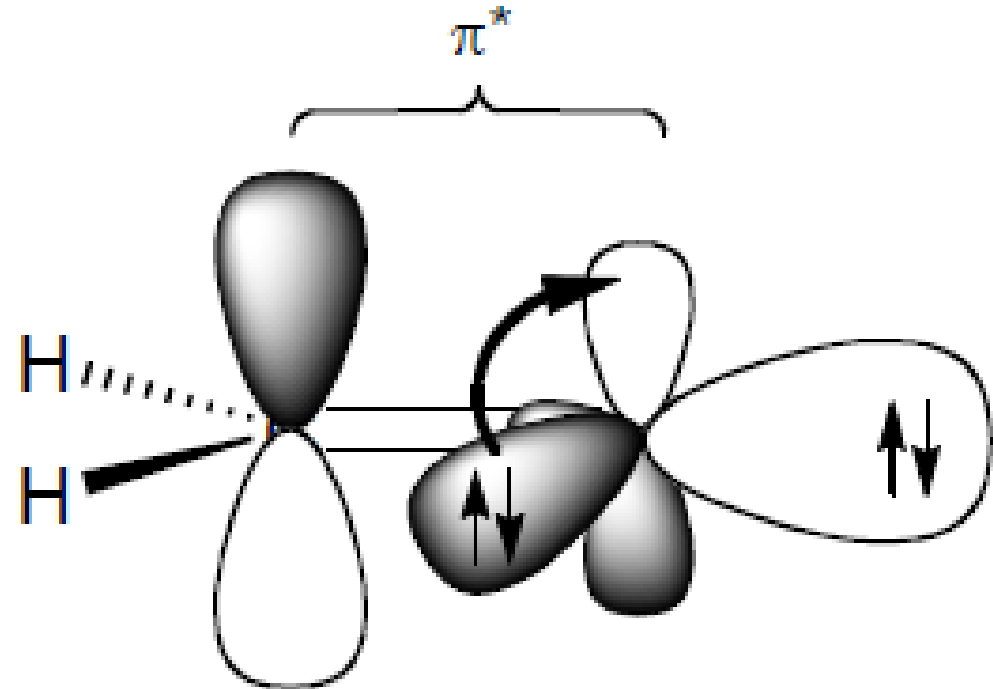
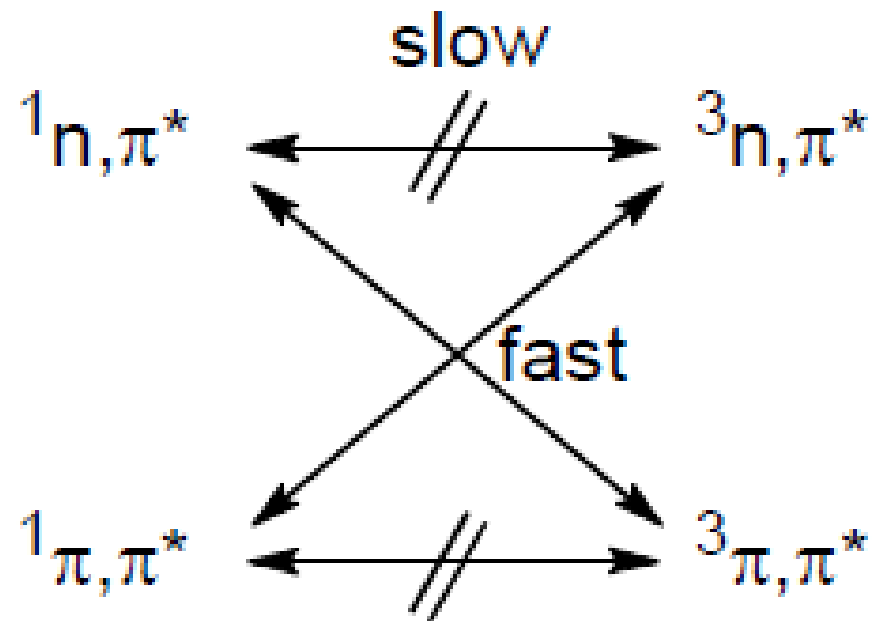


The n, π^* -transition of formaldehyde.

