PC VIII: Femtochemistry and/or Photochemistry

Organization

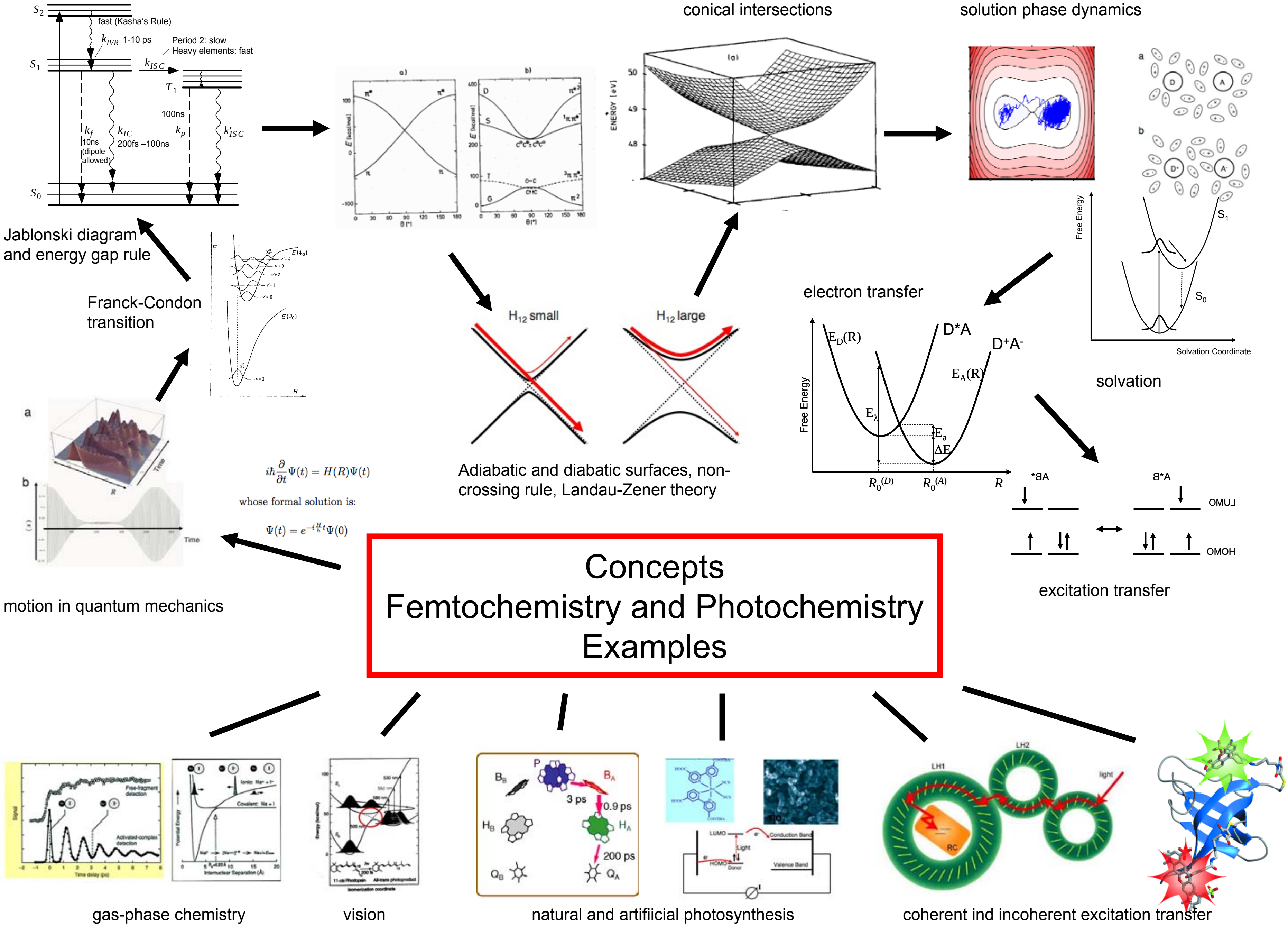
Physikalische Chemie VIII: Spektroskopie II

- Some exercises with *Mathematica*
- Exercises 2 weeks
- Debriefing: Thursday 8.00-10.00 in room 34-K-01 or 13K24 (through 13 K 26), every second week, start Oct. 4
- Return exercises Wednesday before 12.00
- Computer-Exam
- Script (password PCseven7)

Tutor: Fivos Perakis 34 K 30

Femtochemistry: Basic Concepts

- Examples of Photochemical Reactions
- Experimental Methods
- Motion in Quantum Mechanics: Wavepackets
- Franck-Condon Transition
- Jablonski Diagram, Fermi Golden Rule, Energy Gap Law
- Prototype Potential Energy Surfaces
- Non-Crossing Rule, Avoided Crossings, Conical Intersections
- Born Oppenheimer Approximation and its Breakdown
- Adiabatic and Diabatic Surfaces
- Mixed Quantum-Classical Methods, Landau Zener Theory
- Solvation
- Electron Transfer Theory
- Excitation Transfer: Exciton- and Förster Transfer



Jablonski diagram
and energy gap rule
Franck-Condon
transition
motion in quantum mechanics
$i\hbar\frac{\partial}{\partial t}\Psi(t) = H(R)\Psi(t)$
whose formal solution is:
$\Psi(t) = e^{-i\frac{H}{\hbar}t}\Psi(0)$
H_{12} small
H_{12} large
Adiabatic and diabatic surfaces, non-crossing rule, Landau-Zener theory
conical intersections
solution phase dynamics
electron transfer
solvation
excitation transfer
Concepts
Femtochemistry and Photochemistry
Examples
gas-phase chemistry
vision
natural and artifiicial photosynthesis
coherent ind incoherent excitation transfer

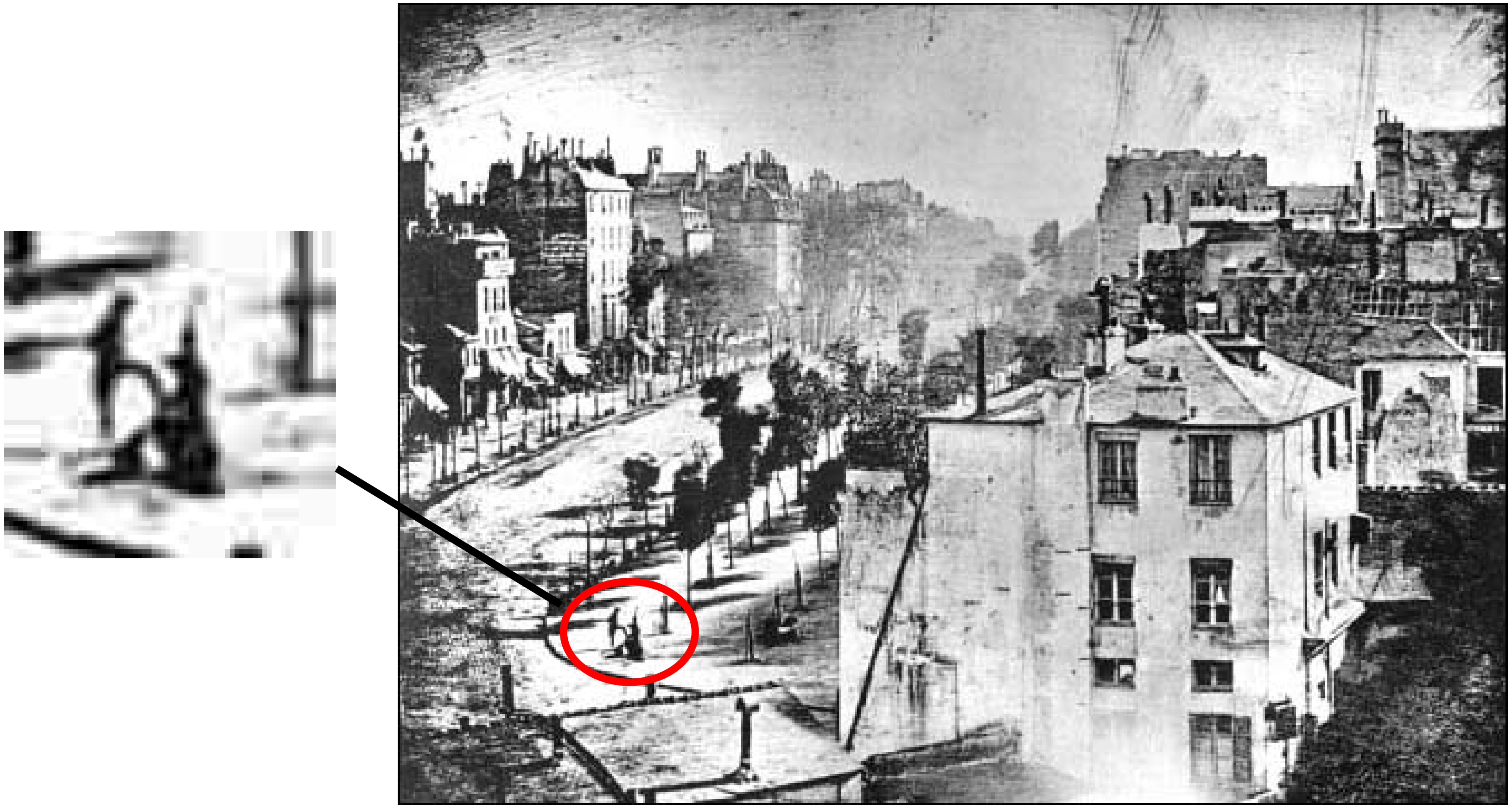
Femtochemistry

Nobel Prize 1999

Ahmed Zewail

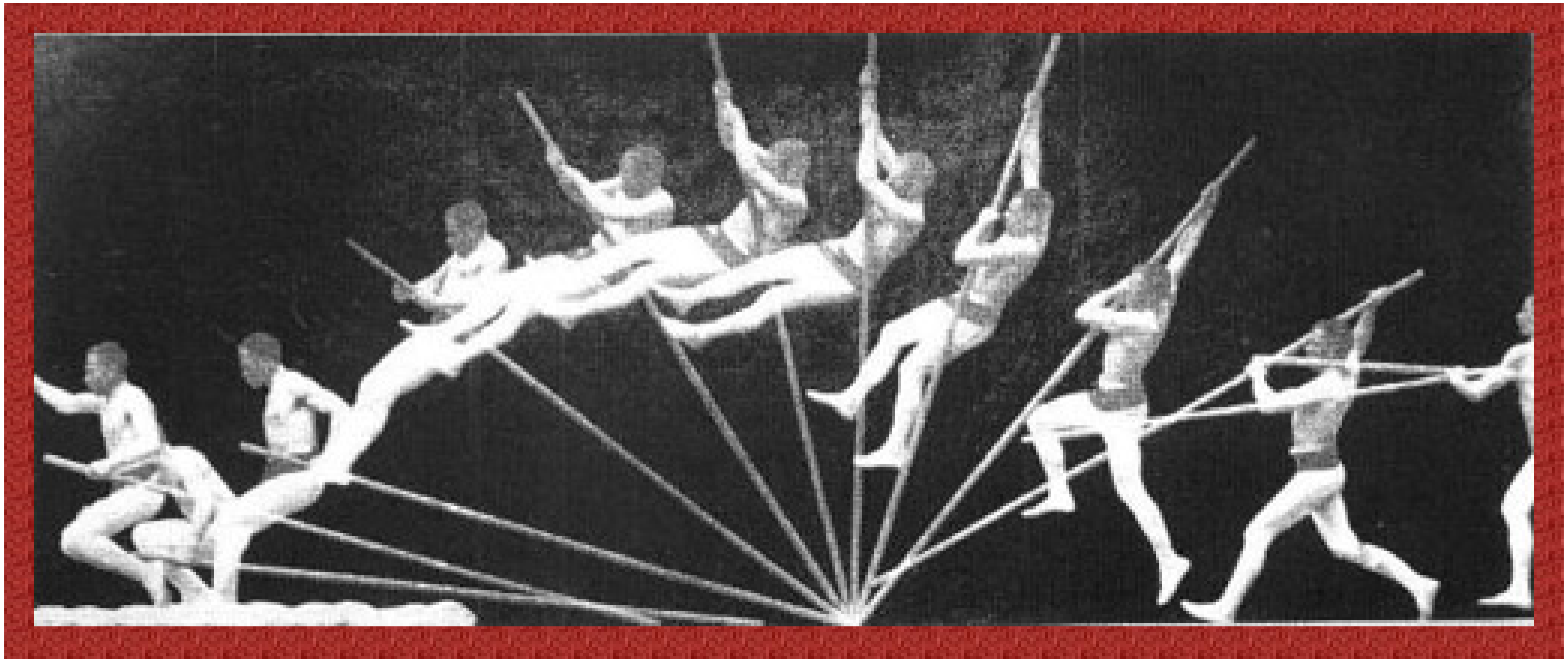
The First Time-Resolved Photo

Louis Jacques Mande Daguerre, 1839
Exposure Time: 10-20 min



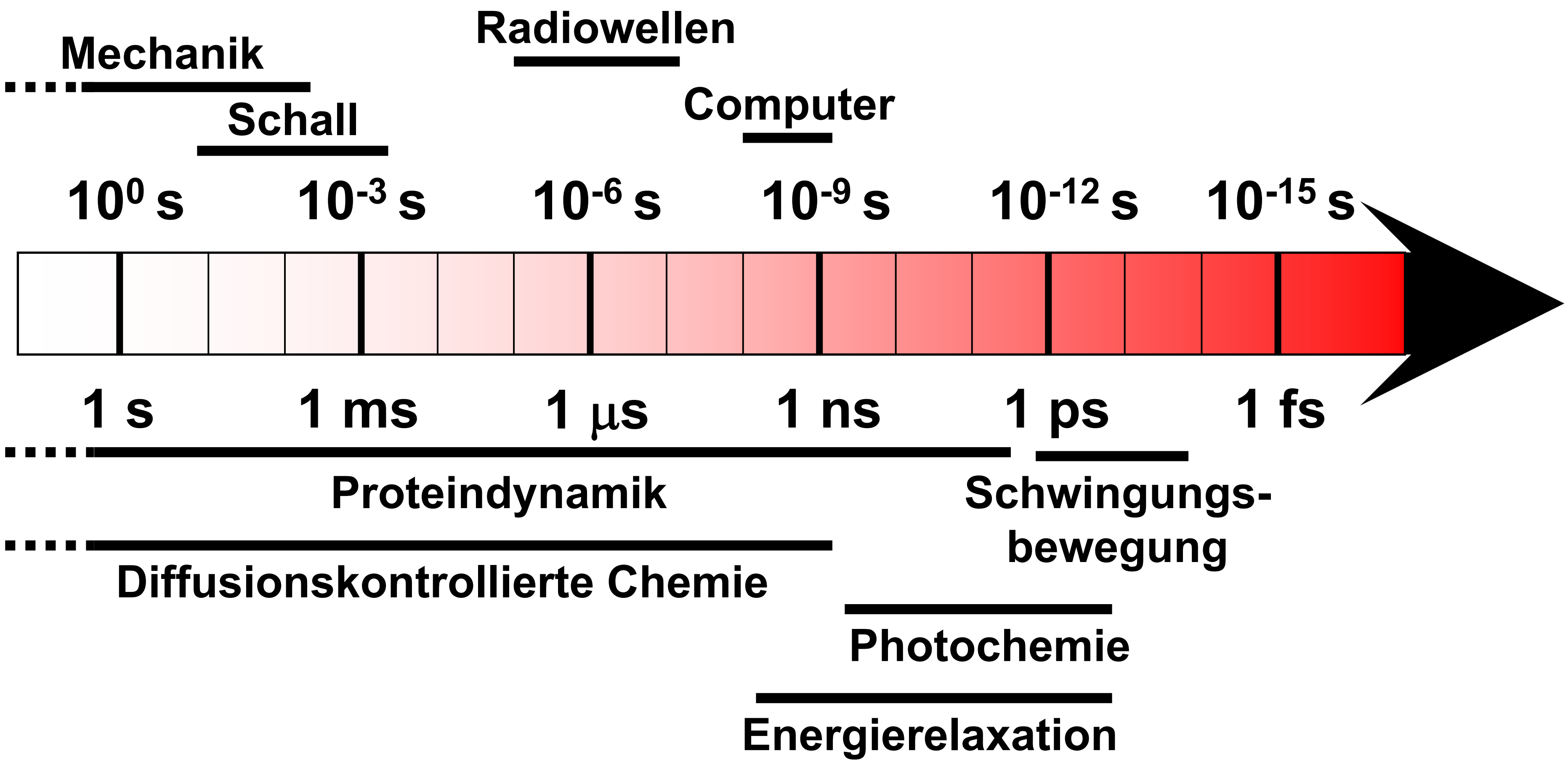
http://www.rleggat.com/photohistory/history/daguerr.htm

Stroboskop



Zeitauflösung: 1 ms
ca. 1880

Zeitpfeil

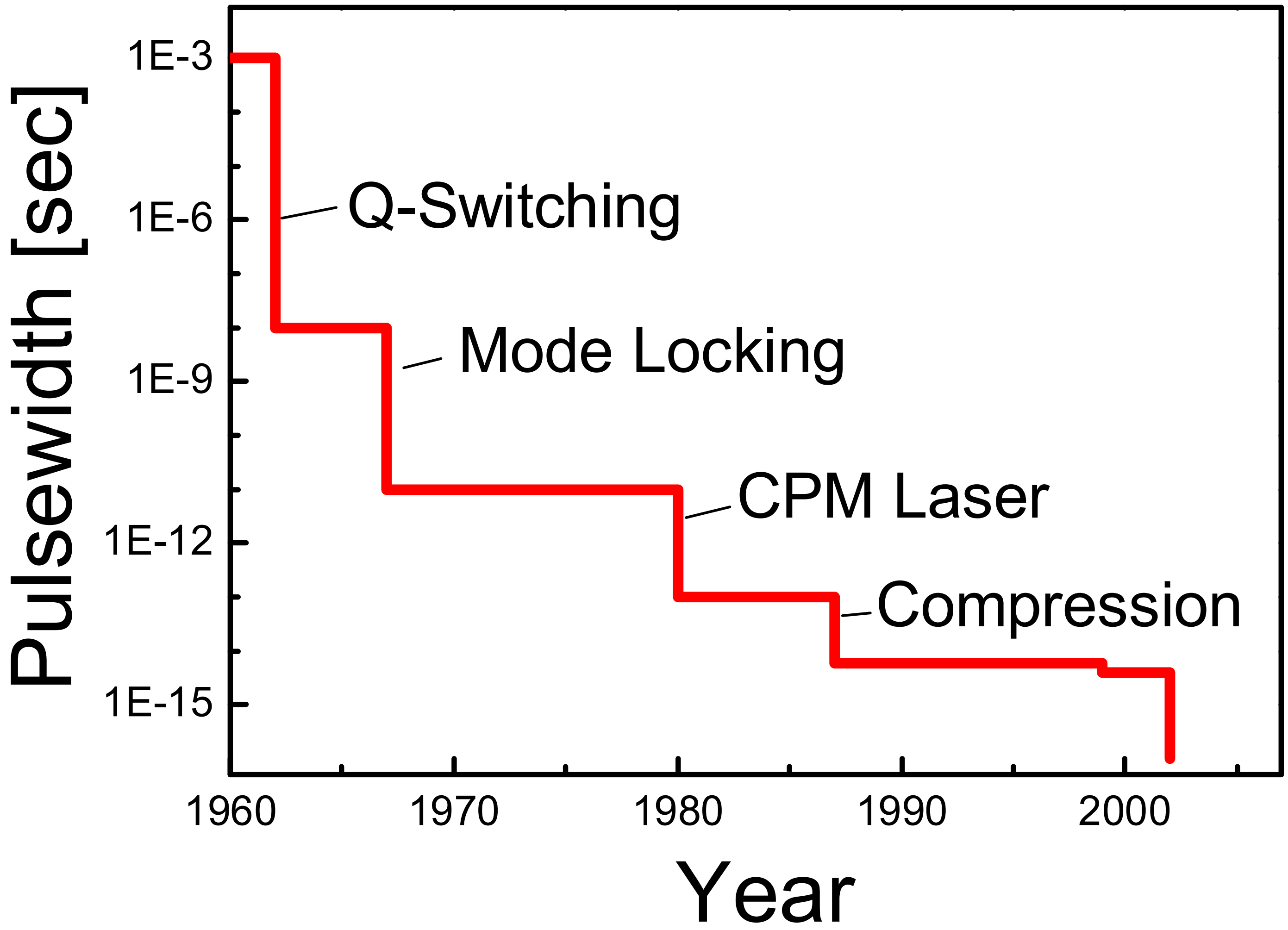


Radiowellen
Mechanik
Computer
Schall
10^{0} s
10^{-3} s
10^{-6} s
10^{-9} s
10^{-12} s
10^{-15} s
1 s
1 ms
1 µs
1 ns
1 ps
1 fs
Proteindynamik
Schwingungs-
bewegung
Diffusionskontrollierte Chemie
Photochemie
Energierelaxation