Benzophenone State Diagram



El-Sayed's Rules for Intersystem Crossing



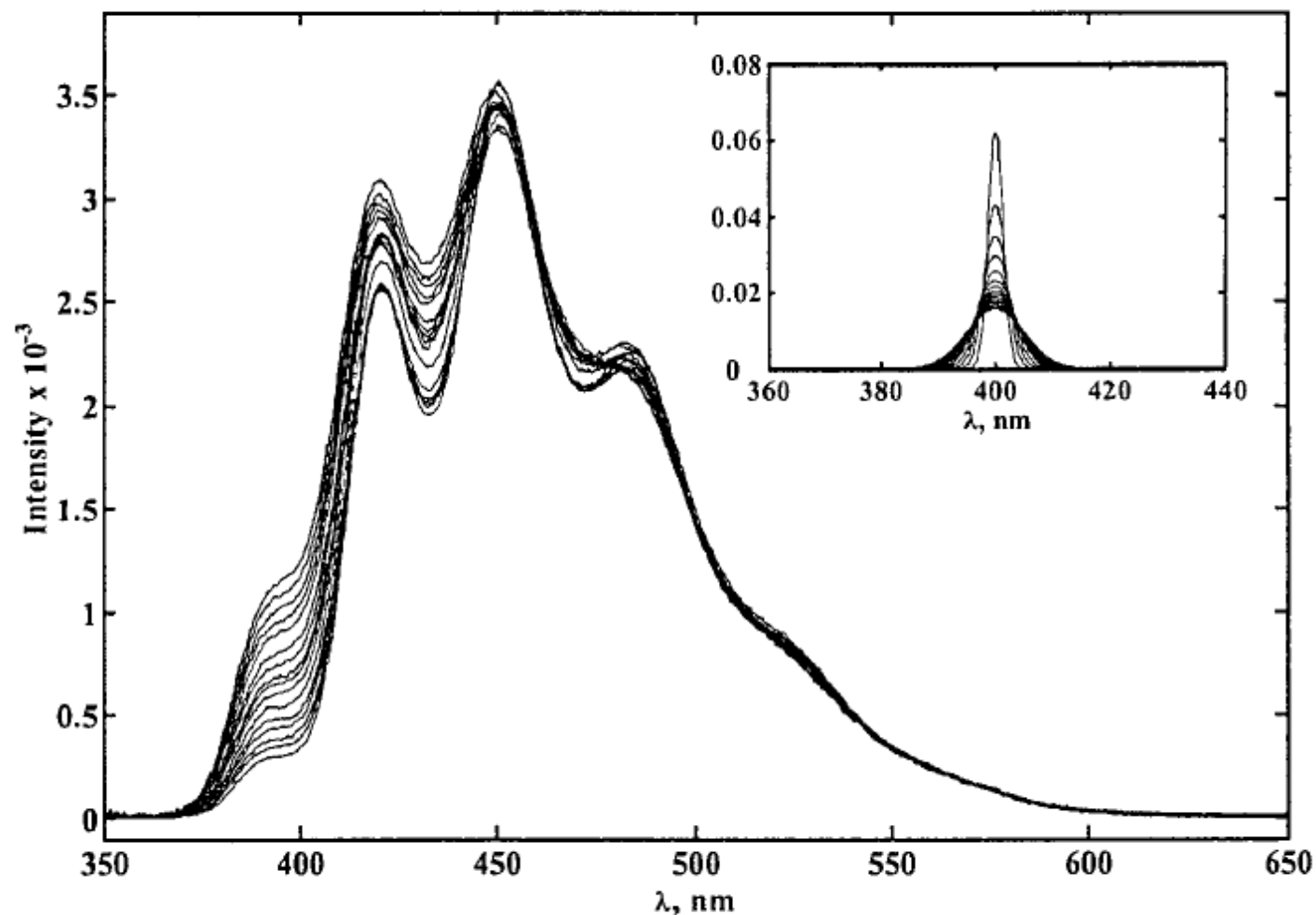


Figure 1. Benzophenone luminescence spectra (self-absorption-corrected, instrumental-response-uncorrected) at different temperatures (Table 1) from the degassed CCl₄ solution. The inset shows the set of Gaussian functions used to compensate the spectra for thermal broadening.

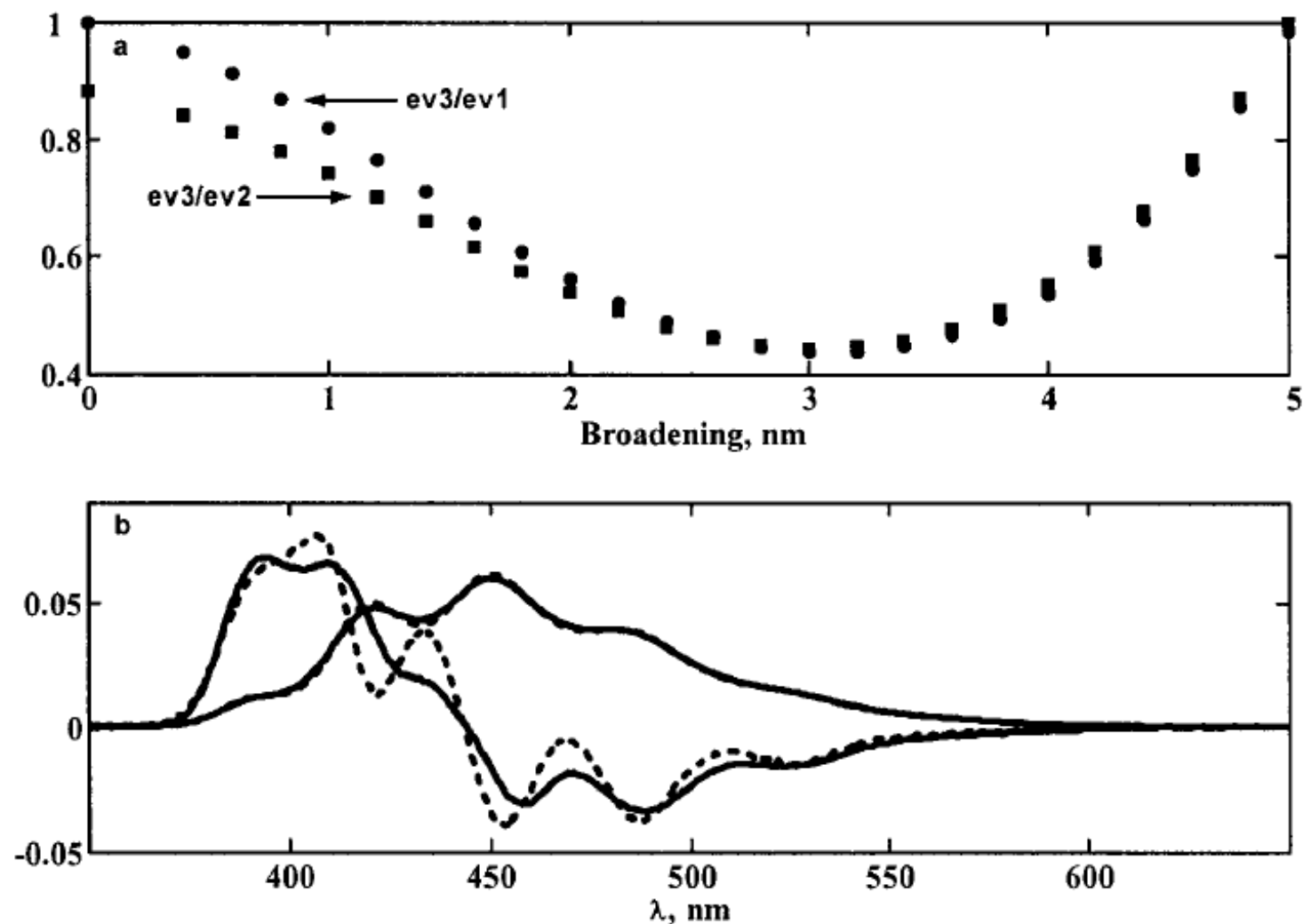


Figure 3. (a) Ratios of the third to the first eigenvalue (circles) and the third to the second eigenvalue (squares) as a function of the compensating broadening parameter k . (b) First and second eigenvectors before the compensation for thermal broadening (dashed lines) and after the compensation (solid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

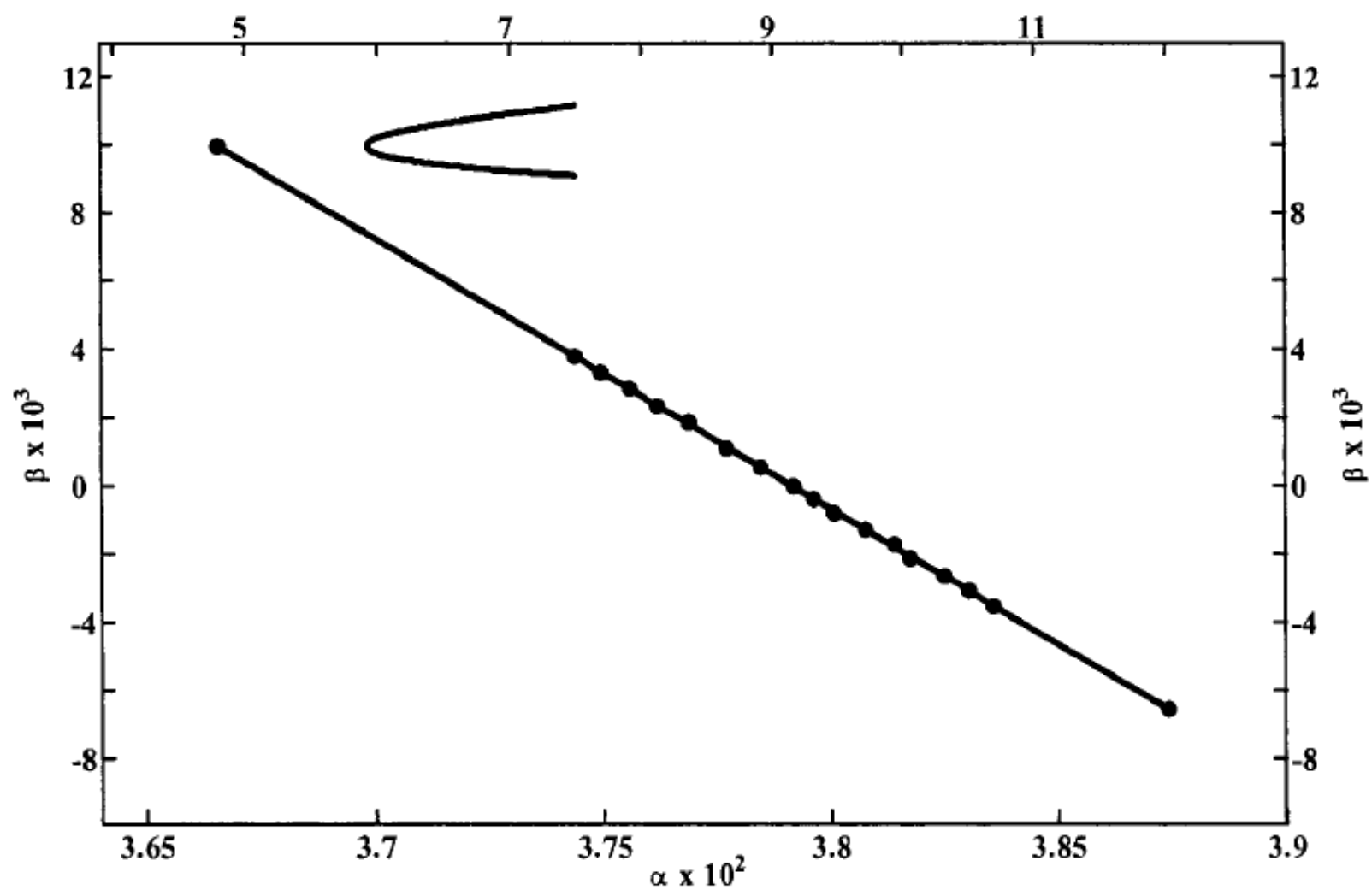


Figure 5. α, β normalization line for the benzophenone luminescence system. The standard deviation for the van't Hoff plot as a function of β is also shown. The minimum determines the β_{DF} value corresponding to the spectrum of the pure delayed benzophenone fluorescence.

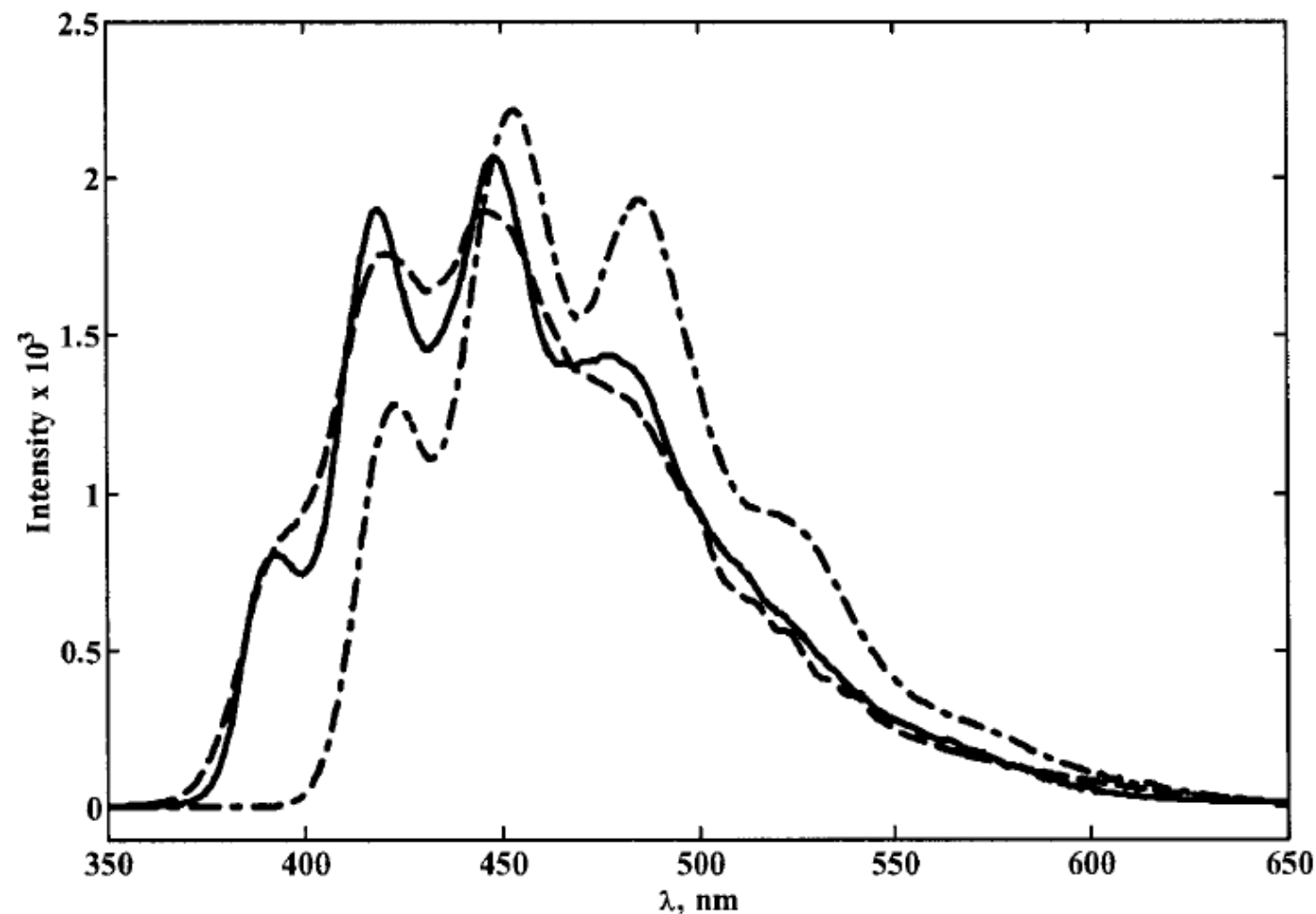
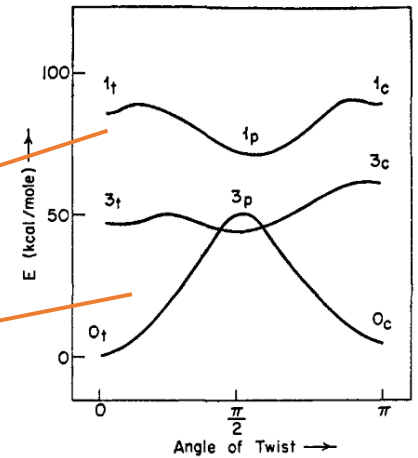
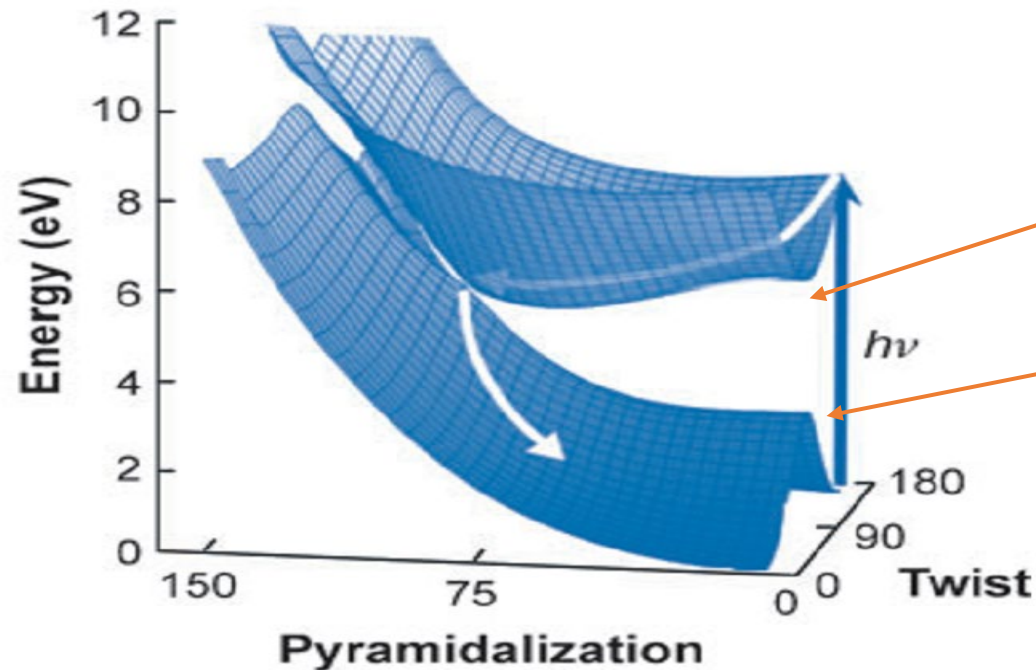
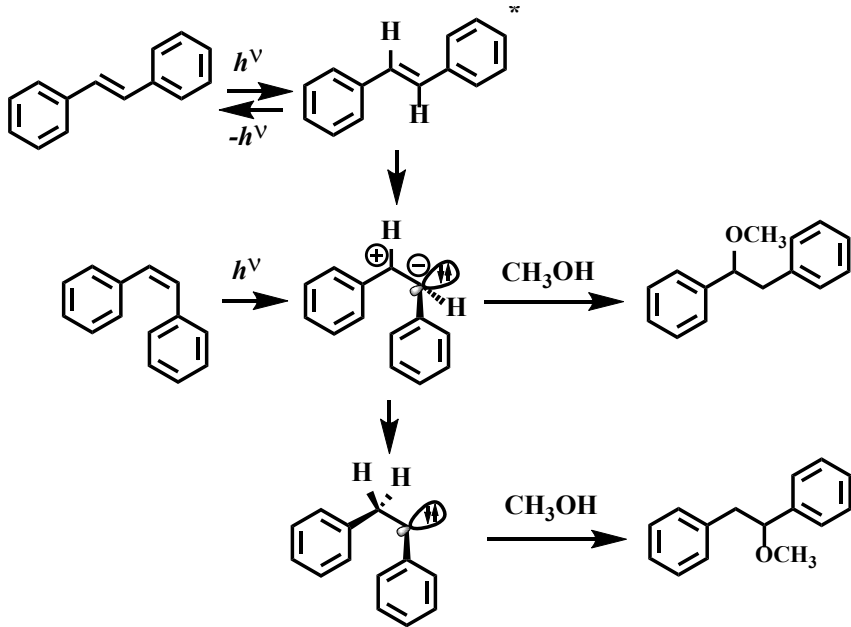