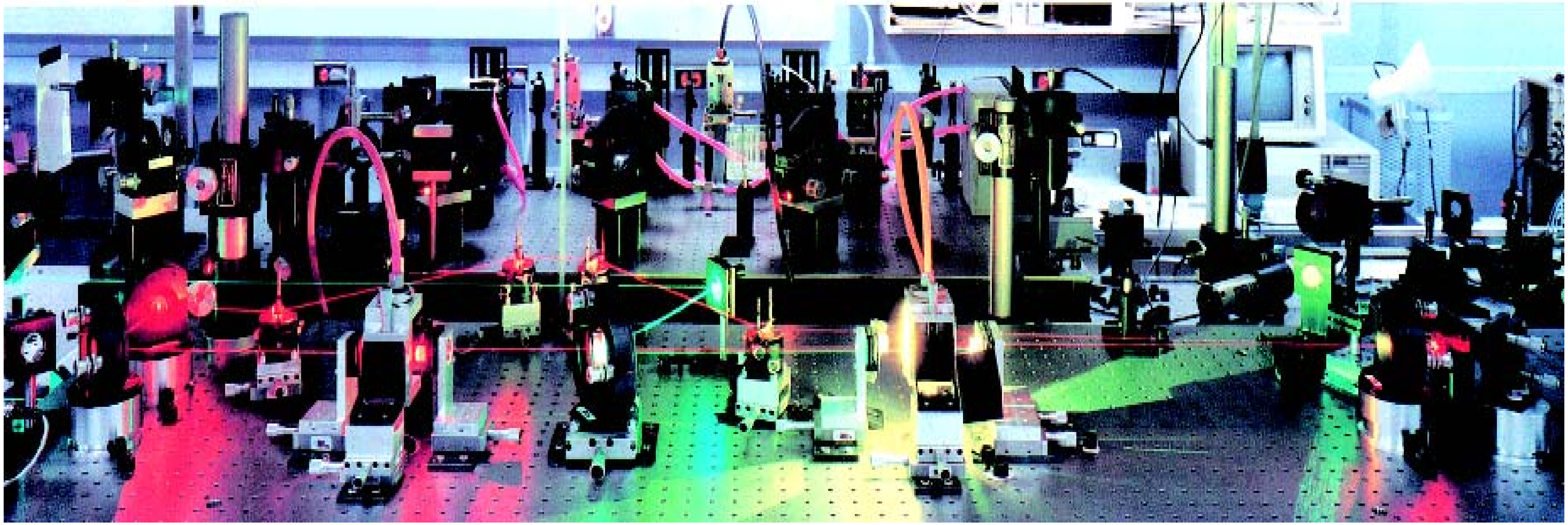
100 Femtosekunden

Lichtgeschwindigkeit: 300.000 km/s	
1 s:	**Erde → Mond**
8 min:	**Erde → Sonne**
100 fs:	**Dicke eines dünnen Blatt Papiers**

Short Pulses with Lasers

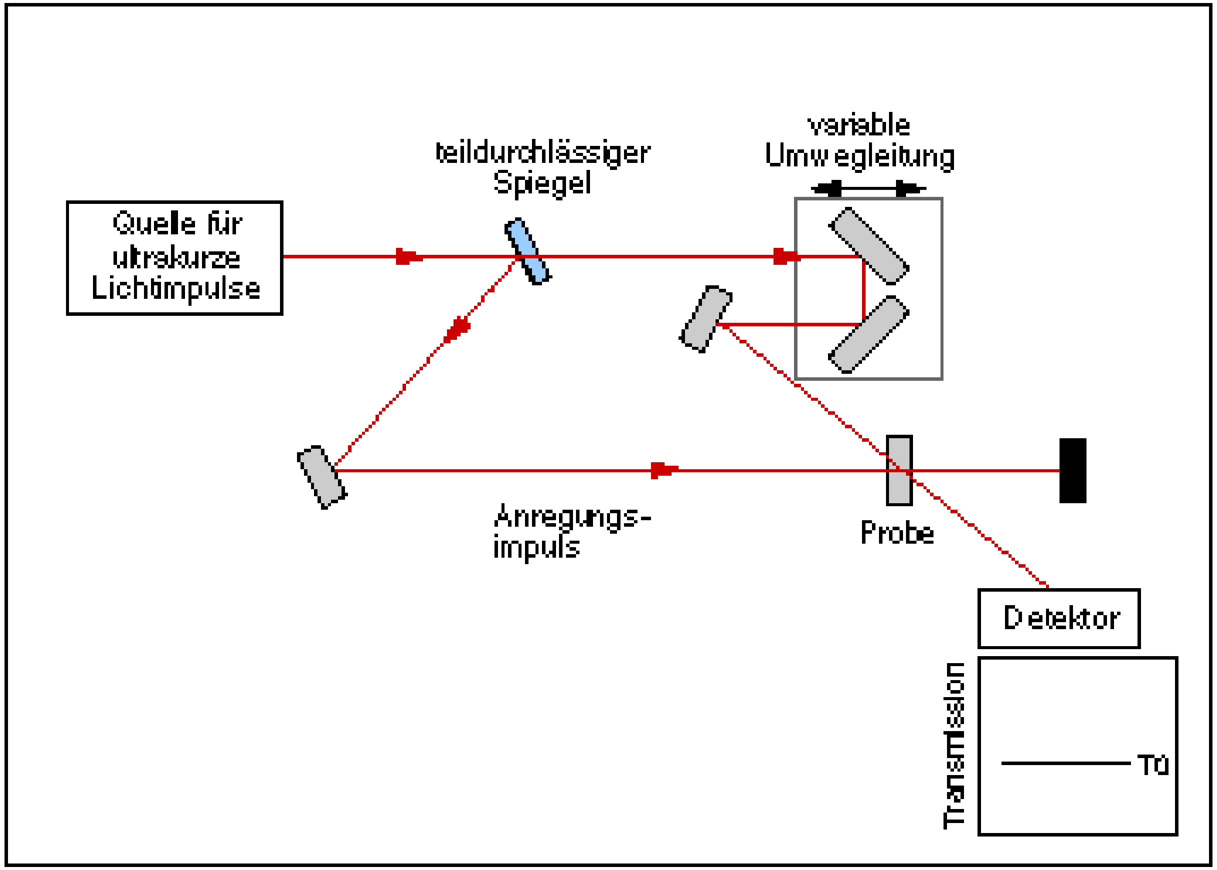


Femtosecond Lasers

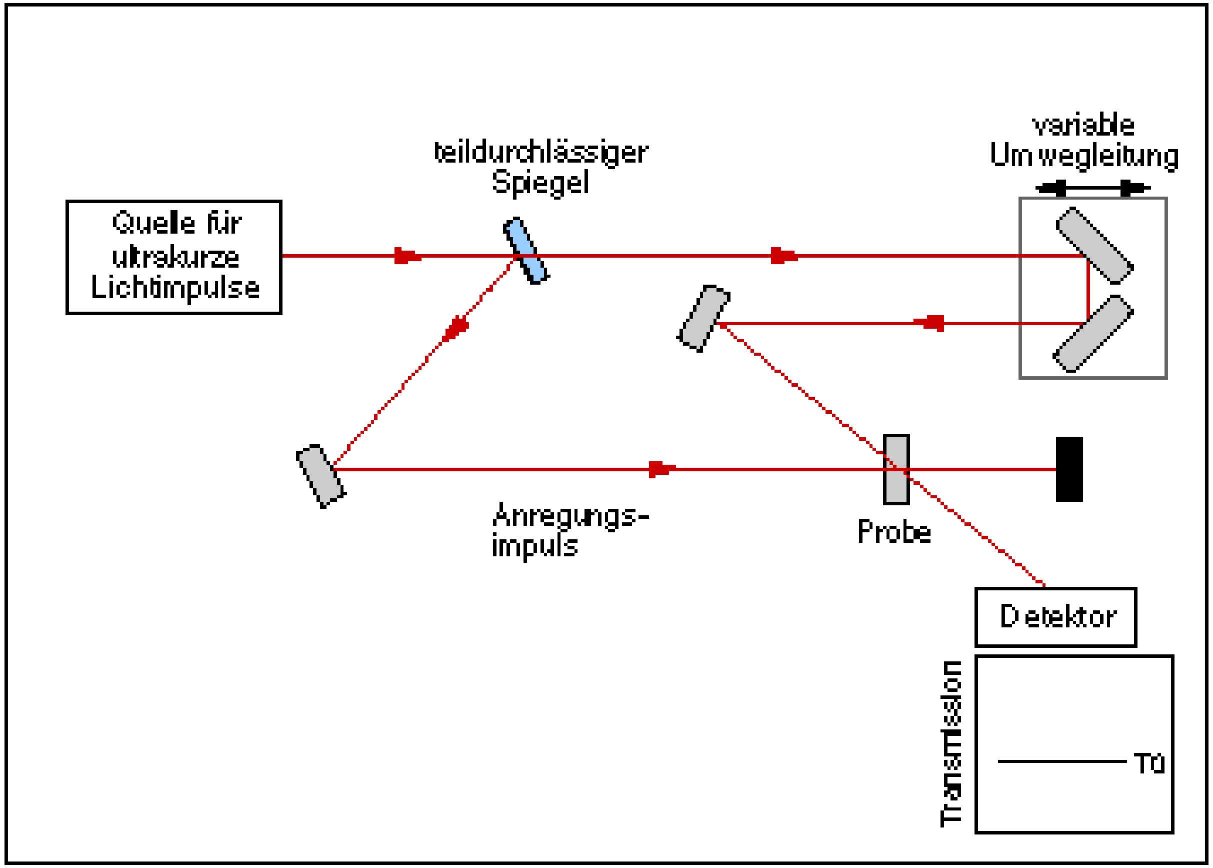


CPM Laser 1980

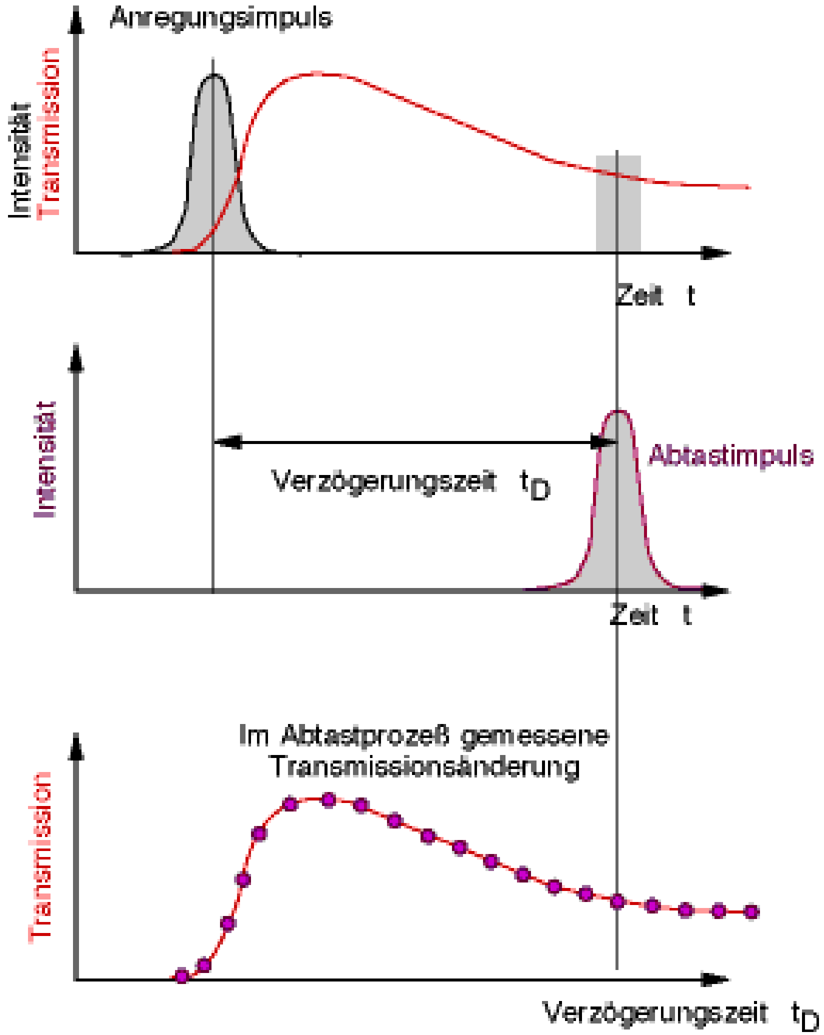
Pump-Probe Spectroscopy



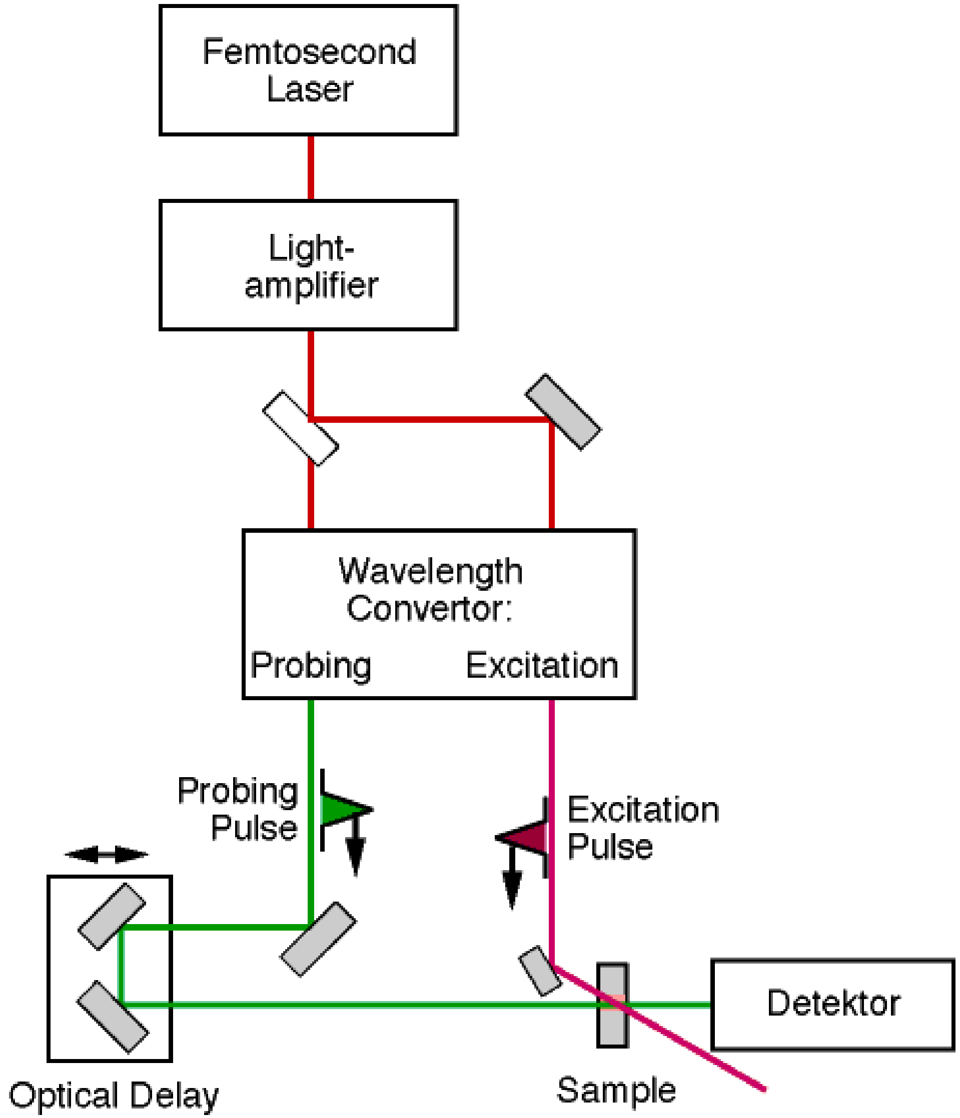
Pump-Probe Spectroscopy



Pump-Probe Spectroscopy



Pump-Probe Spectroscopy



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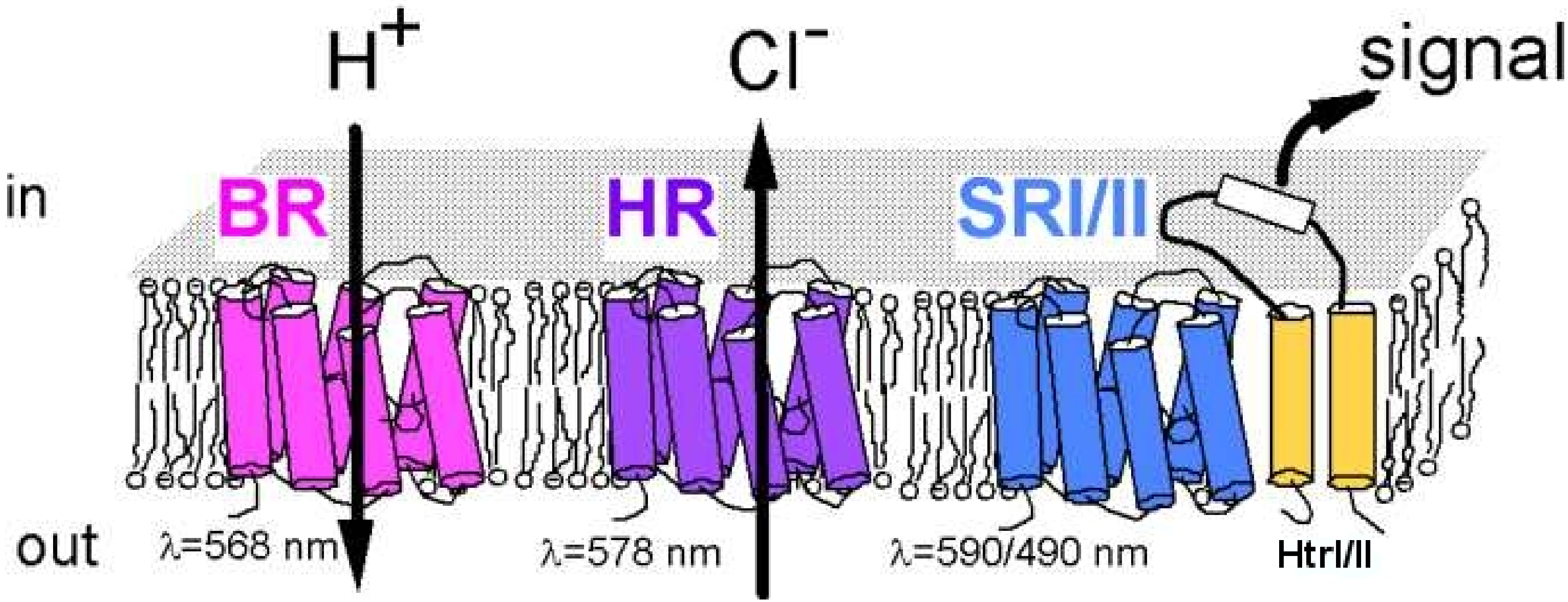
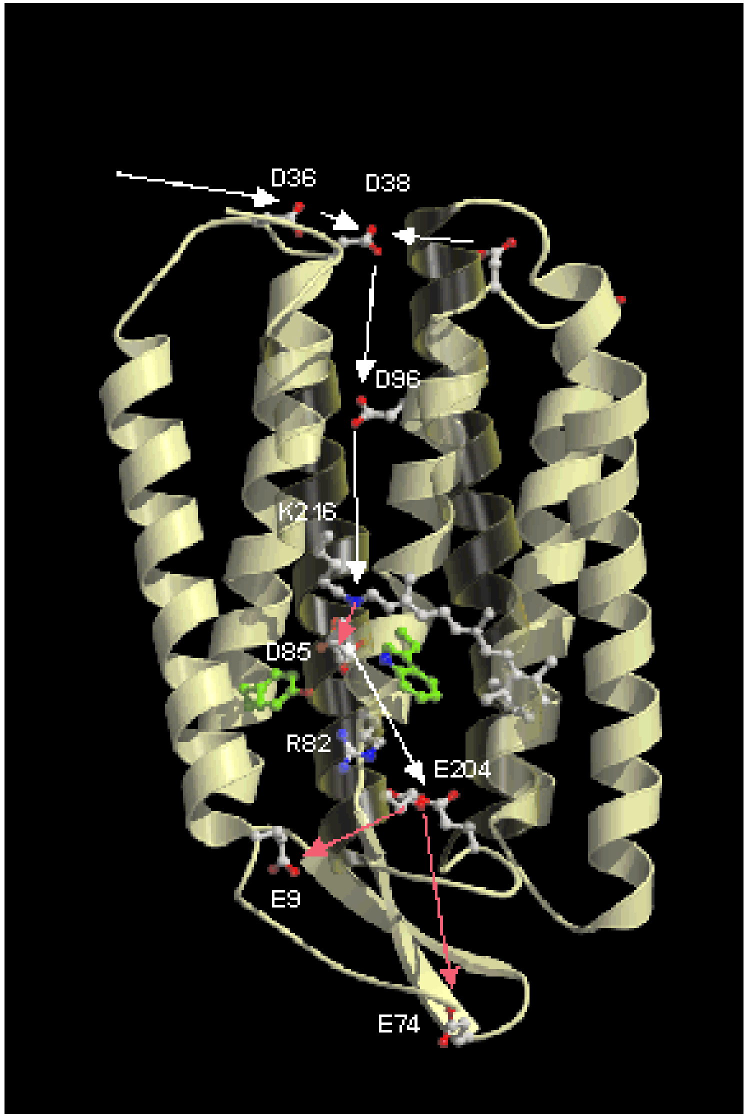
Photochemical Reactions in Nature: Isomerization of Bacteriorhodopsin