Figure 9. Emission spectra of benzophenone in CCl₄ corrected for nonlinearity in instrumental response and normalized to unit area: phosphorescence (dashed–dotted line), delayed fluorescence (solid line), and prompt fluorescence (dashed line). The first two spectra are obtained by extrapolation of the 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 $\lambda_{\text{exc}} = 326$ nm.

Multidimensional Isomerization – Conical Intersections – Trapping Twisted Intermediates

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



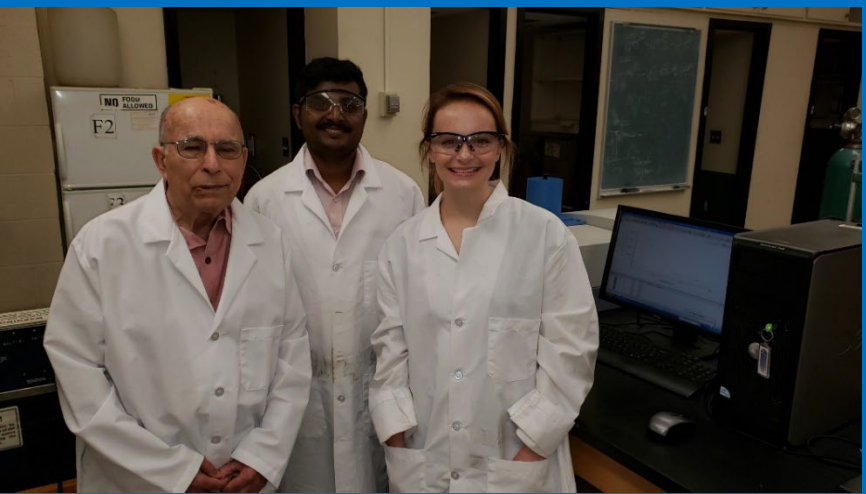
Saltiel, J.; Gupta, S. Photochemistry of the Stilbenes in Methanol. Trapping the Common Phantom Singlet State. *J. Phys. Chem. A* **2018**, *122*, 6089-6099.

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



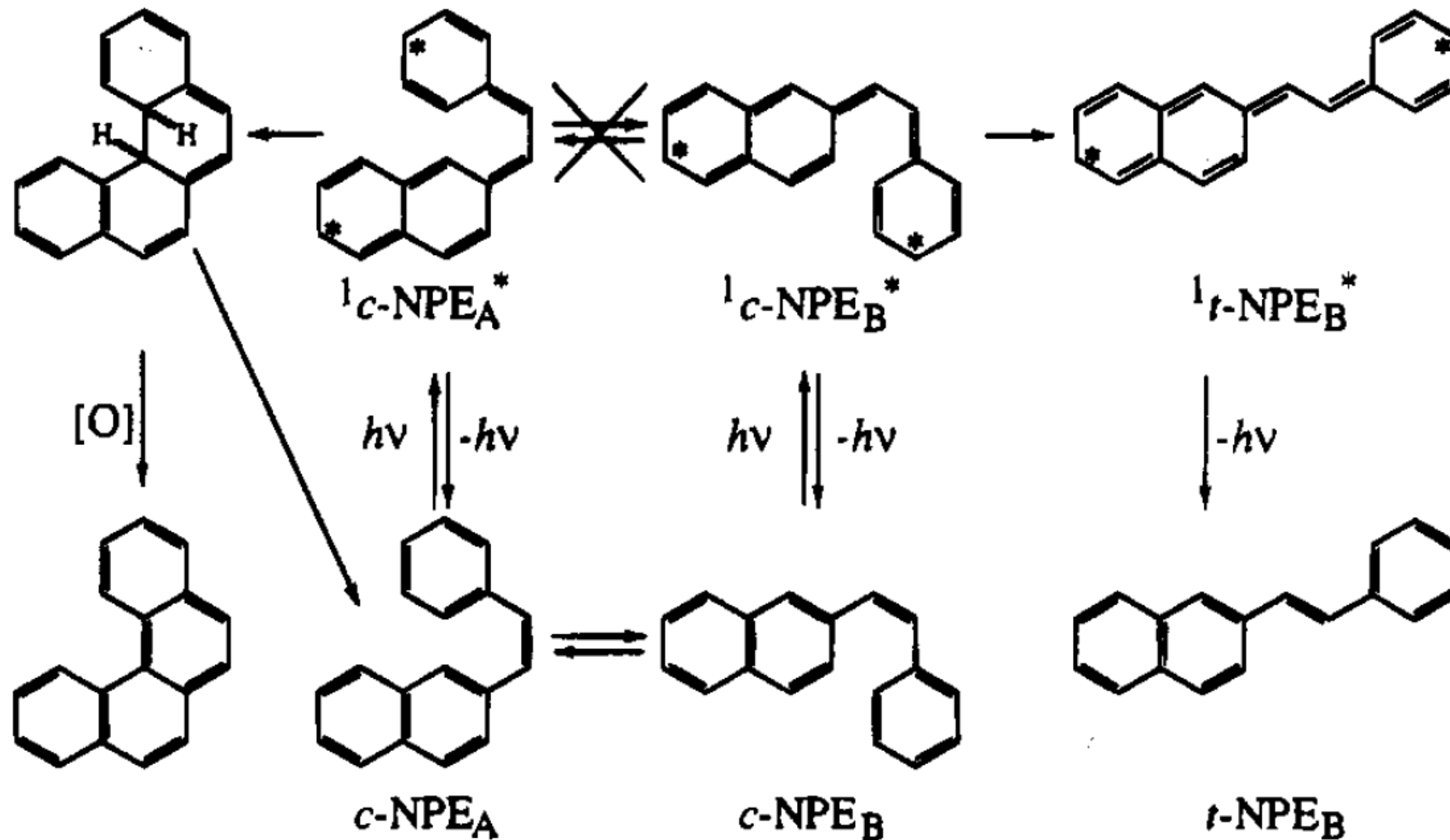


Acknowledgments

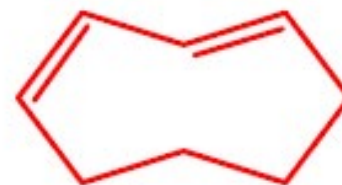
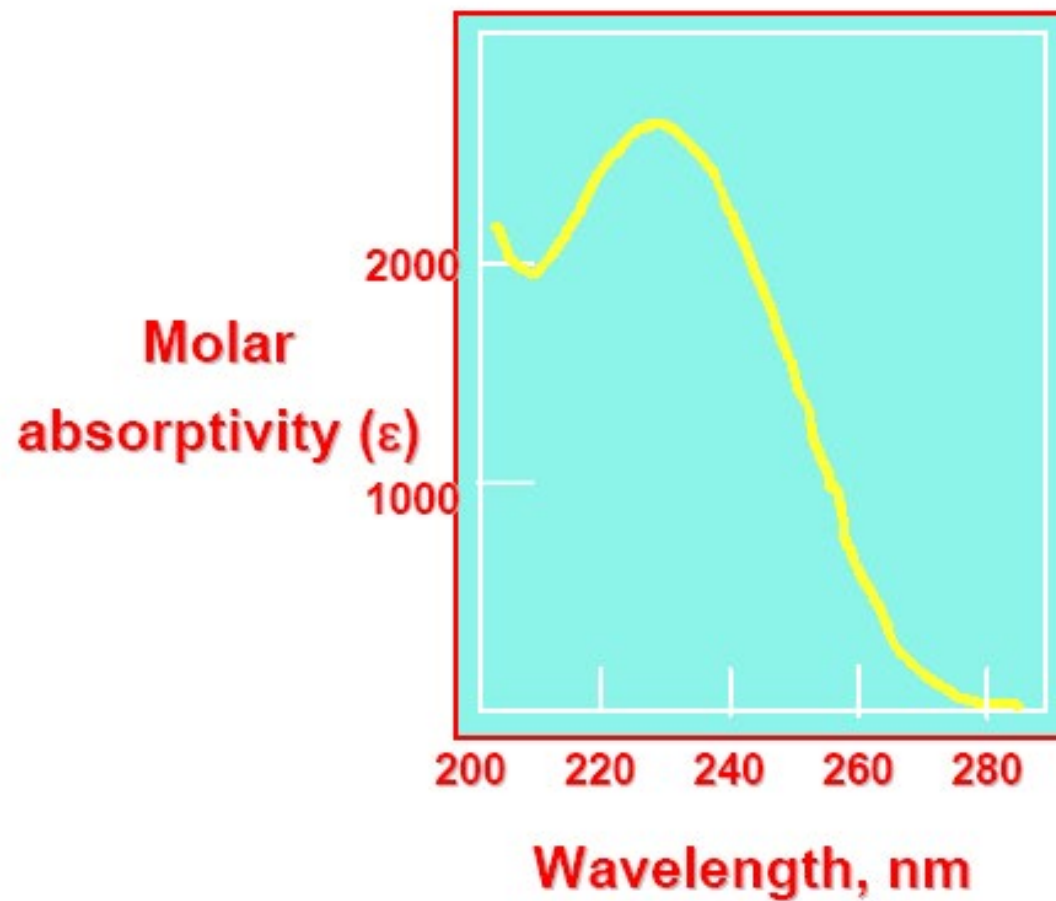


PCA-SM
C. Redwood
L. Zimanyi
Experimental
Gosia Bayda,
Shipra Gupta
Sumesh Krishnan
Support
NSF (1965-2020)