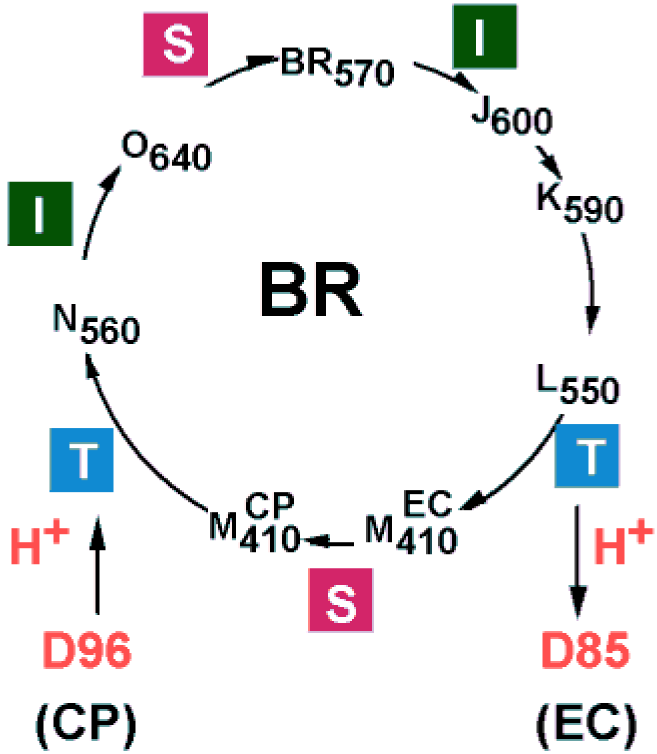
Wikipedia, Halobacteria in the salt lake Chokrak (Ukraine)

Photochemical Reactions in Nature: Isomerization of Bacteriorhodopsin



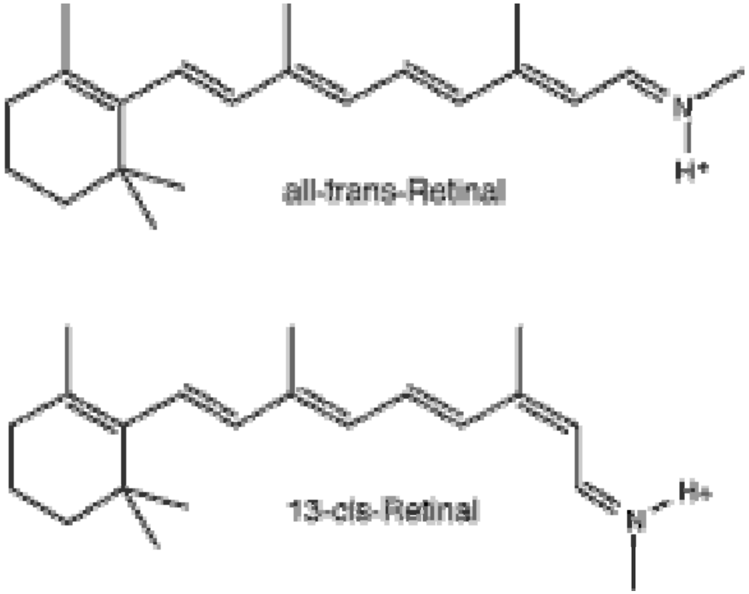
Photochemical Reactions in Nature: Isomerization of Bacteriorhodopsin

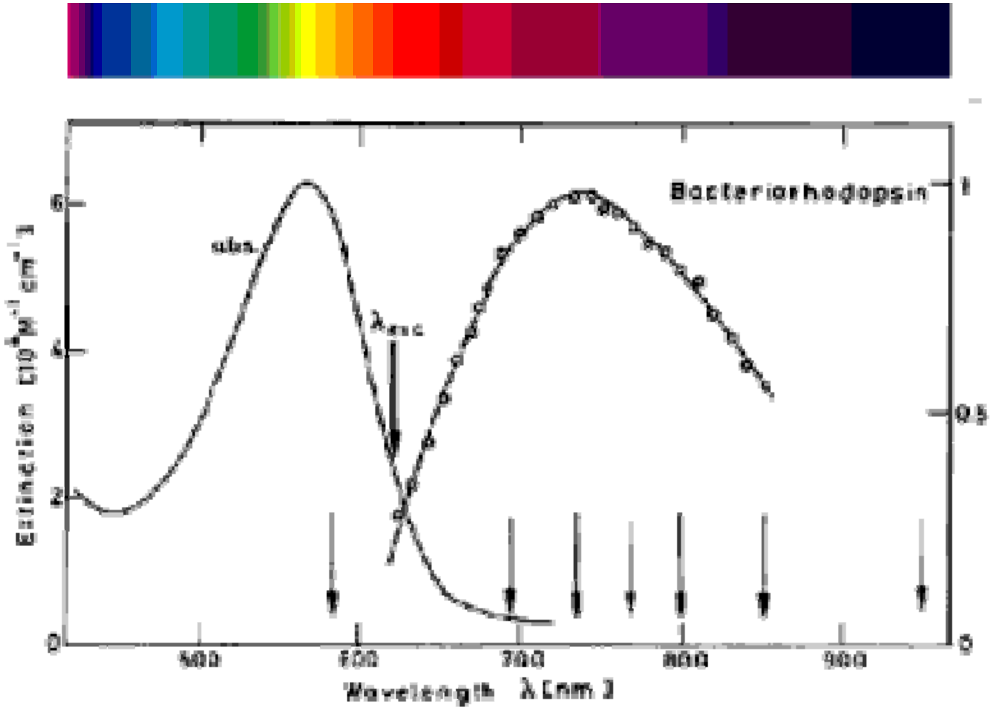




http://www.biochem.mpg.de/oesterhelt/photobiology/br.html

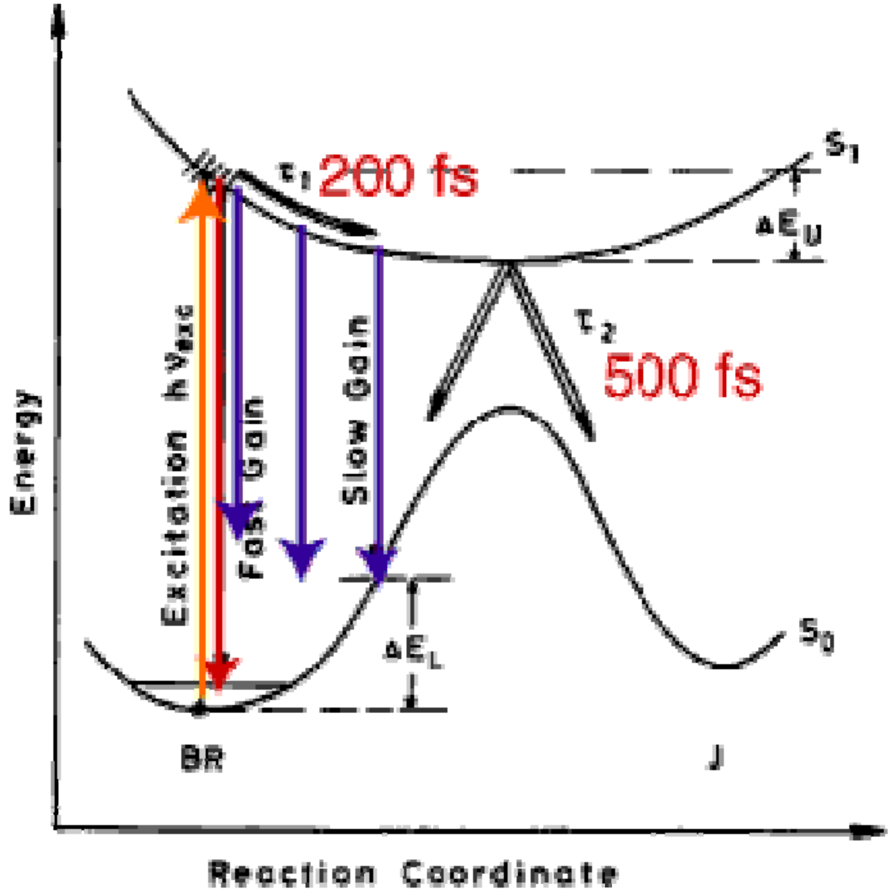
Photochemical Reactions in Nature: Isomerization of Bacteriorhodopsin

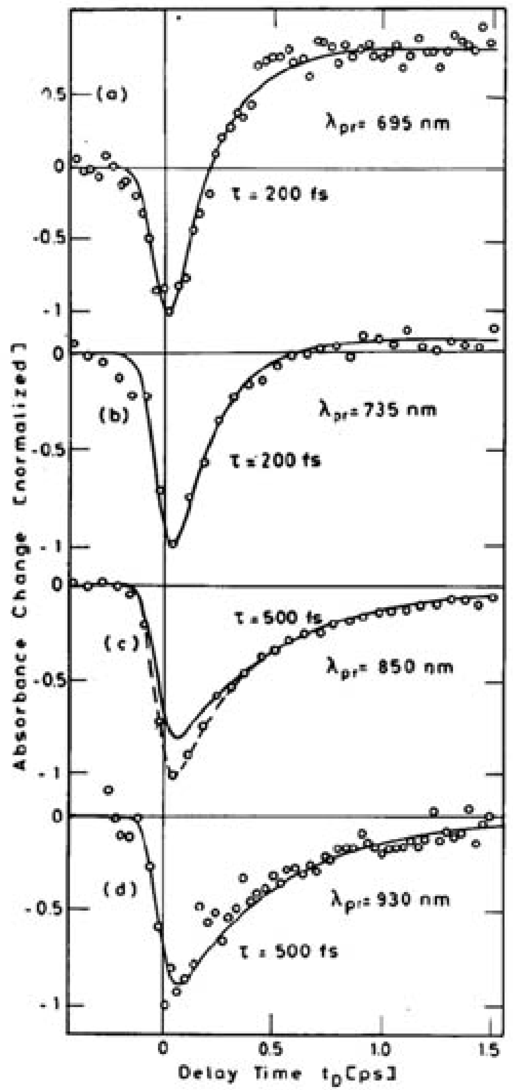




Dobler, W. Zinth, W. Kaiser, D. Oesterhelt *Excited-state reaction dynamics of Bacteriorhodopsin studied by femtosecond spectroscopy.* Chem. Phys. Lett. 144 (Feb. 1988) 215

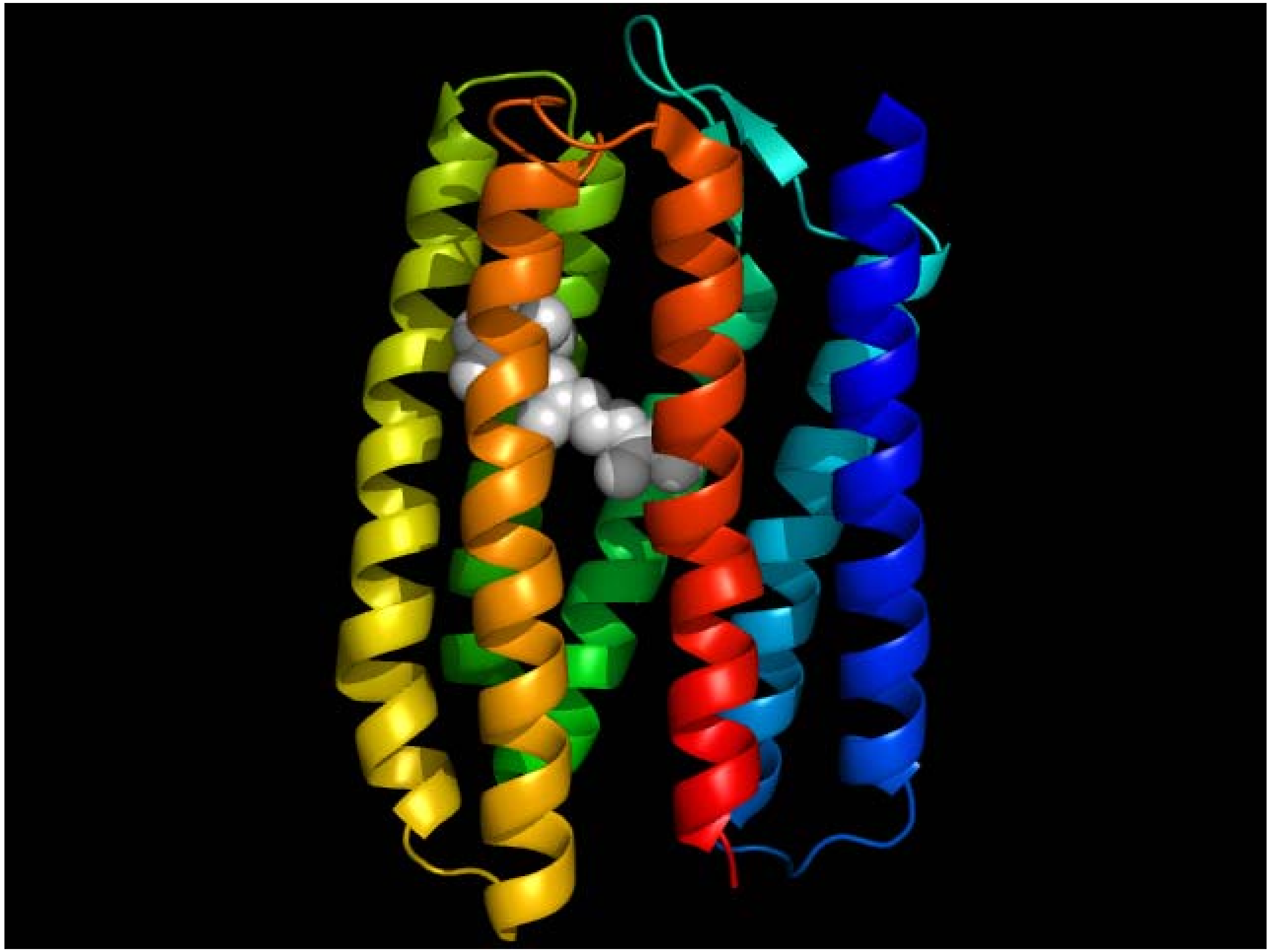
Photochemical Reactions in Nature: Isomerization of Bacteriorhodopsin





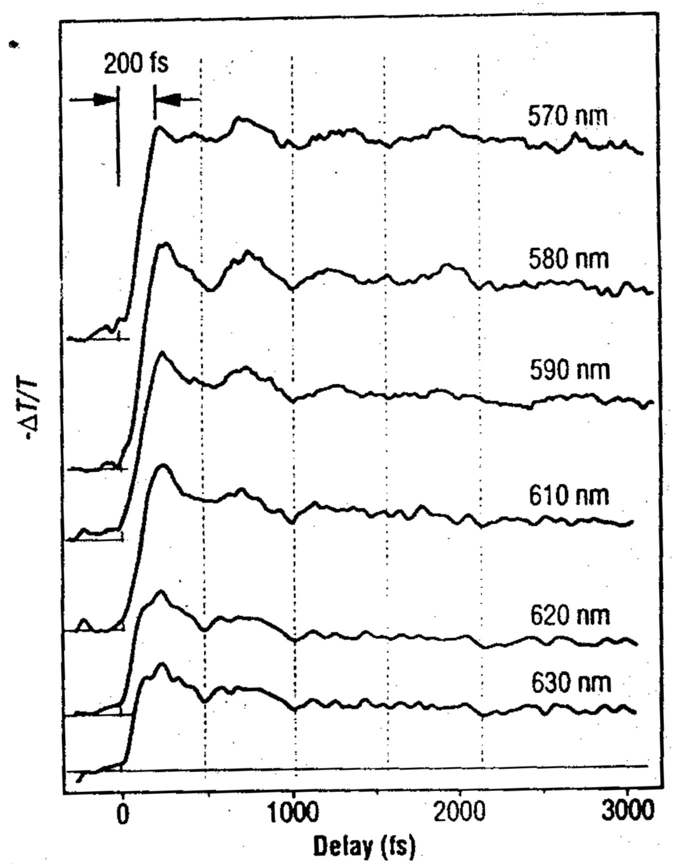
Dobler, W. Zinth, W. Kaiser, D. Oesterhelt *Excited-state reaction dynamics of Bacteriorhodopsin studied by femtosecond spectroscopy.* Chem. Phys. Lett. 144 (Feb. 1988) 215

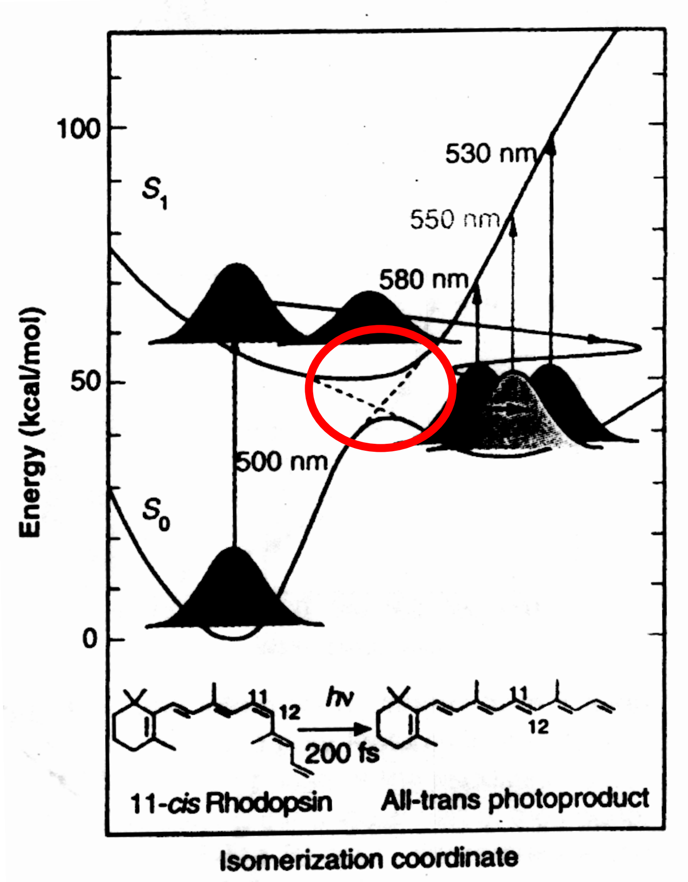
Vision: Isomerization in Rhodopsin



movie

Photochemical Reactions in Nature: Isomerization of Rhodopsin

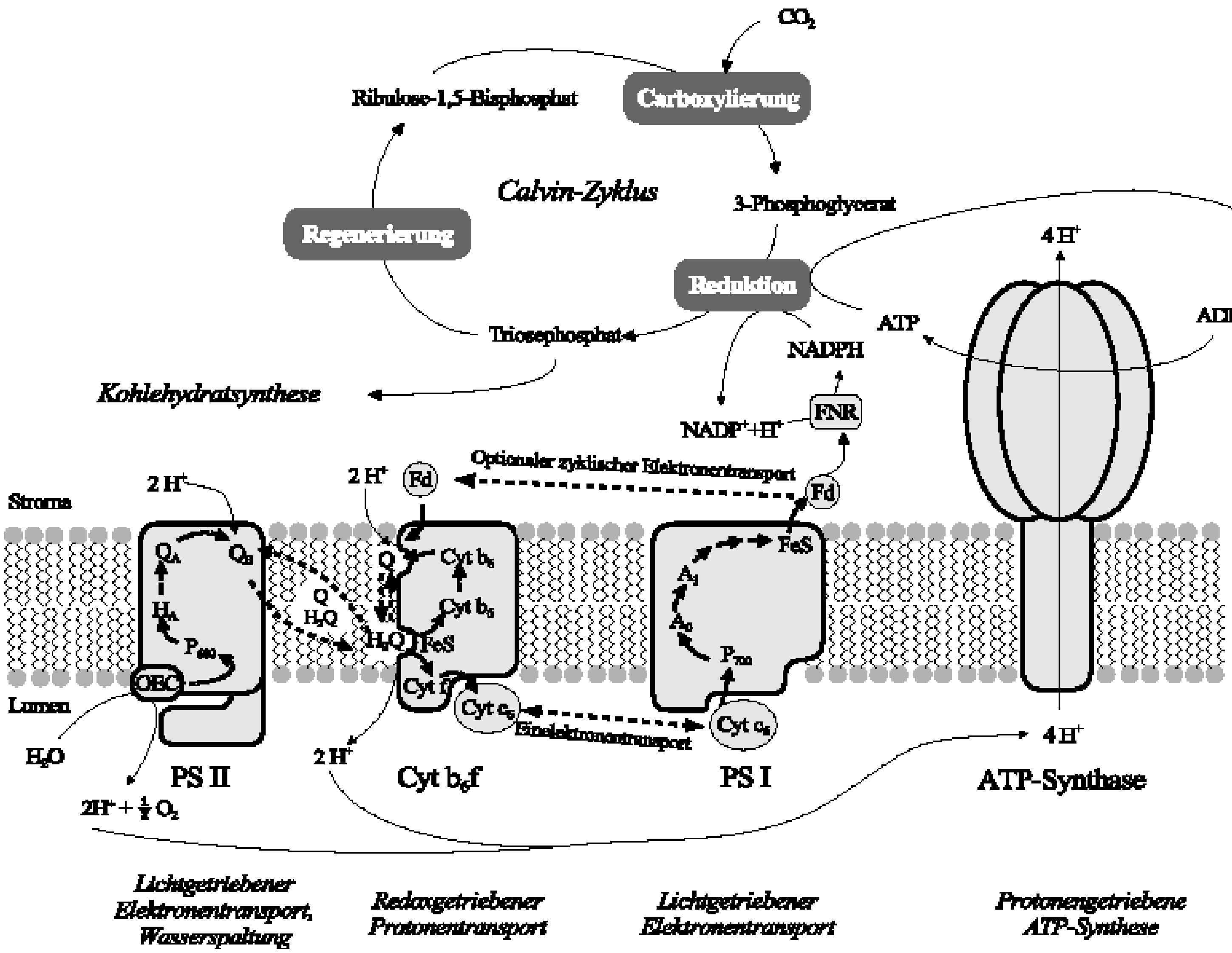




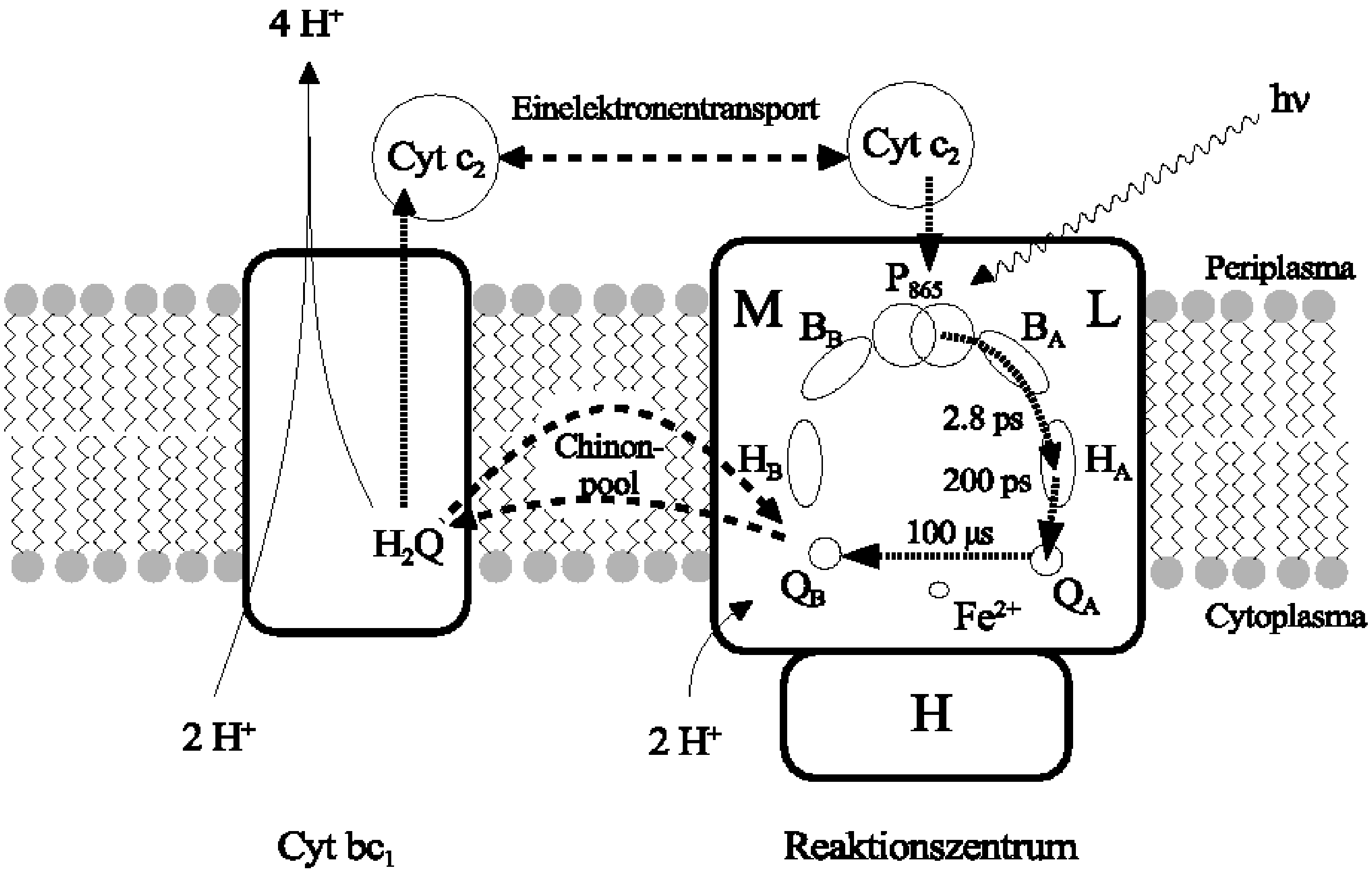
Q. Wang, R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank, Science 266 (1994) 422

Photochemical Reactions in Nature: Electron Transfer in Photosynthesis

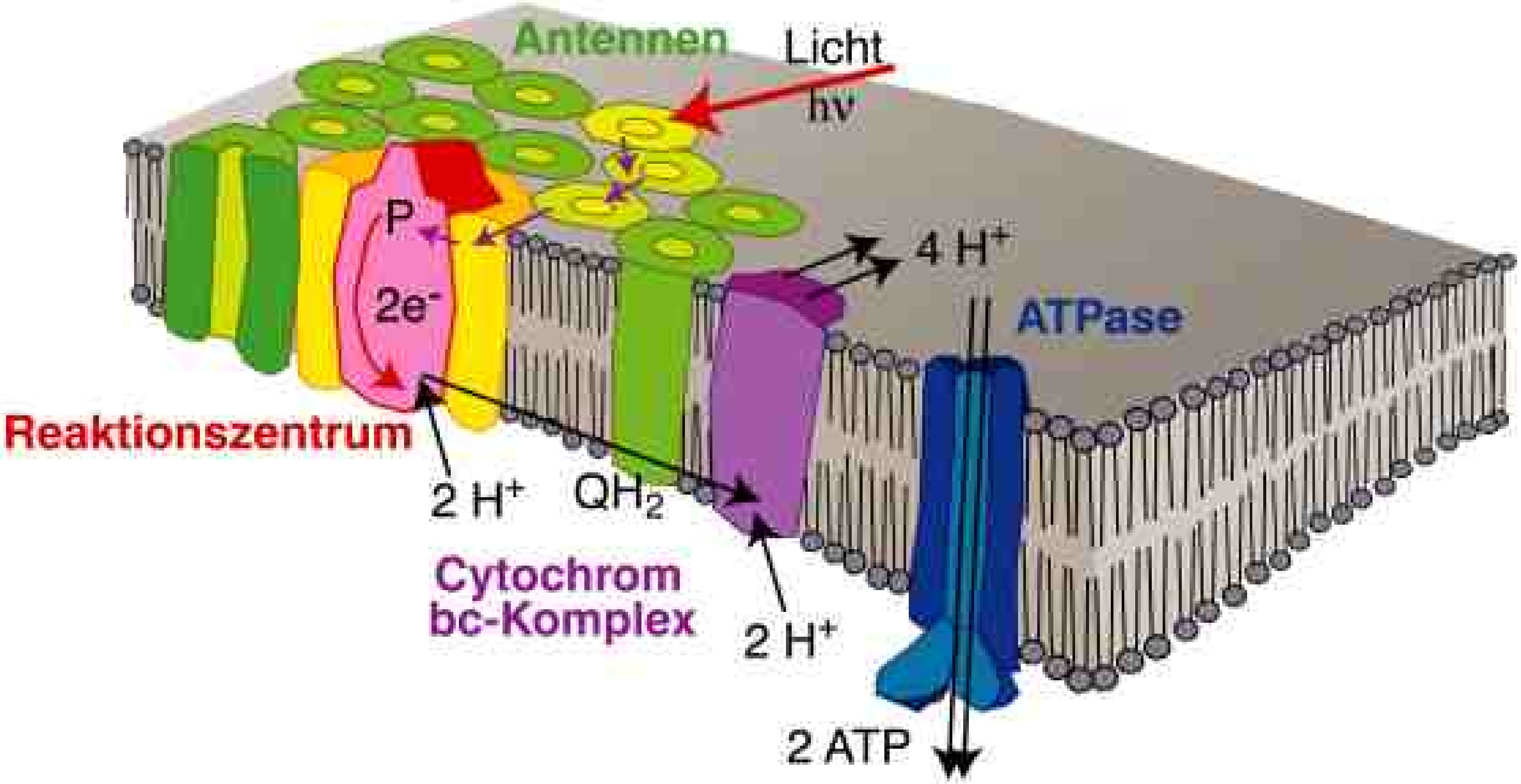
Photochemical Reactions in Nature: Photosynthesis in Green Plants



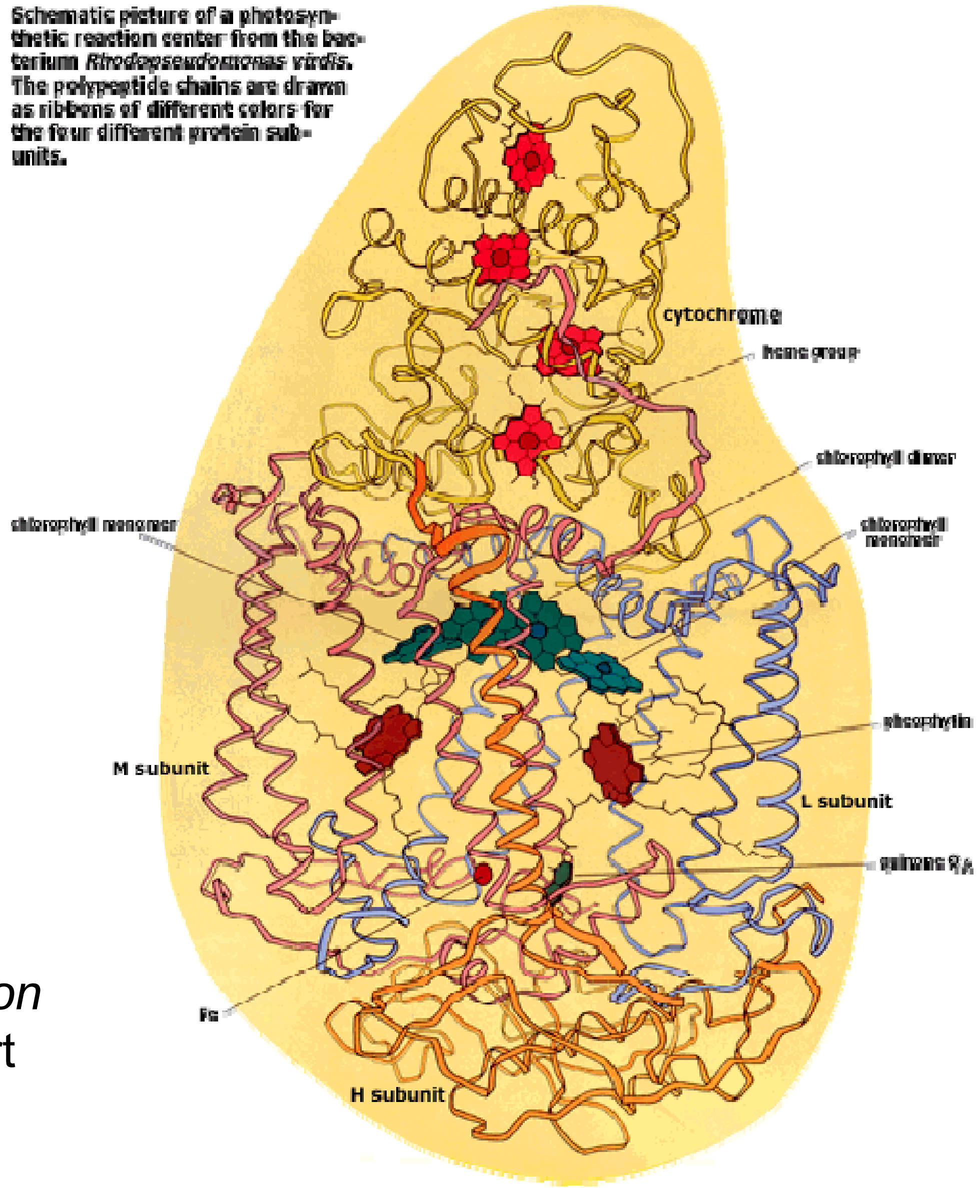
Photochemical Reactions in Nature: Bacterial Photosynthesis



Photochemical Reactions in Nature: Bacterial Photosynthesis



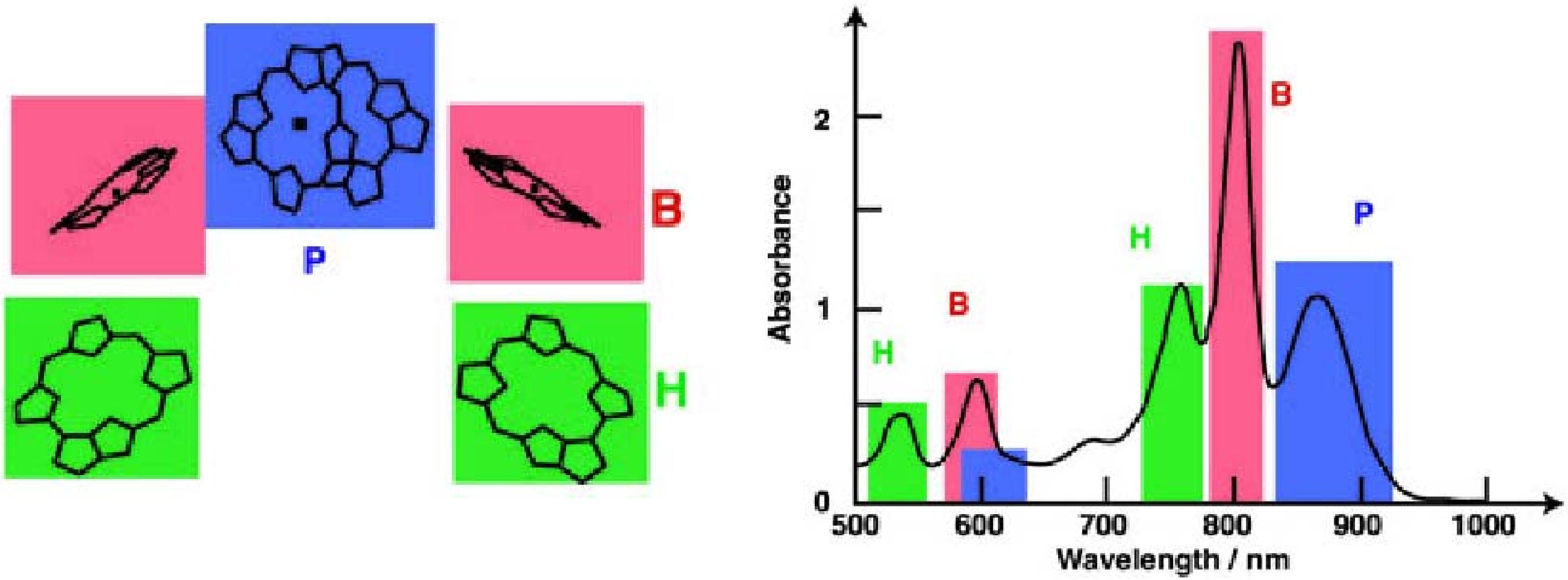
Photochemical Reactions in Nature: Bacterial Photosynthesis



Schematic picture of a photosynthetic reaction center from the bacterium *Rhodopseudomonas viridis.* The polypeptide chains are drawn as ribbons of different colors for the four different protein subunits.