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



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



λ_{\max} 230 nm

ϵ_{\max} 2630

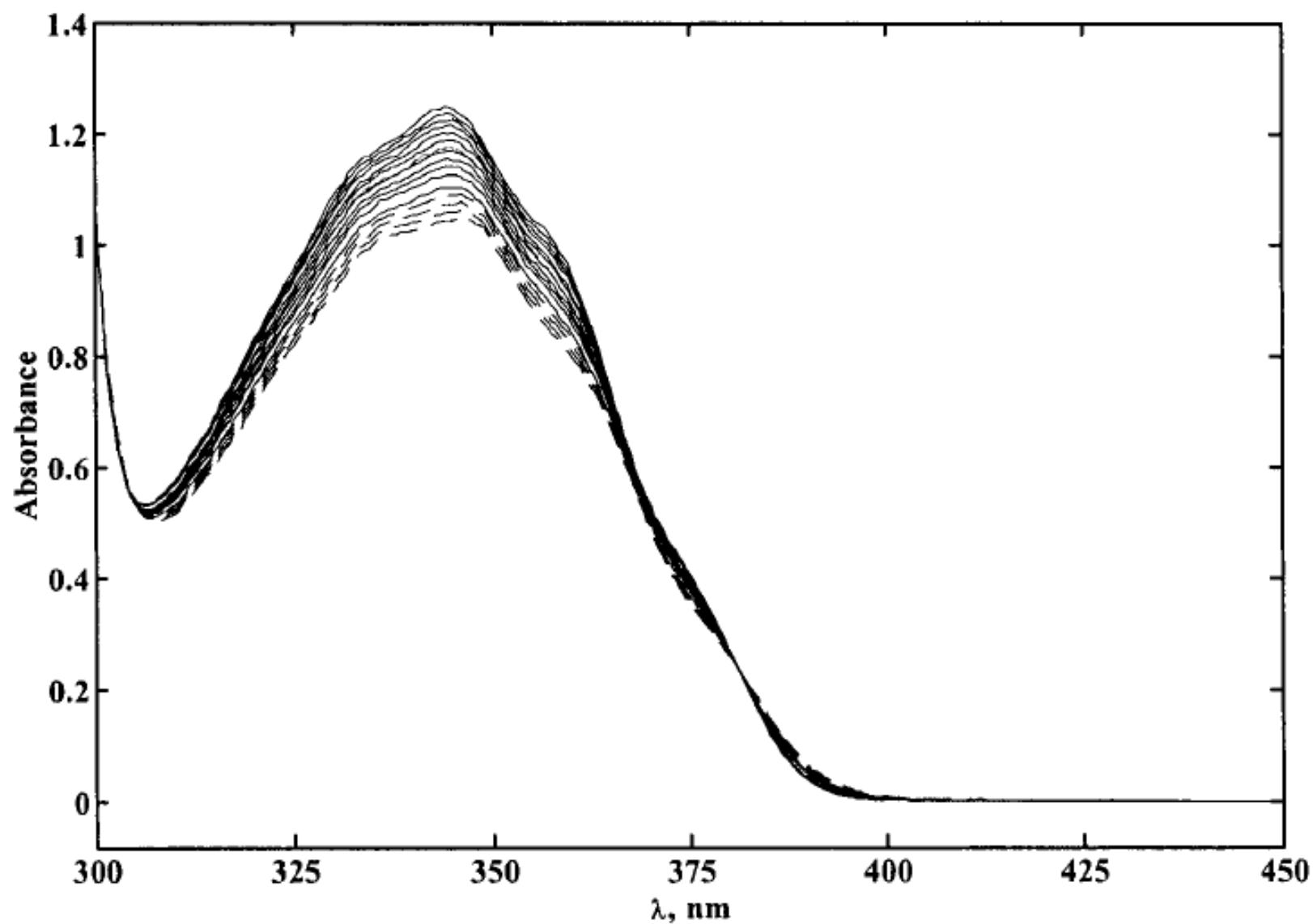
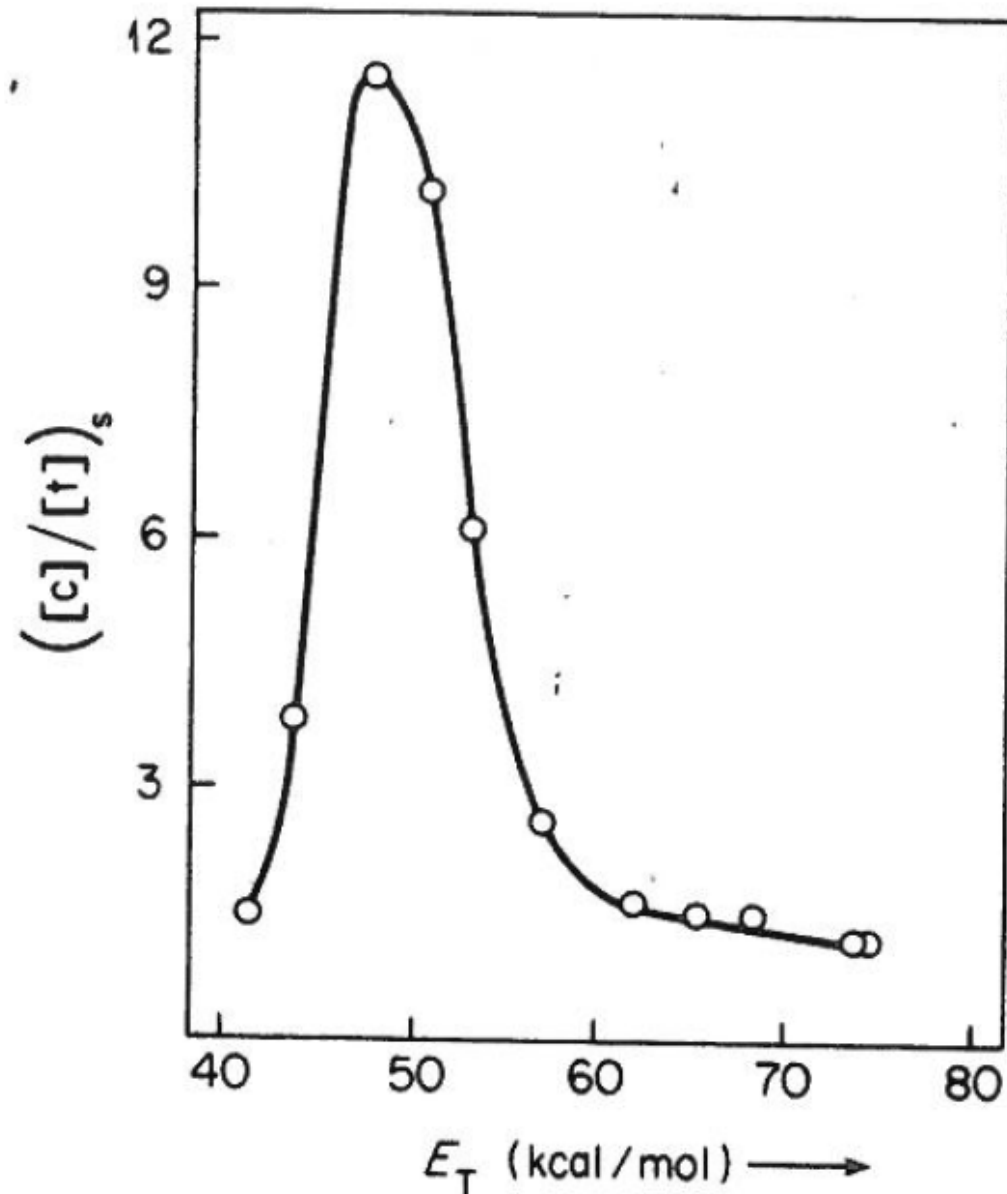


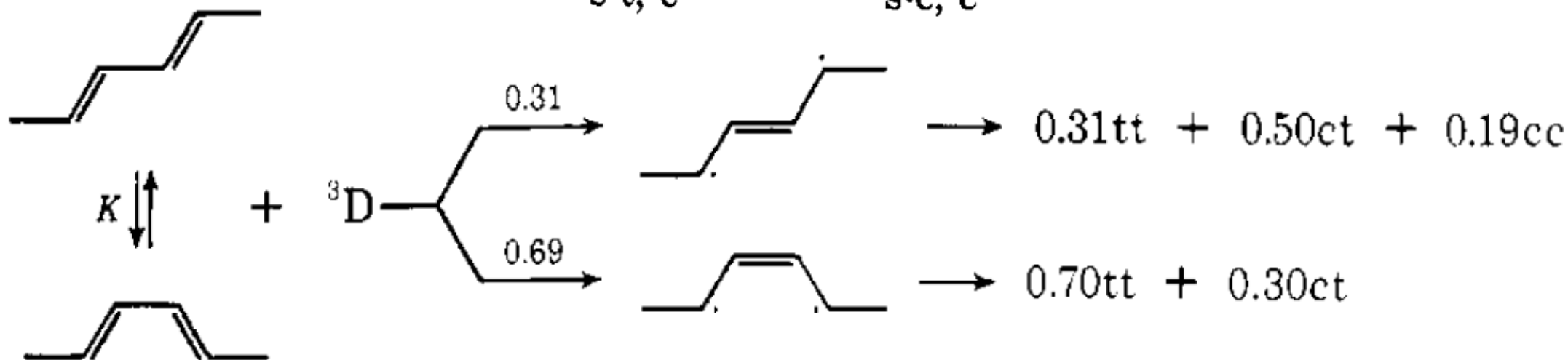
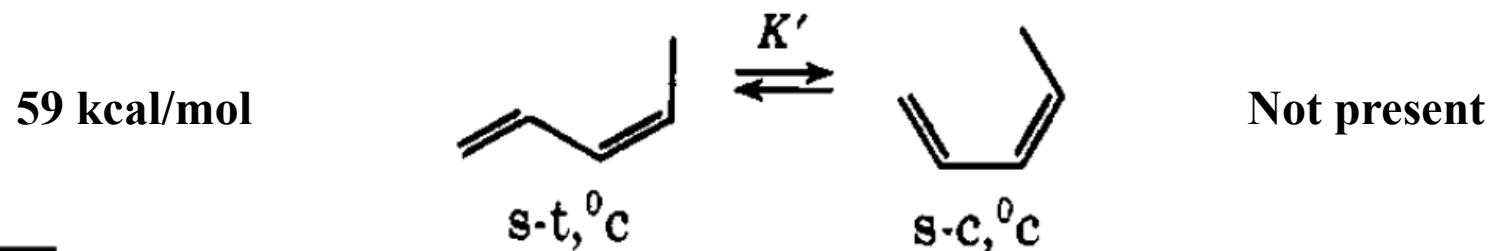
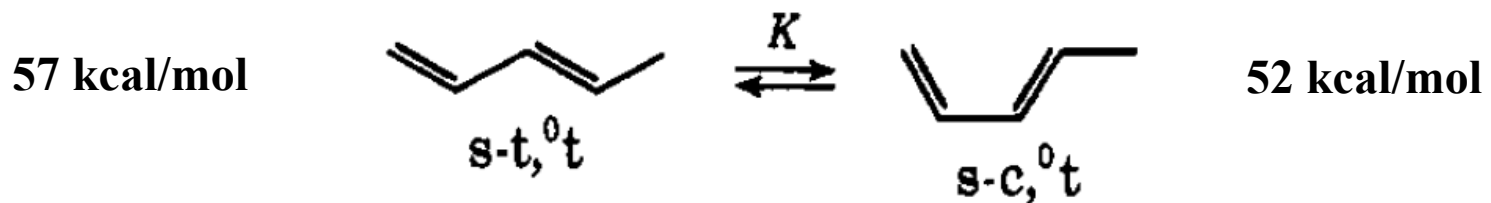
Figure 2. Temperature dependence of the n, π^* absorption spectrum of a 0.0093 M benzophenone solution in CCl_4 : experimental spectra (14.7–68.1 °C), solid lines; extrapolated spectra (73.5–88.5 °C), dashed lines (see the Supporting Information).

The Saitel Plot for Stilbene Triplet Photoisomerization



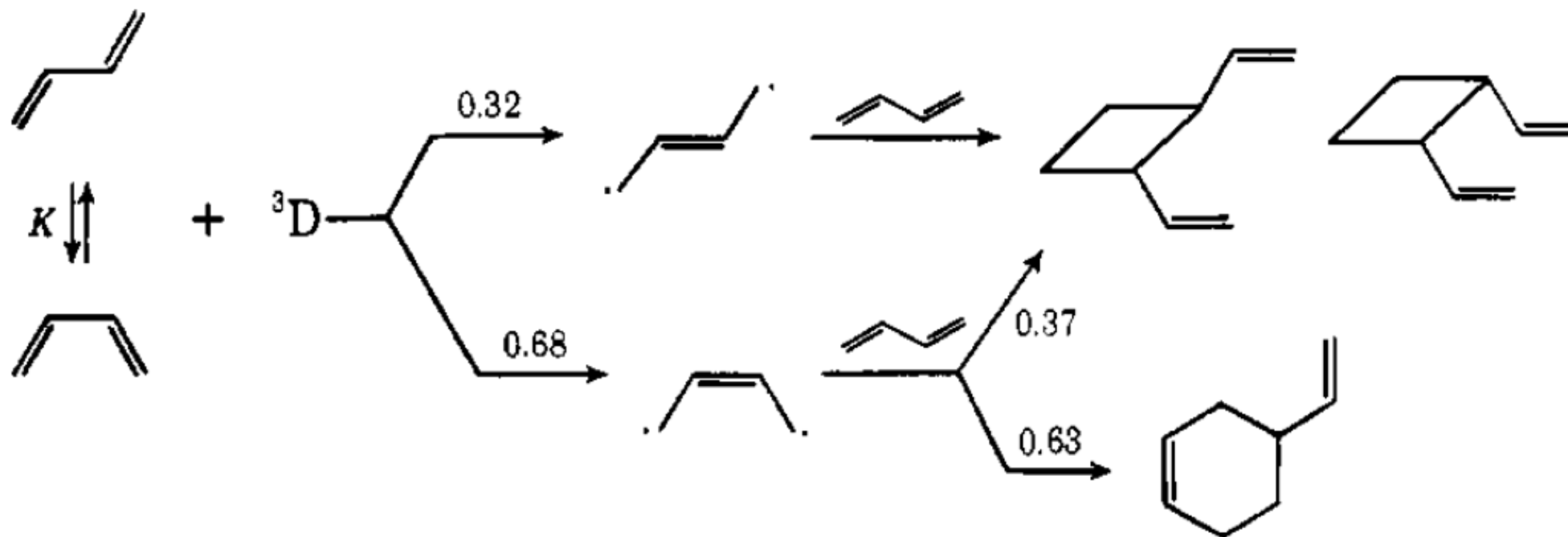
1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized photoisomerization