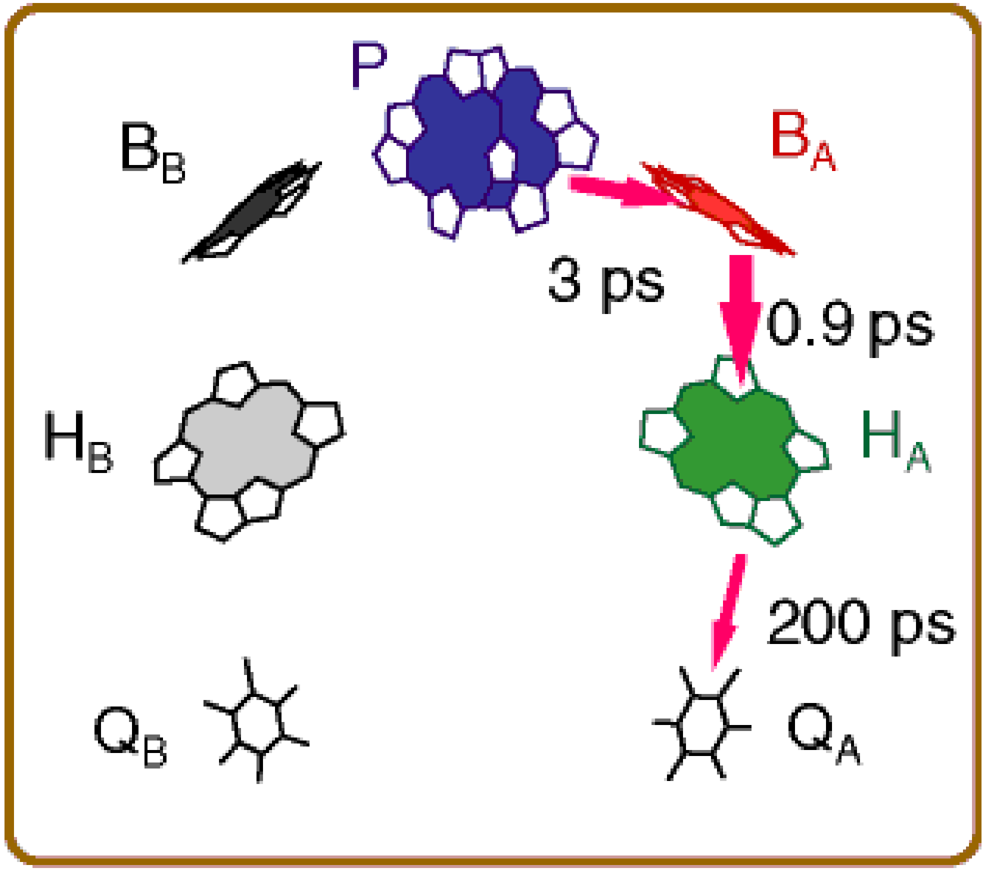
Nobel Prize in Chemistry 1988 *The structure of a photosynthetic reaction center*, Johann Deisenhofer, Robert Huber and Hartmut Michel

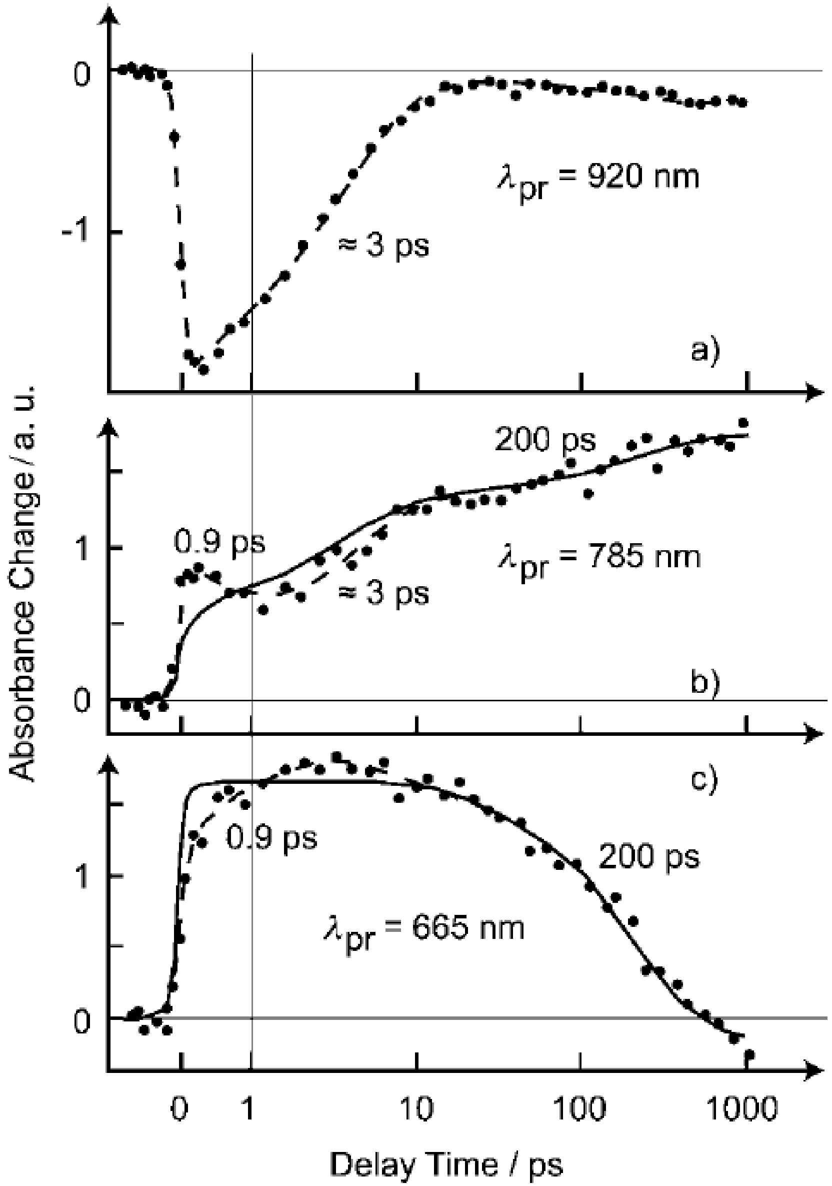
Photochemical Reactions in Nature: Electron Transfer in Photosynthesis



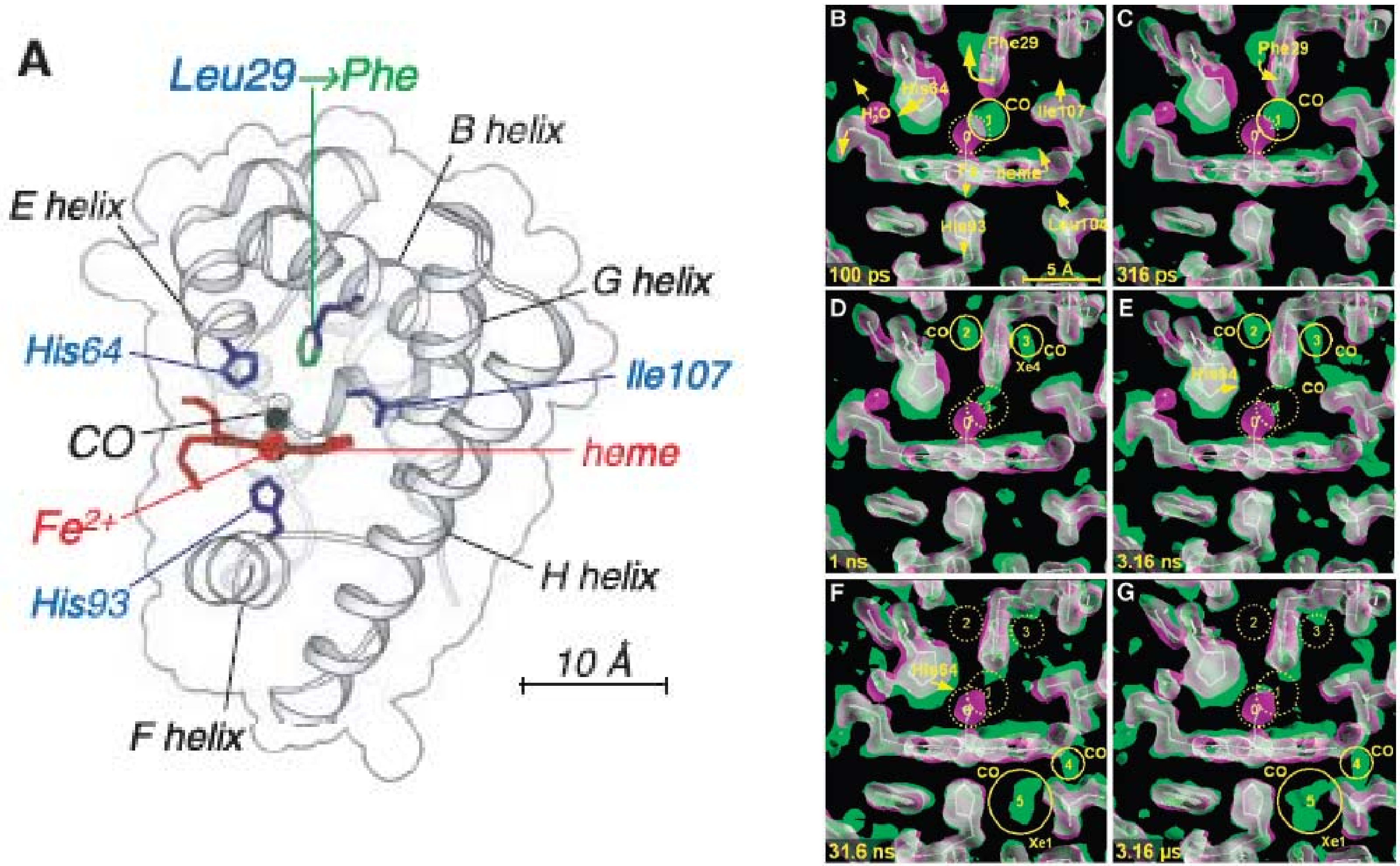
W. Zinth, J. Wachtveitl ChemPhysChem 2005, 6, 871 – 880

Photochemical Reactions in Nature: Electron Transfer in Photosynthesis





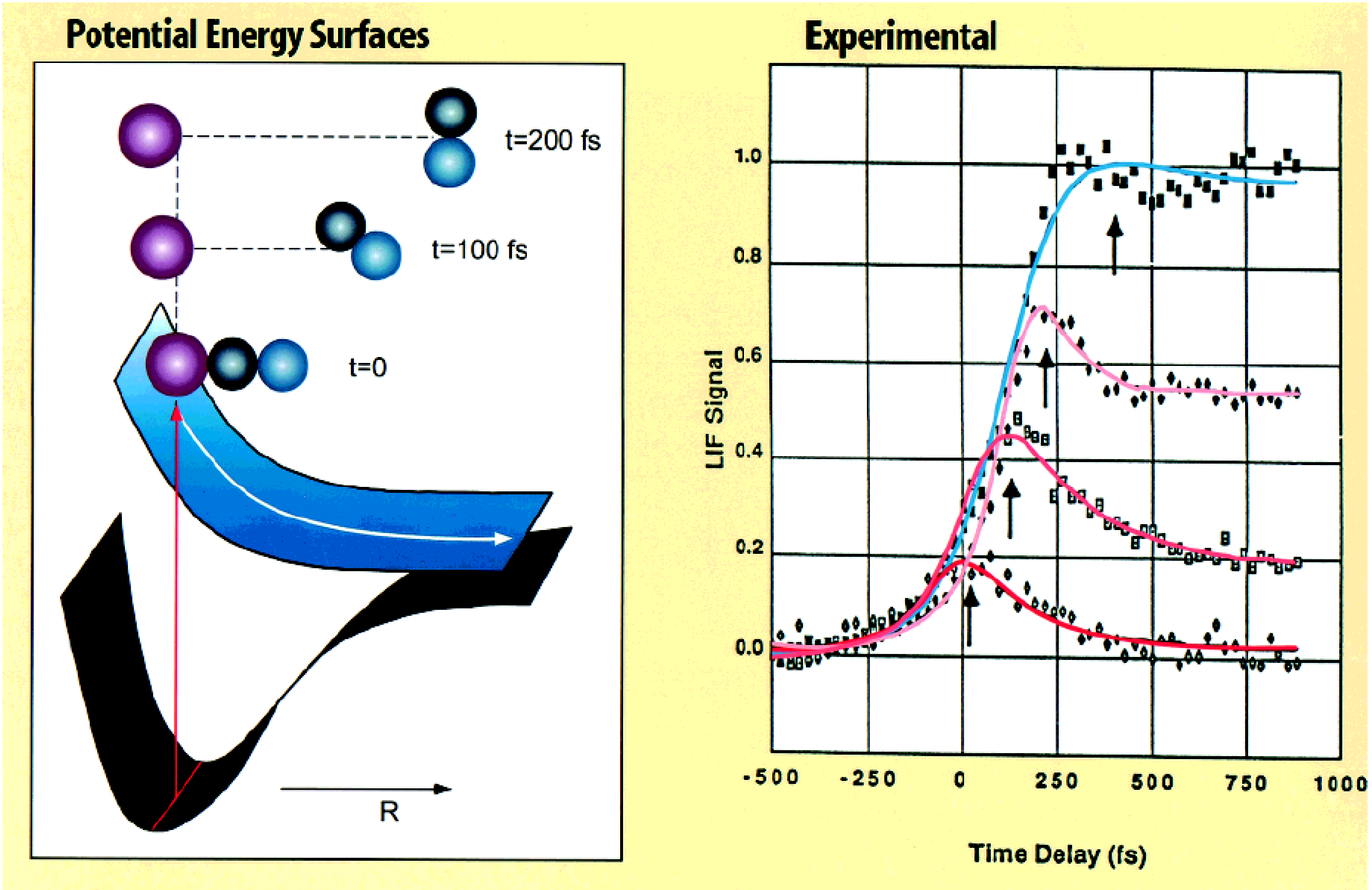
Photochemical Reactions in Nature: Myoglobin



Friedrich Schotte, Manho Lim, Timothy A. Jackson, Ieksandr V. Smirnov, Jayashree Soman, John S. Olson, George N. Phillips Jr., Michael Wulff, Philip A. Anfinrud *Watching a Protein as it Functions with 150-ps Time-Resolved X-ray Crystallography,* Science, 300 1944 (2003)

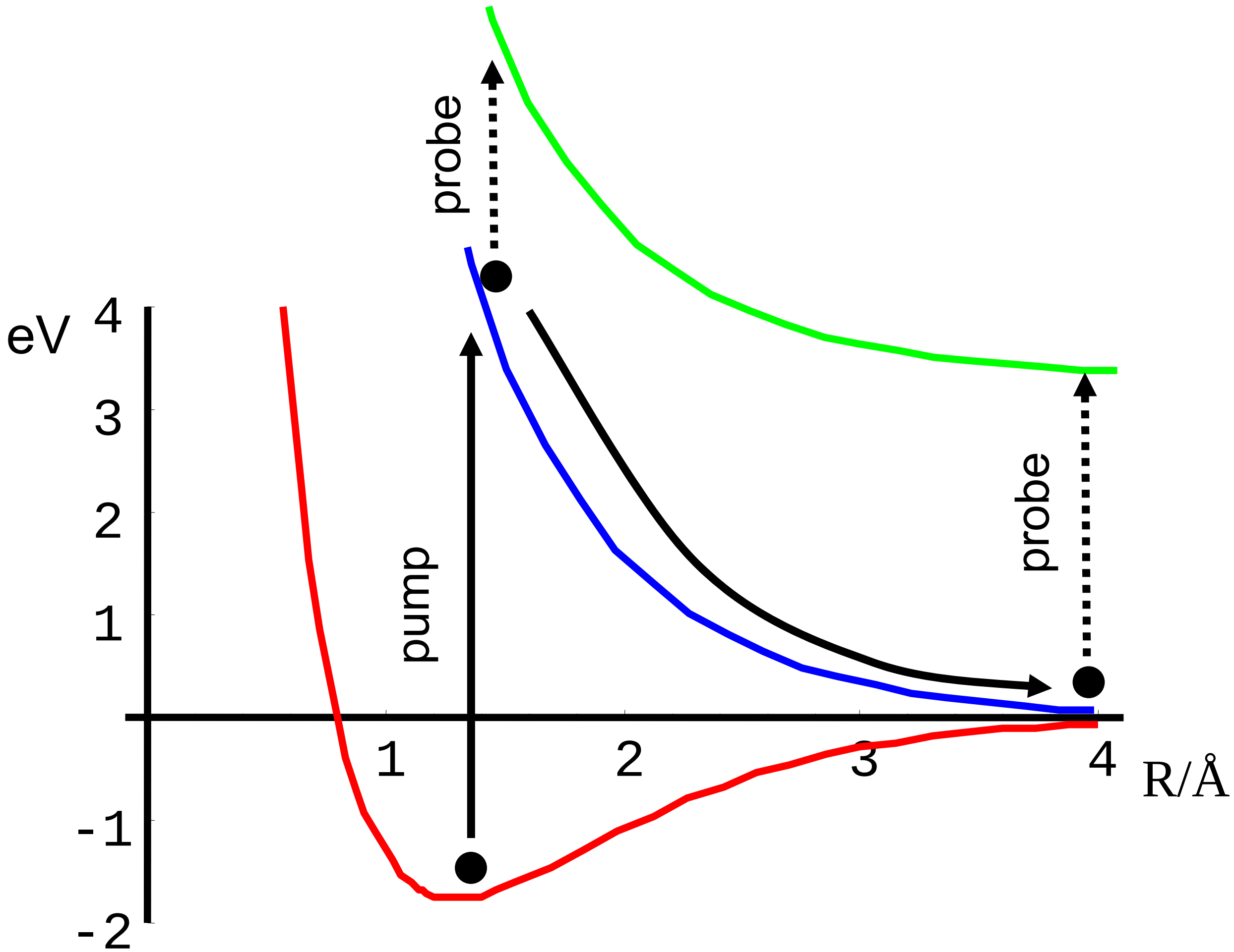
Prototype Photochemical Reactions in Chemistry