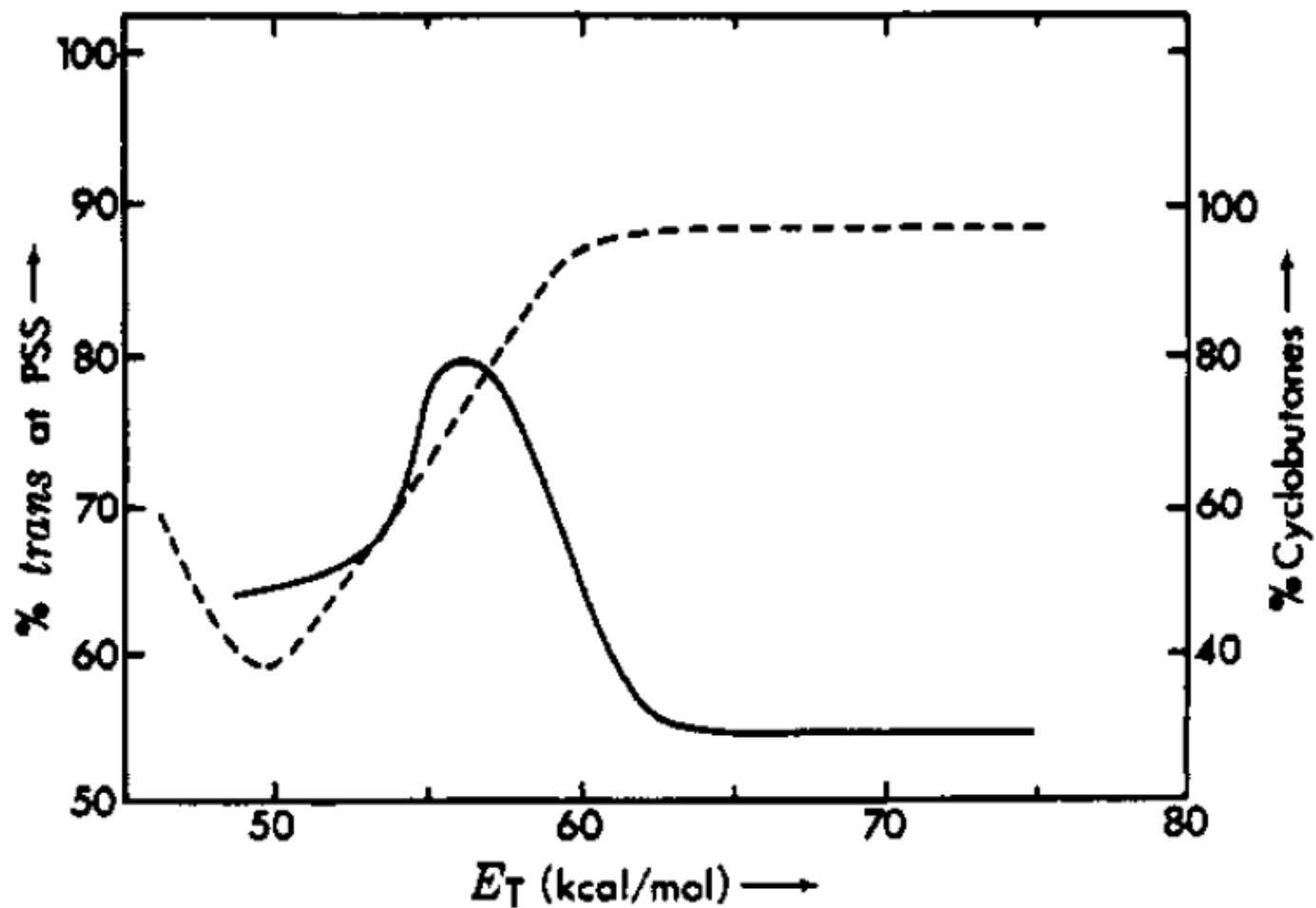


1,3-Diene Triplets: Conformer Specific Photoisomerization and Photodimerization

Fluorenone sensitized dimerization



Saltiel Plots



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

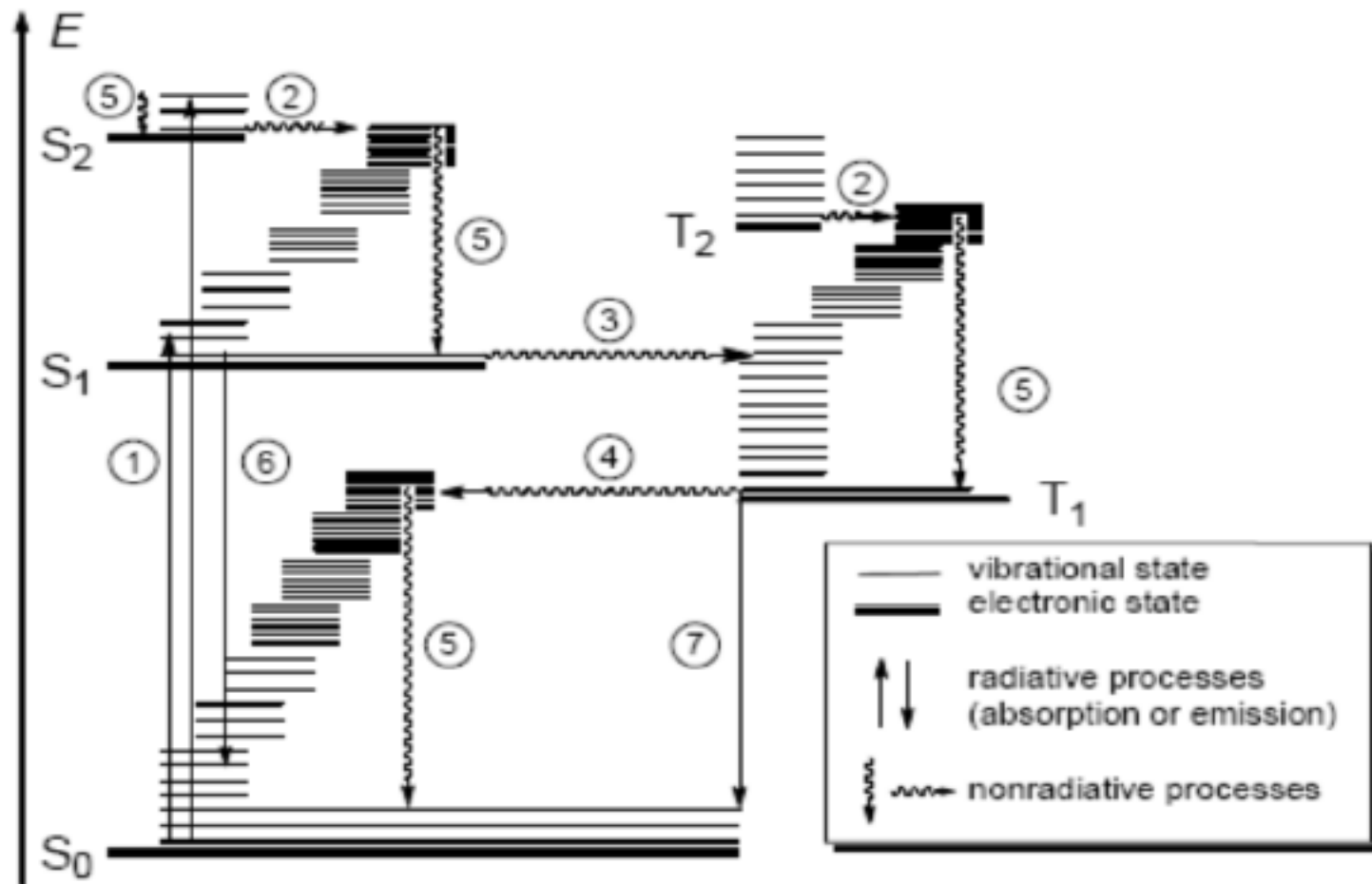


Figure 2-1. State diagram (commonly called Jablonski diagram) depicting molecular states and photophysical processes. The vertical position of thick horizontal lines represents the electronic energy minimum. Vibrational energy levels are shown as thin lines. The width of the horizontal lines and their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