Prototype Photochemical Reaction: ICN

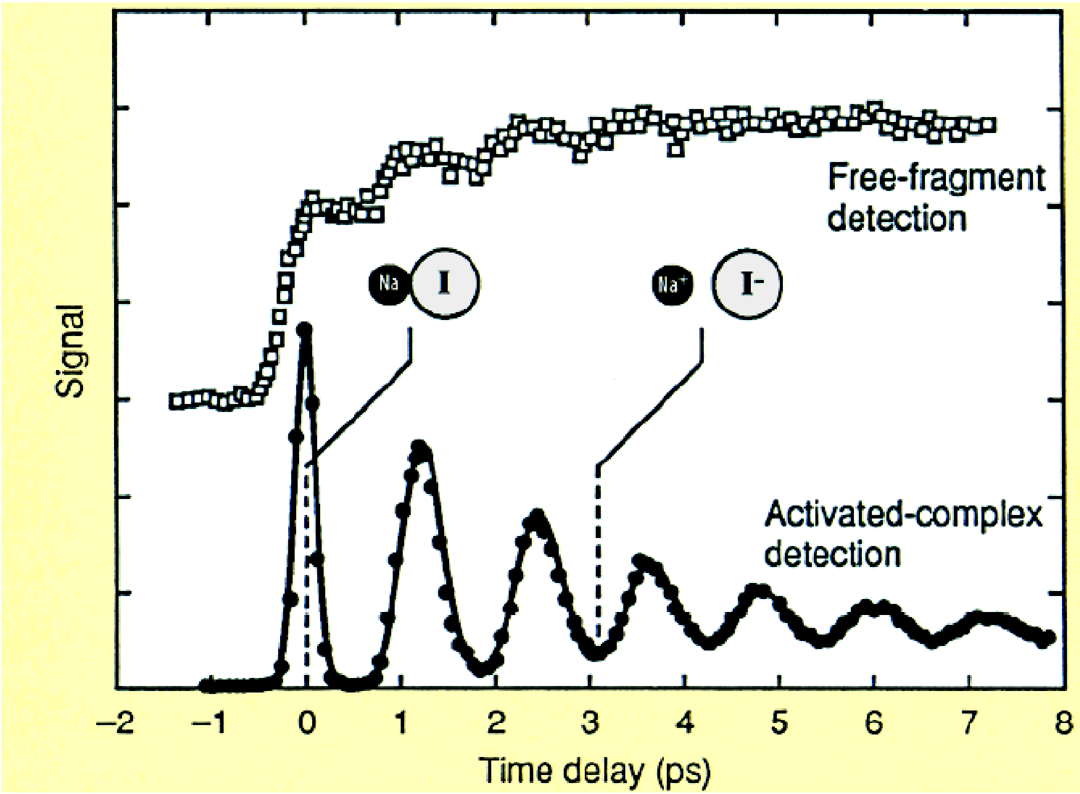


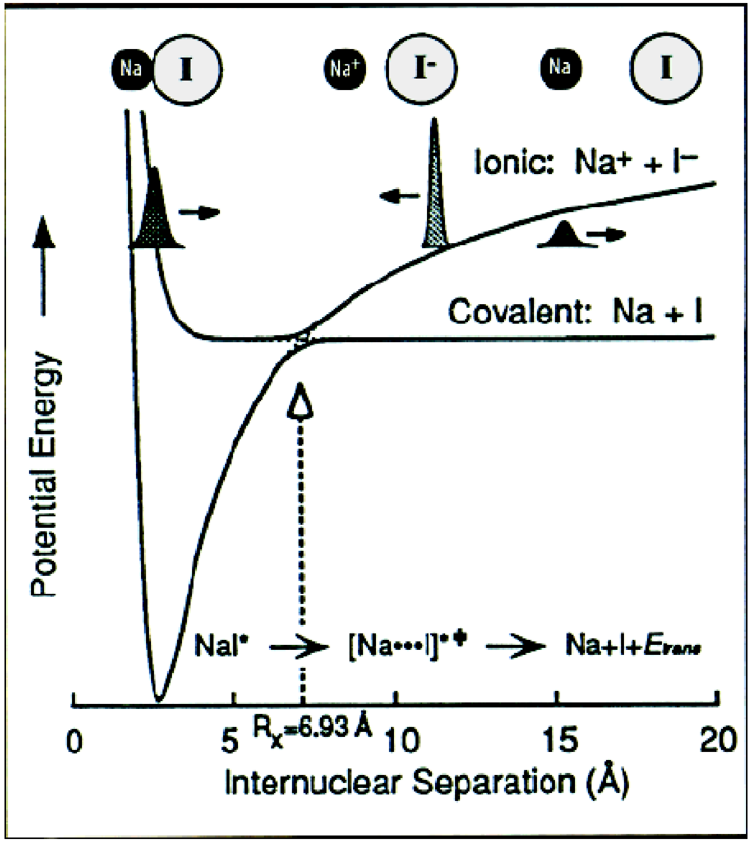
M. Dantus, M. J. Rosker, A. H. Zewail, J. Chem. Phys. 87 (1987) 2395
A. H. Zewail, J. Phys. Chem. A 104 (2000) 5660

Photochemie: H_2^+-Molekül



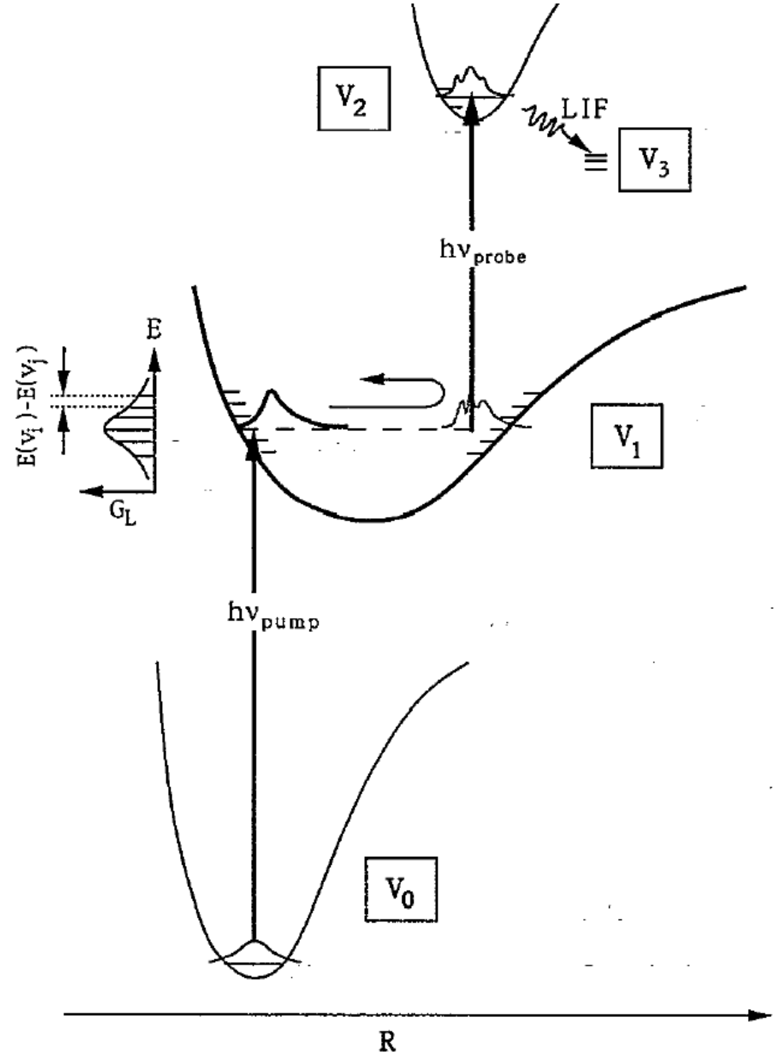
Prototype Photochemical Reaction: NaI

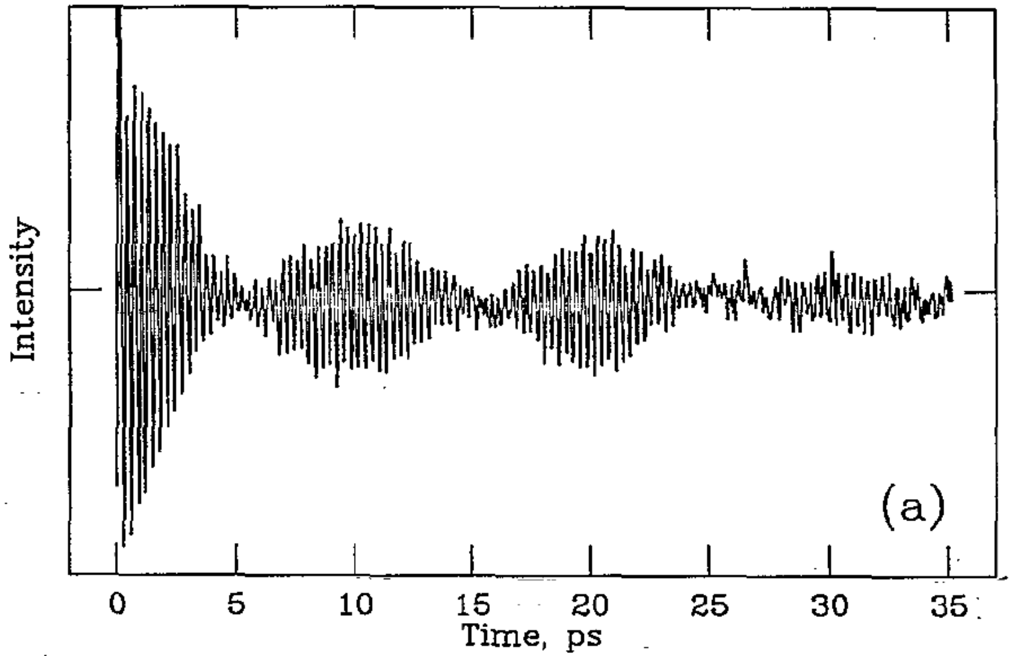




T. S. Rose, M. J. Rosker, A. H. Zewail, J. Chem. Phys. 91 (1989) 7415
A. H. Zewail, J. Phys. Chem. A 104 (2000) 5660

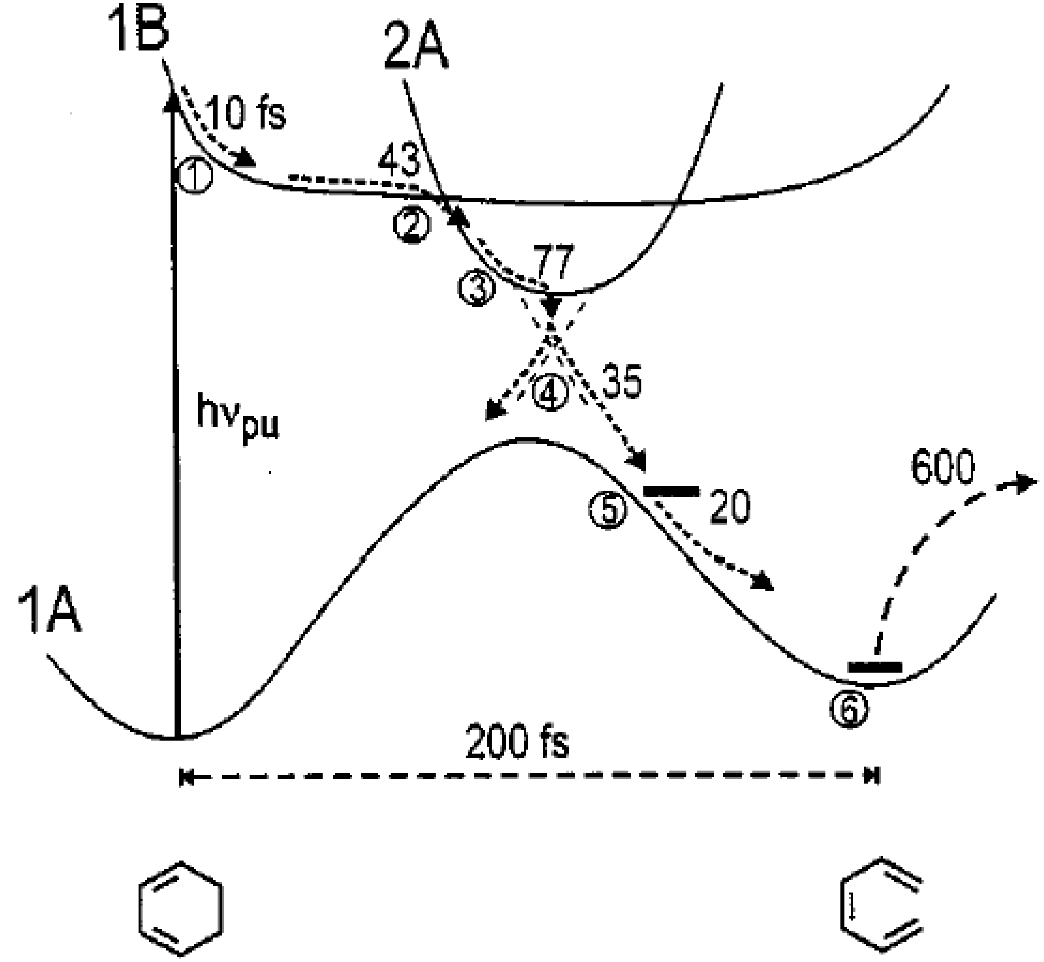
Motion in Quantum Mechanics: I_2





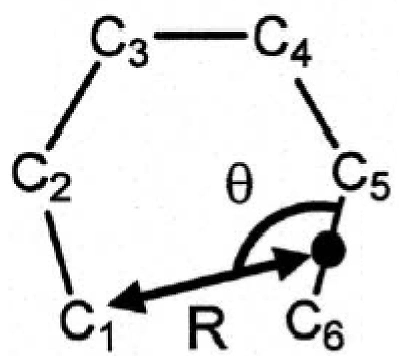
M. Gruebele, A. H. Zewail, J. Chem. Phys. 98 (1993) 883

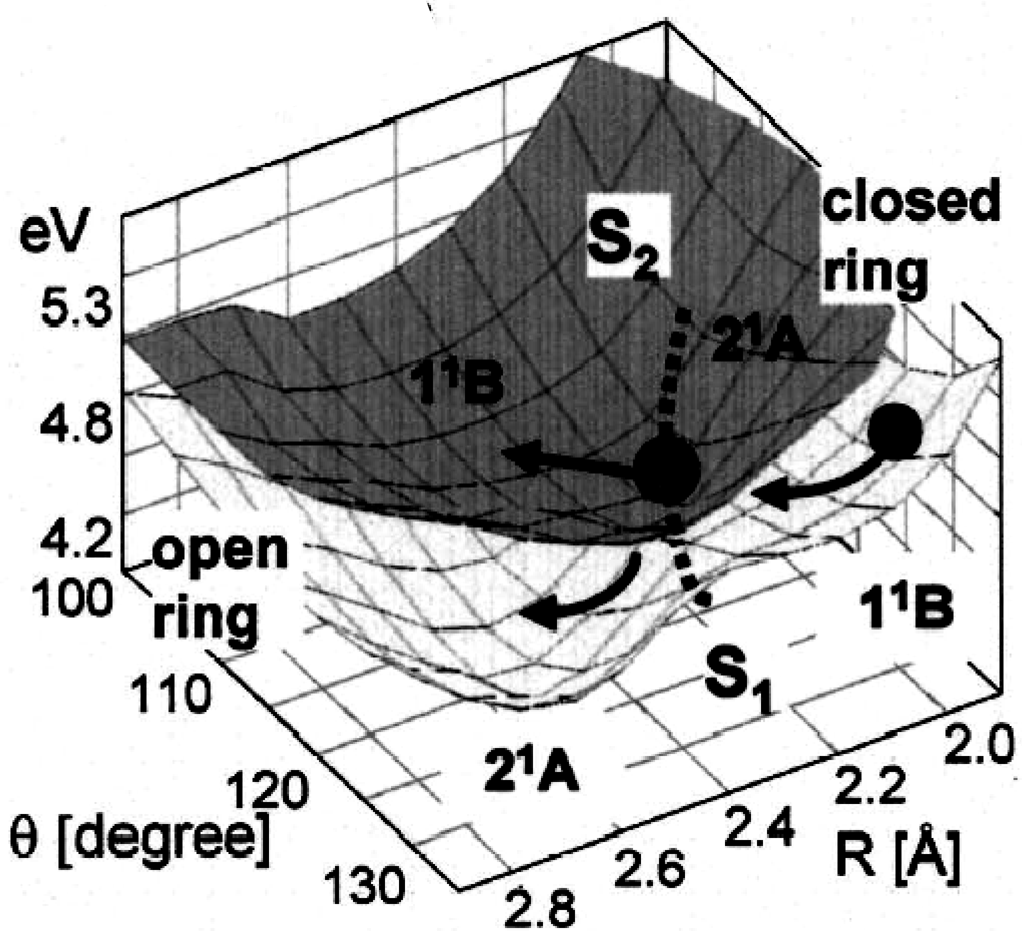
Ring Opening of 1-3-Cyclohexadien



W. Fuß, W. E. Schmid, and S. A. Trushin, Time-resolved dissociative intense-laser field ionization for probing dynamics: Femtosecond photochemical ring opening of 1,3-cyclohexadiene, J. Chem. Phys. 112 (2000) 8347

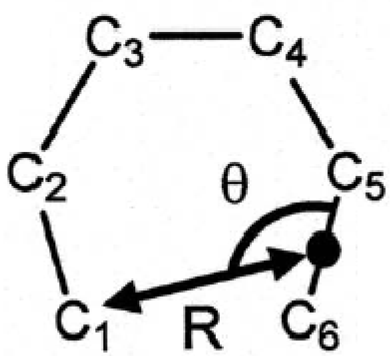
Ring Opening of 1-3-Cyclohexadien

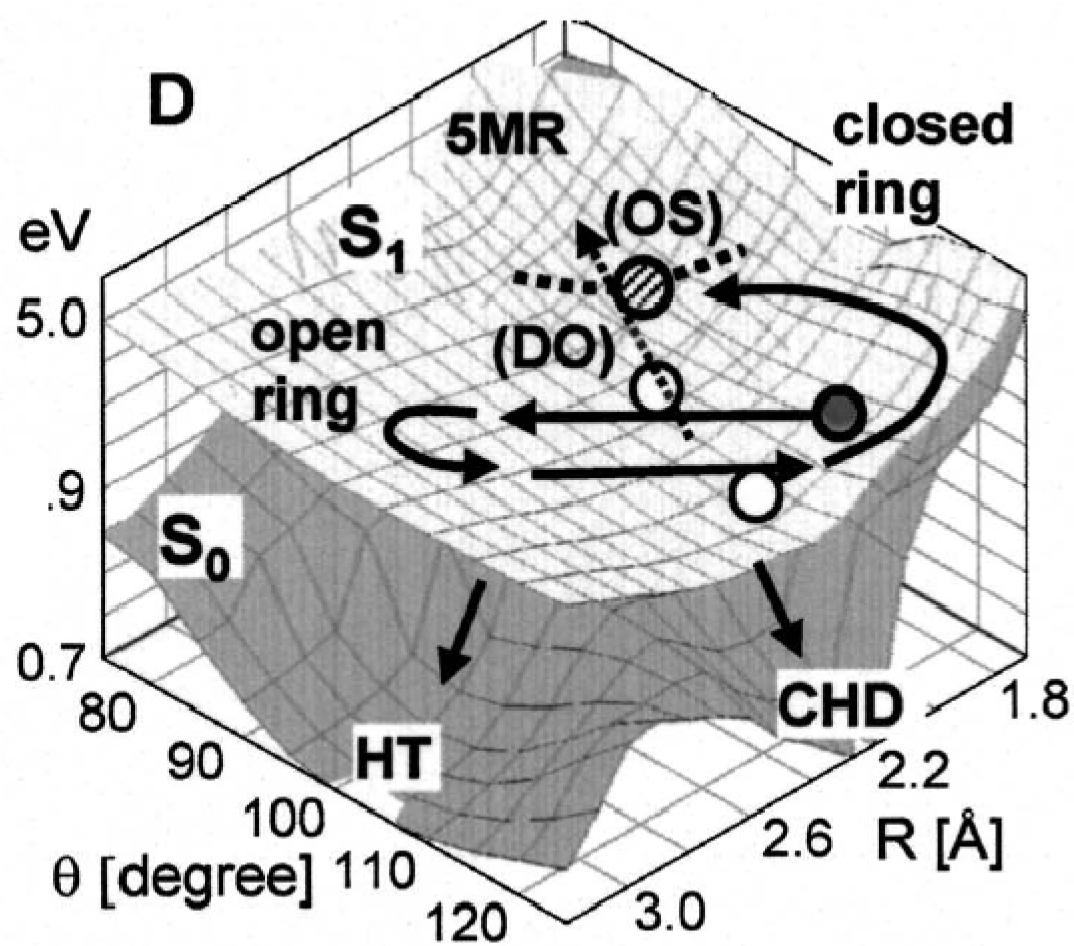




H. Tamuraa S. Nanbu T. Ishida H. Nakamura *Ab initio nonadiabatic quantum dynamics of cyclohexadiene/hexatriene ultrafast photoisomerization* J Chem. Phys. **124**, 084313 2006

Ring Opening of 1-3-Cyclohexadien





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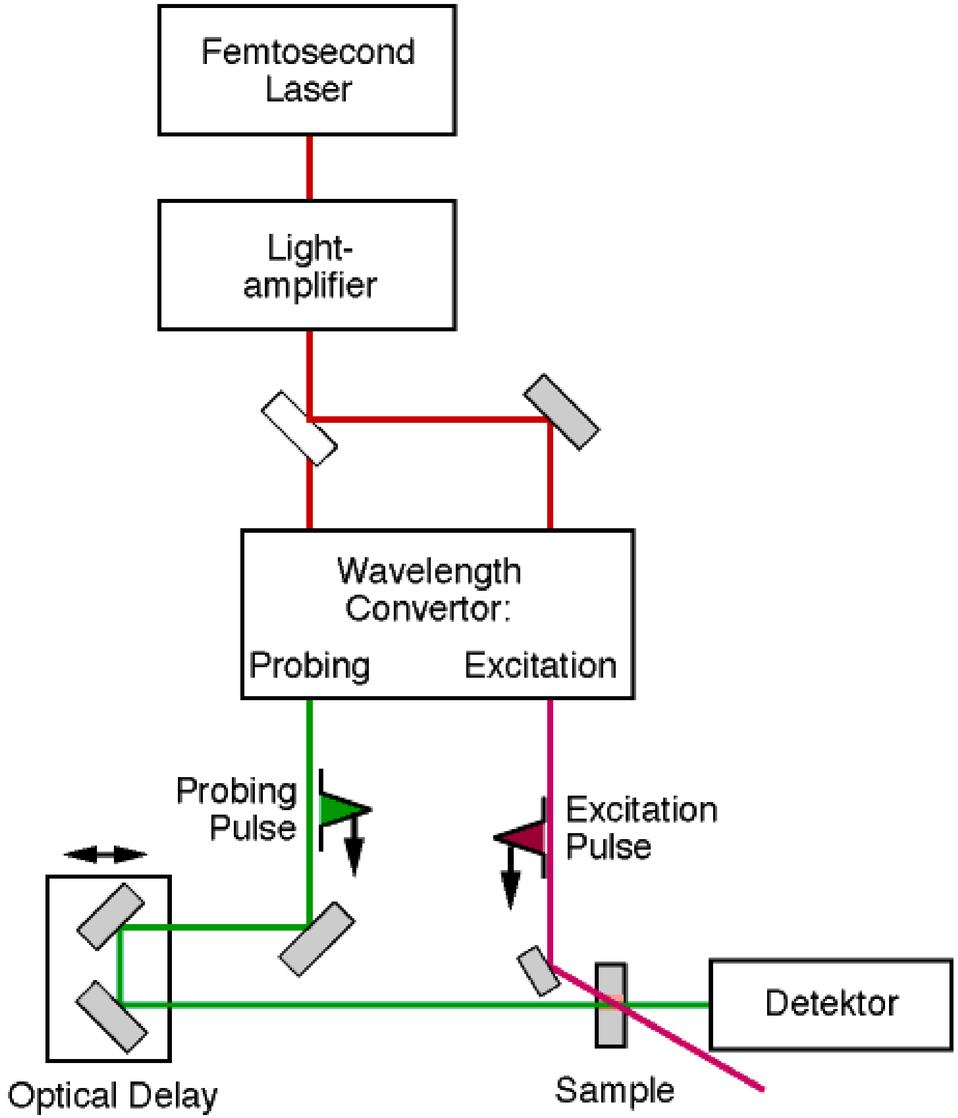
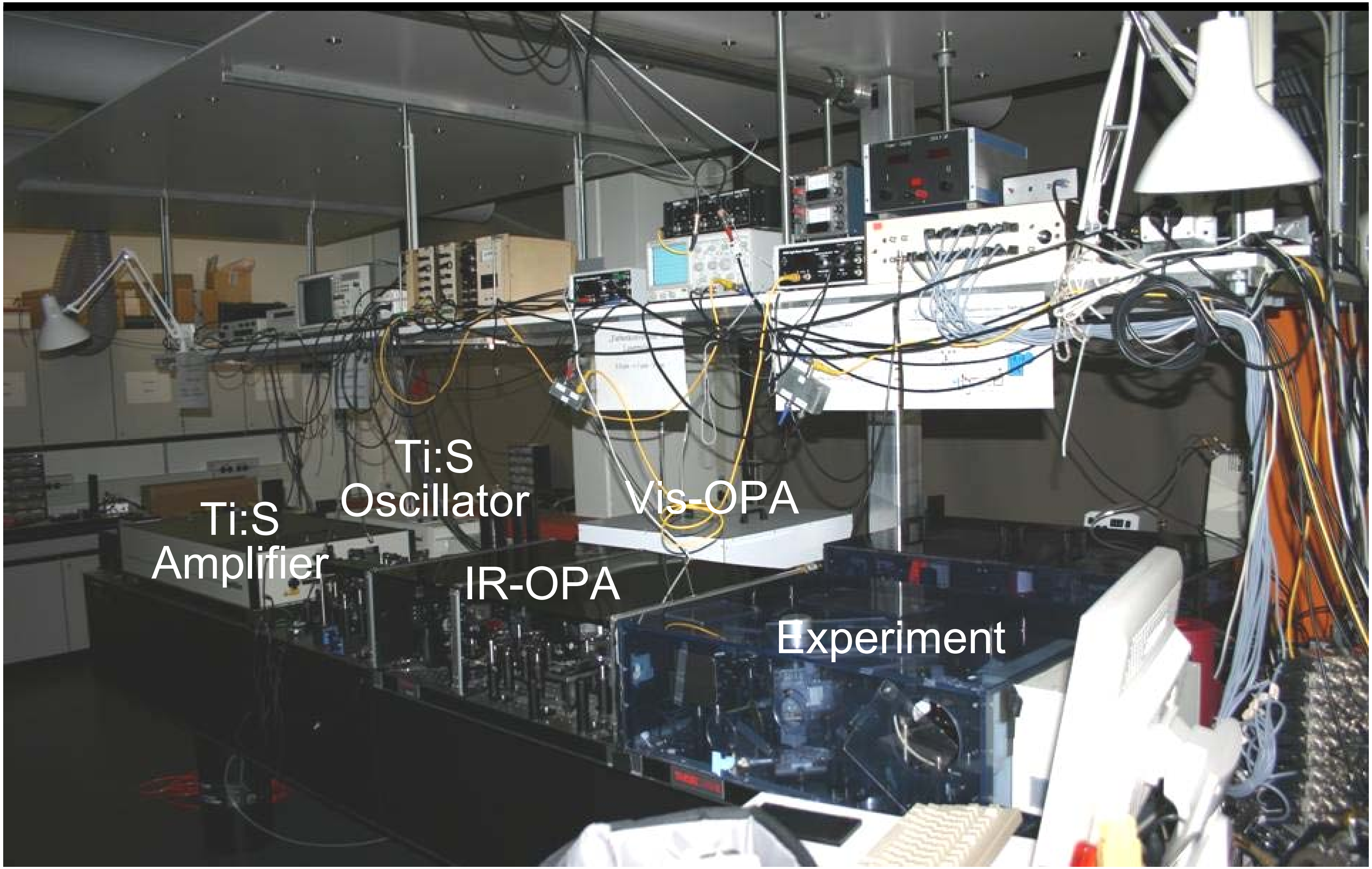
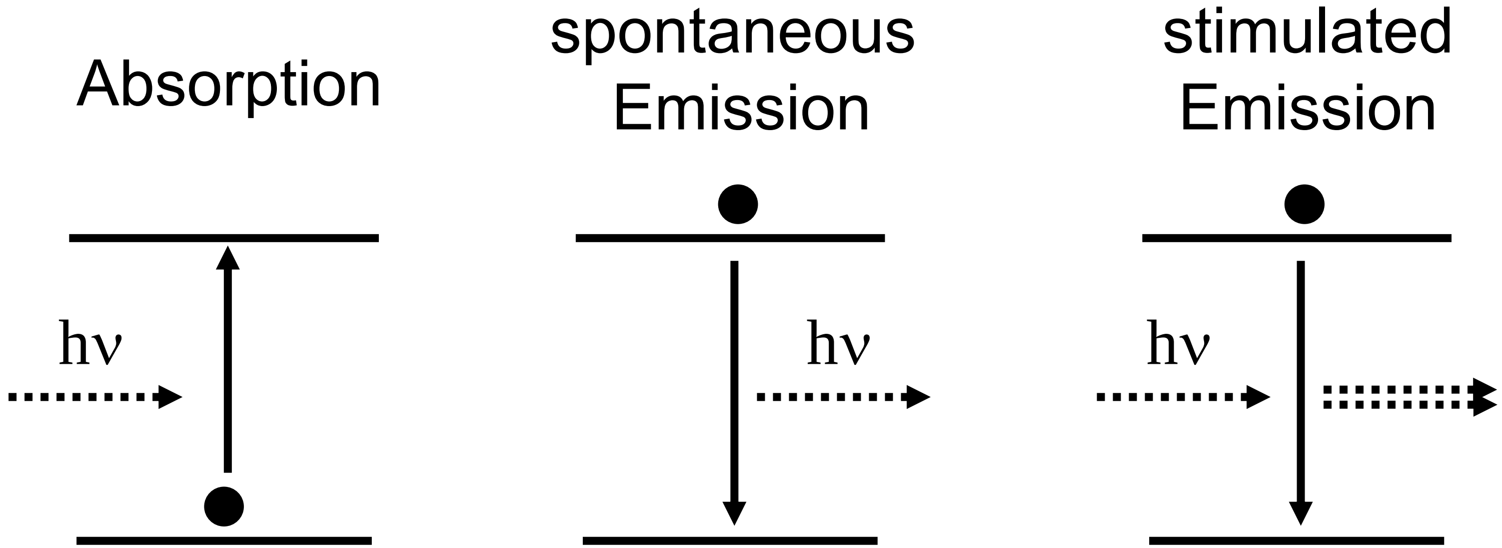
Pump-Probe Spectroscopy



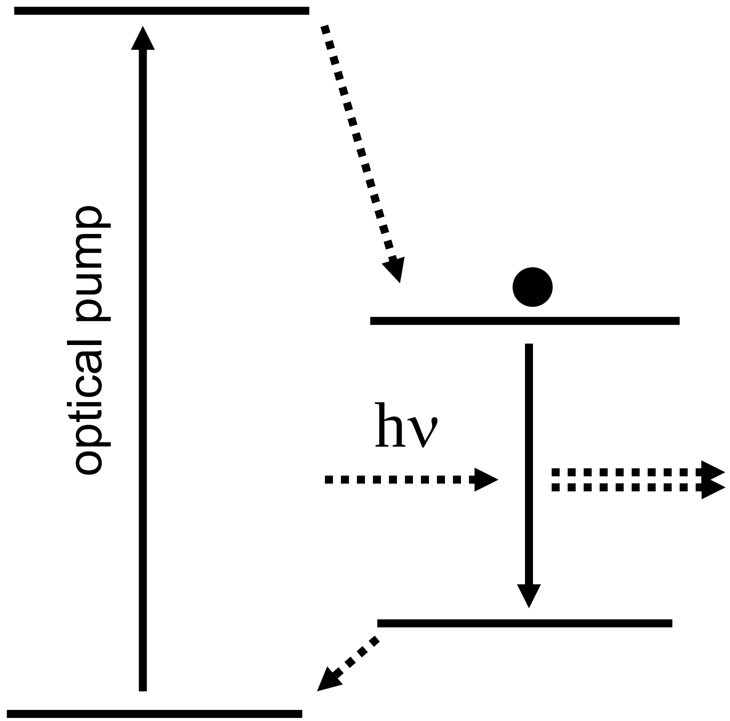
The Laser Lab



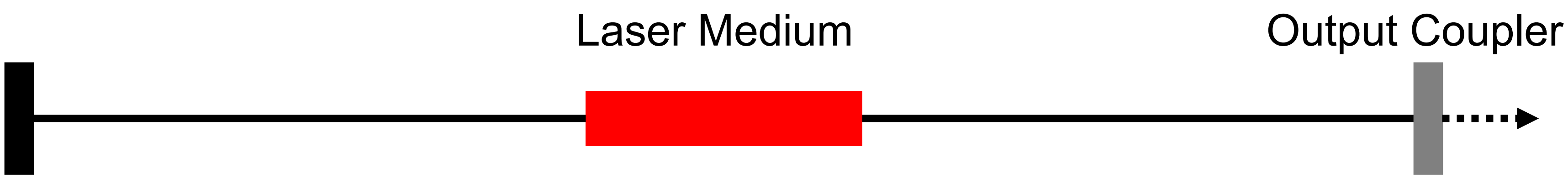
Interaction of Light with Matter



4-Level System

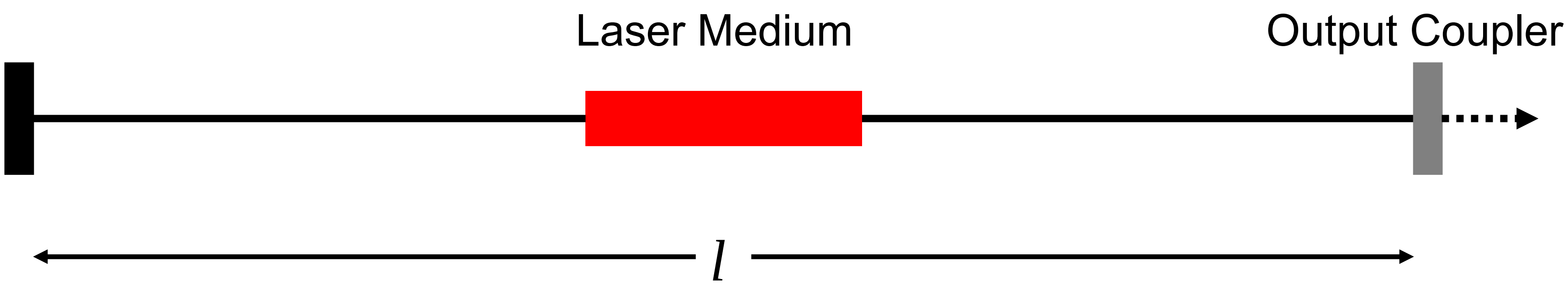


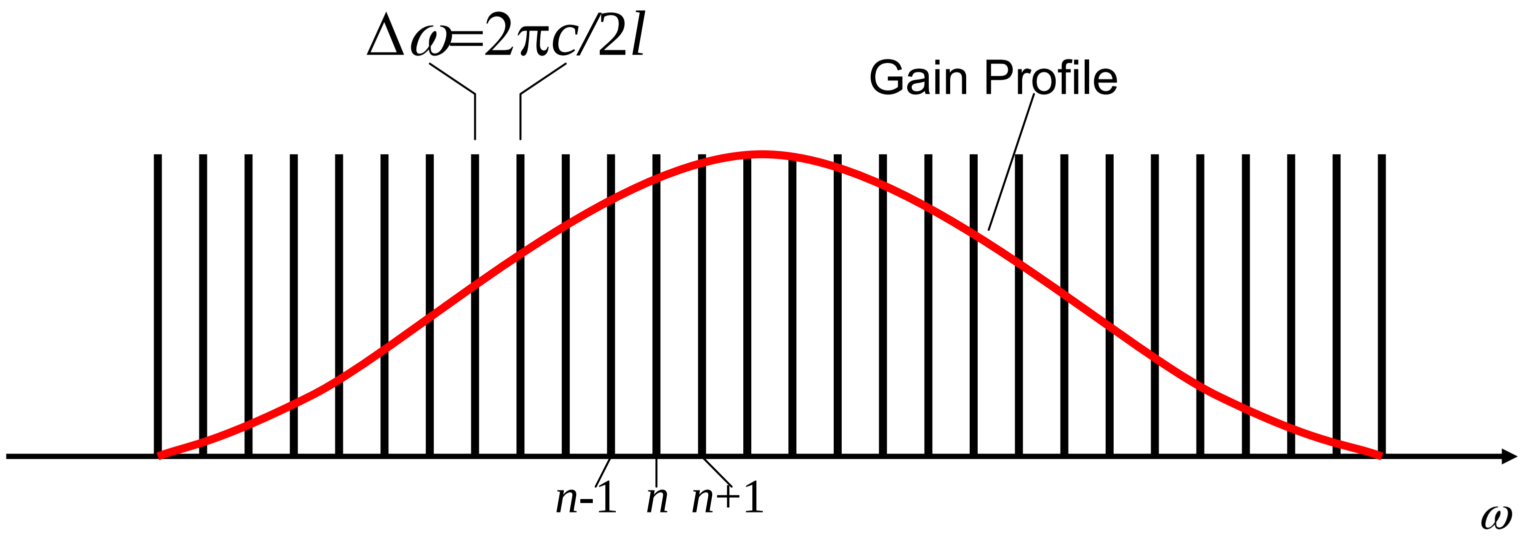
Laser

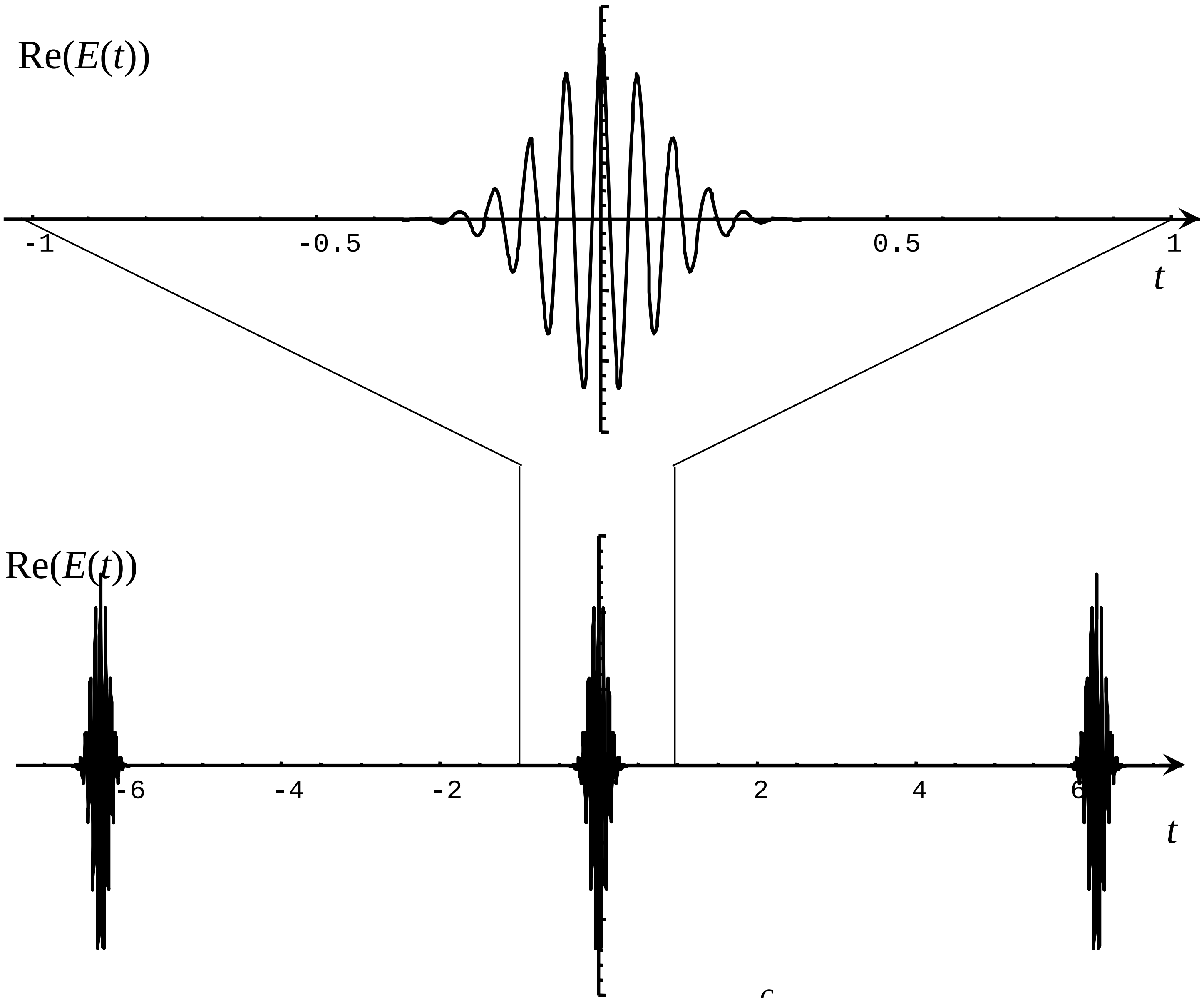


Short Pulses:
- Broad Gain Medium (organic Dyes, Ti:S)
- Mode Locking
- Dispersion Control

Laser

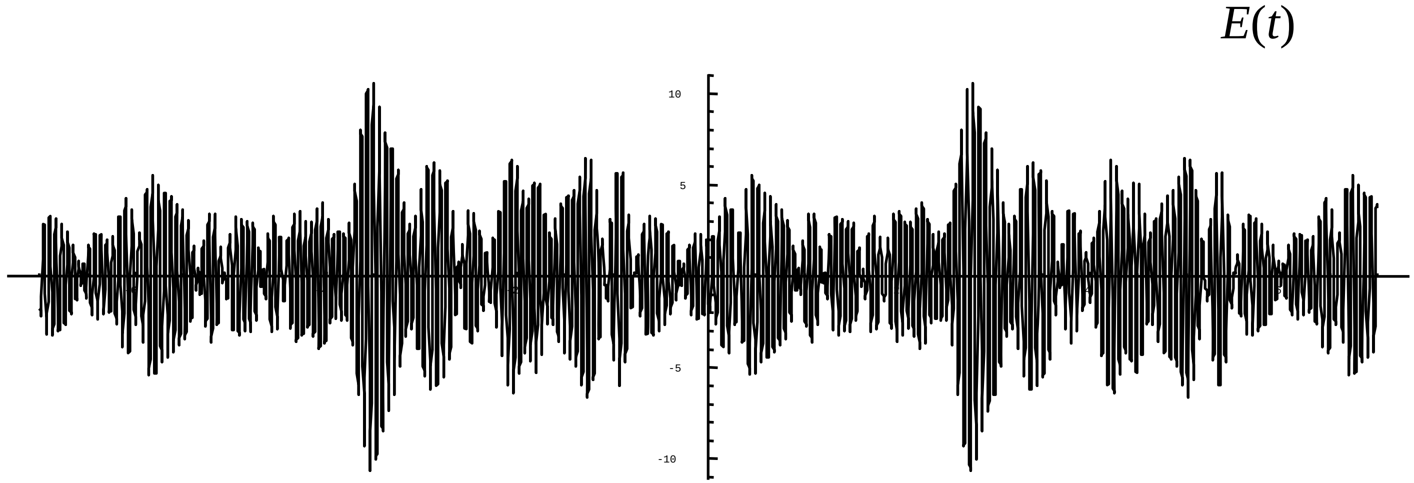




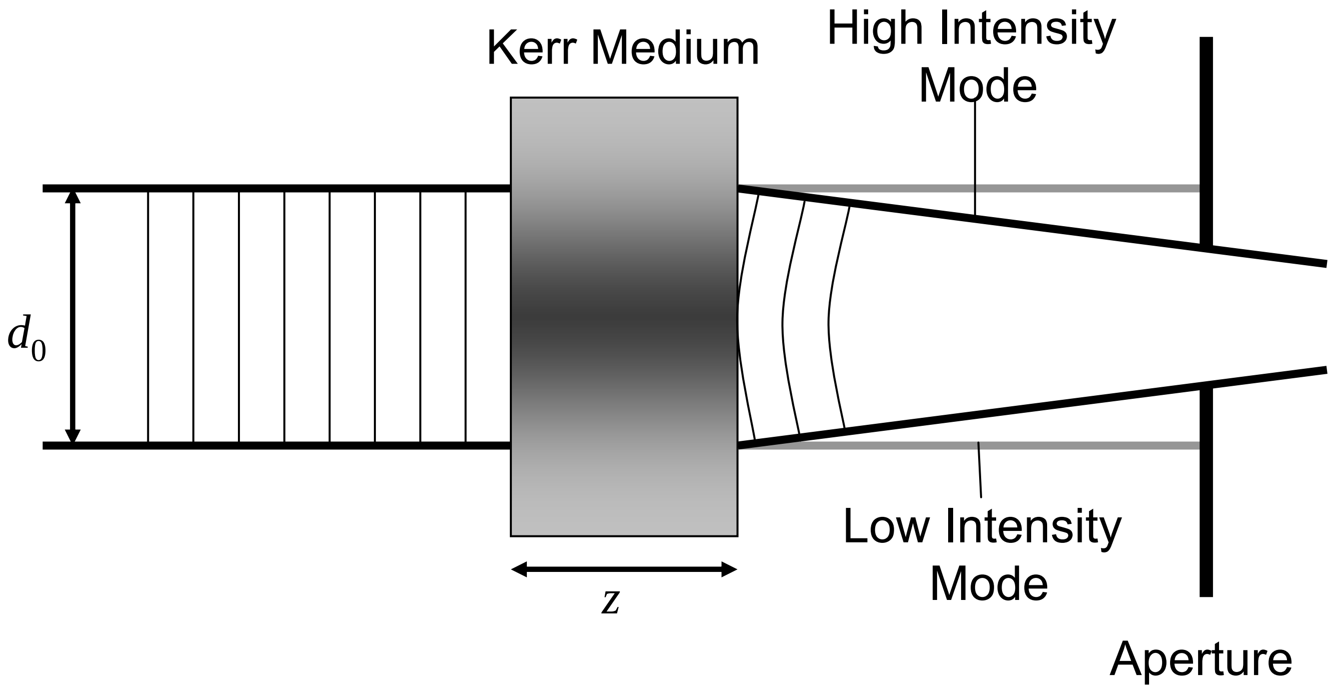


$$E(t) = \sum_n E_n e^{i2\pi n \frac{c}{2l} t}$$

Random Phase



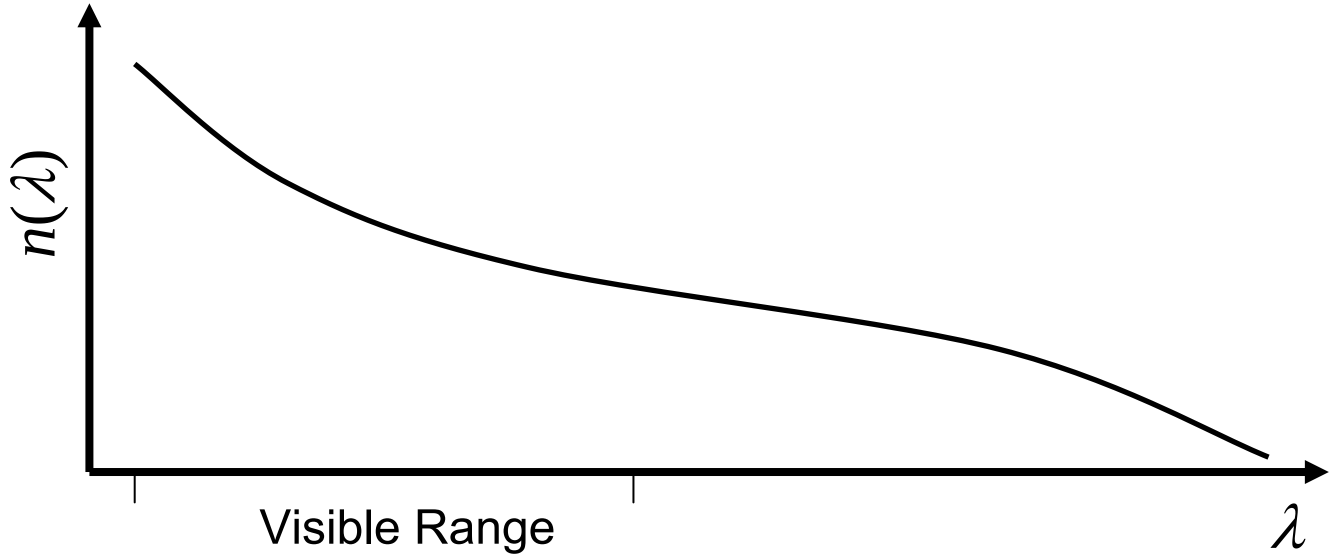
$$E(t) = \sum_n E_n e^{i\varphi_n} e^{i 2\pi n \frac{c}{2l} t}$$



Kerr Effect:

$$n(I) = n_0 + I \times n_2$$

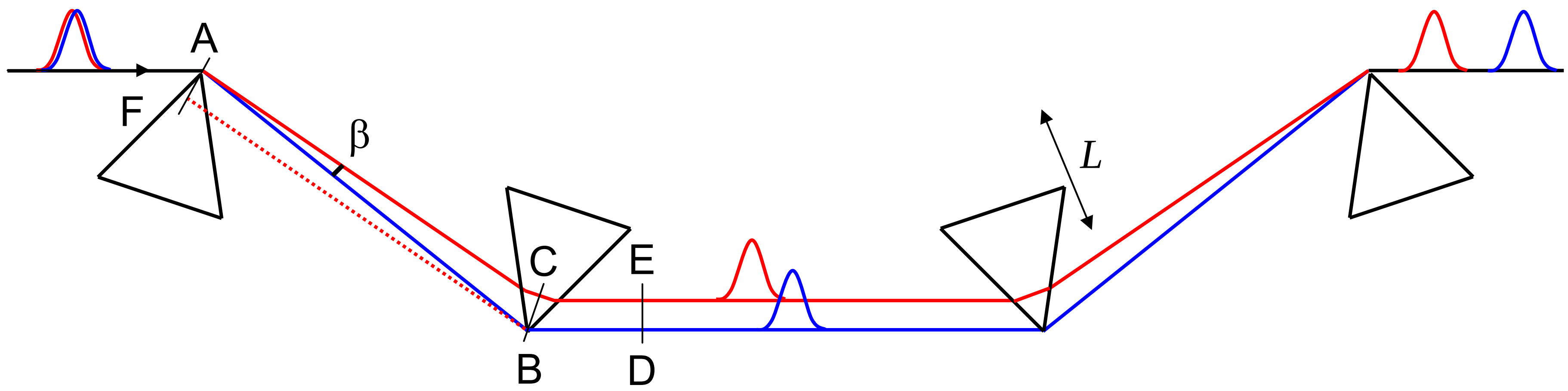
Dispersion



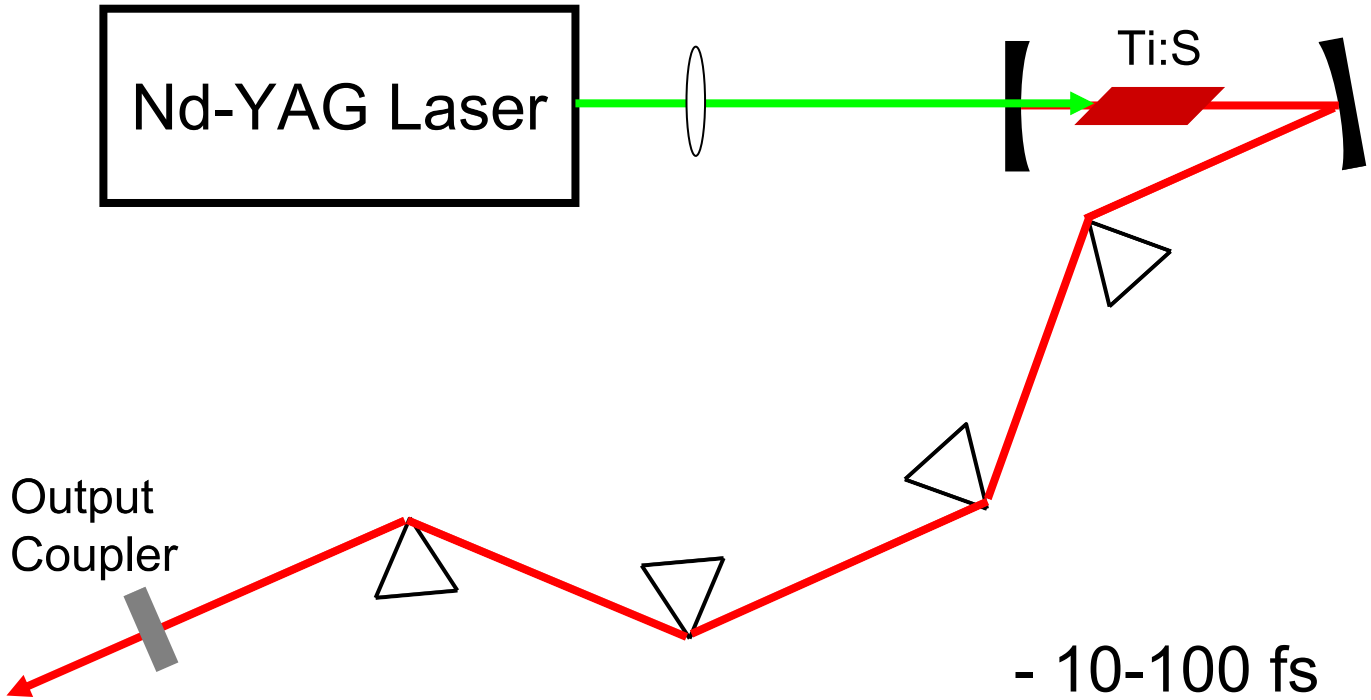
$$v_{ph} = \frac{c}{n(\lambda)}$$

$$v_{gr} = \frac{c}{n(\lambda)} - \frac{\lambda}{c}\frac{dn}{d\lambda}$$

Prism-Compressor



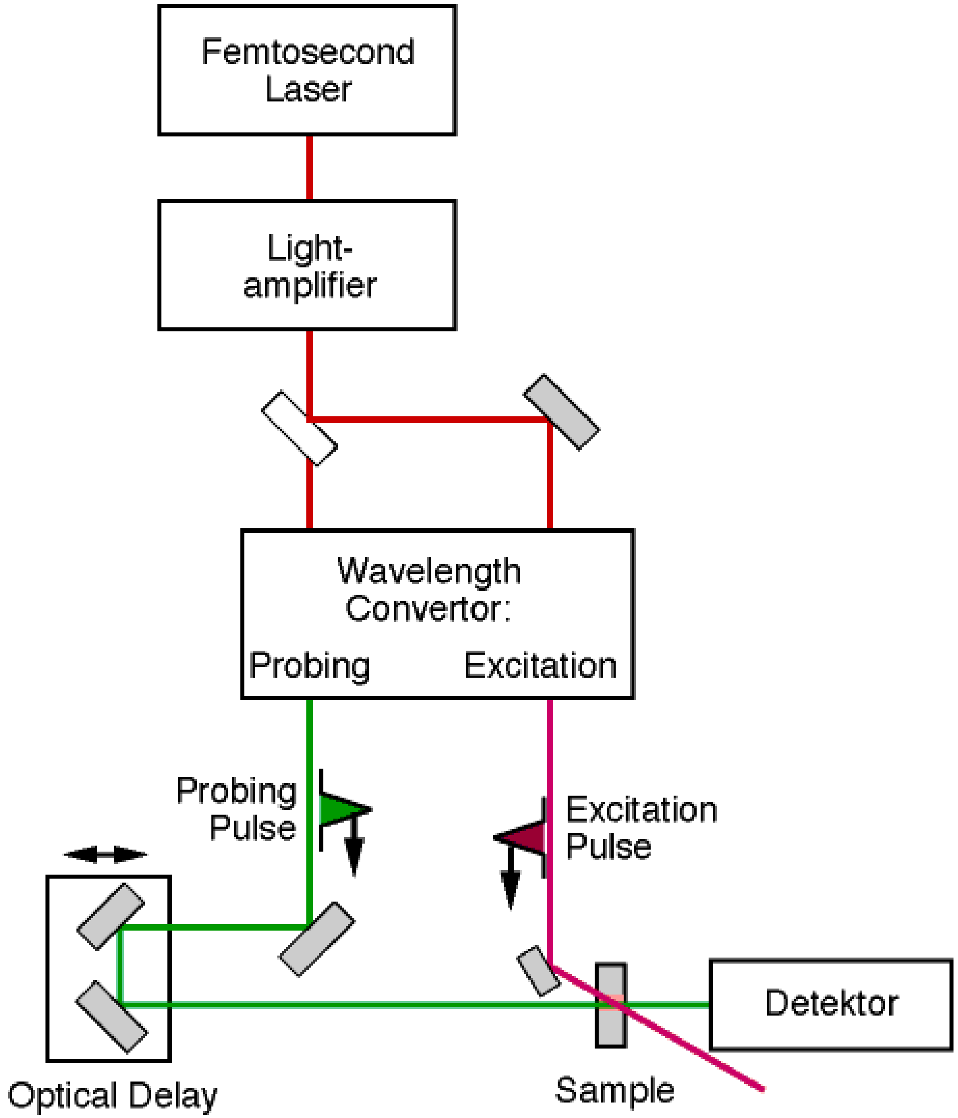
Ti:S Laser



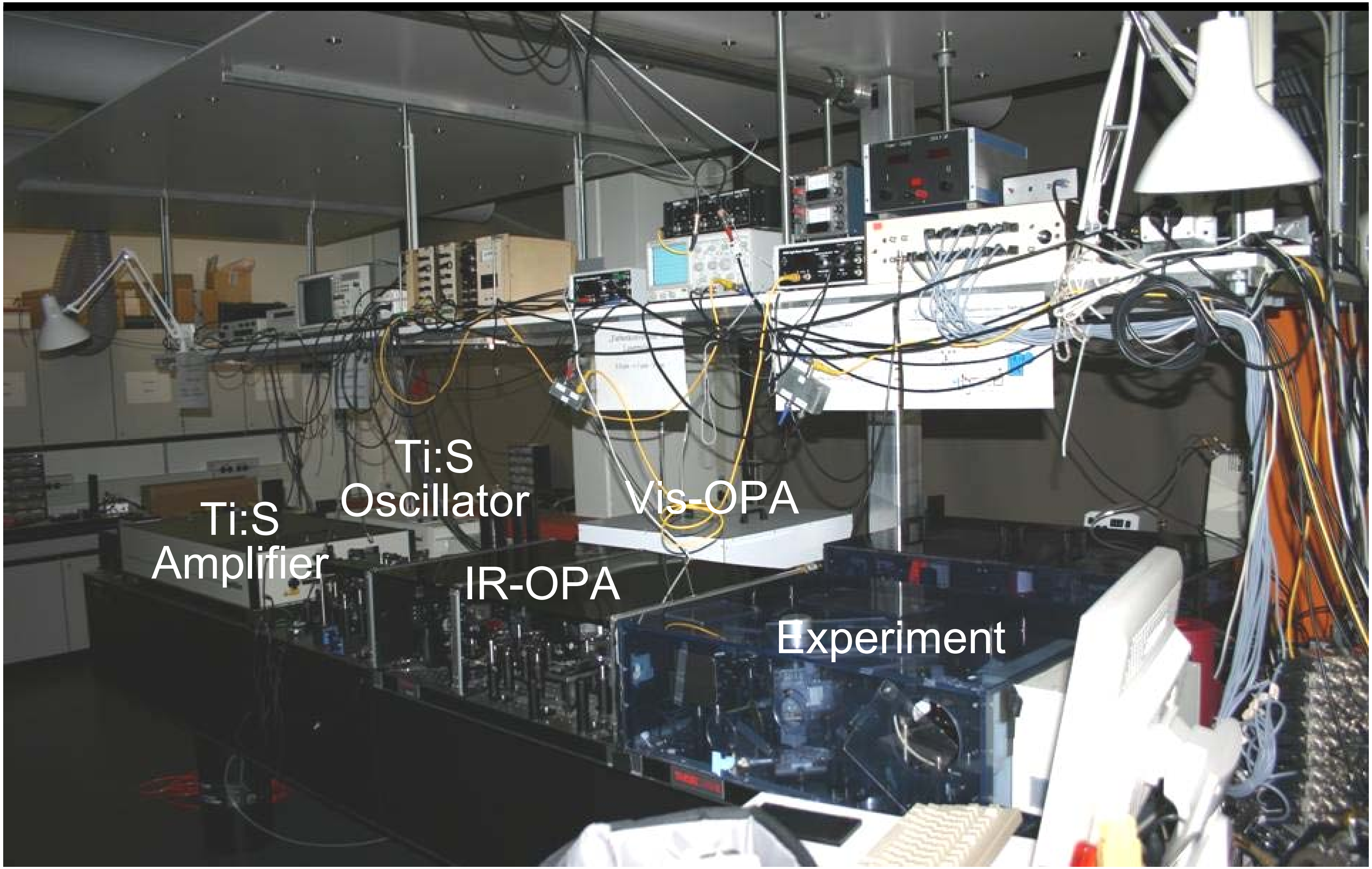
- 10-100 fs
- 750-900 nm
- 100 MHz
- 1 W (average)
- 10 nJ/pulse

Ti:S Laser

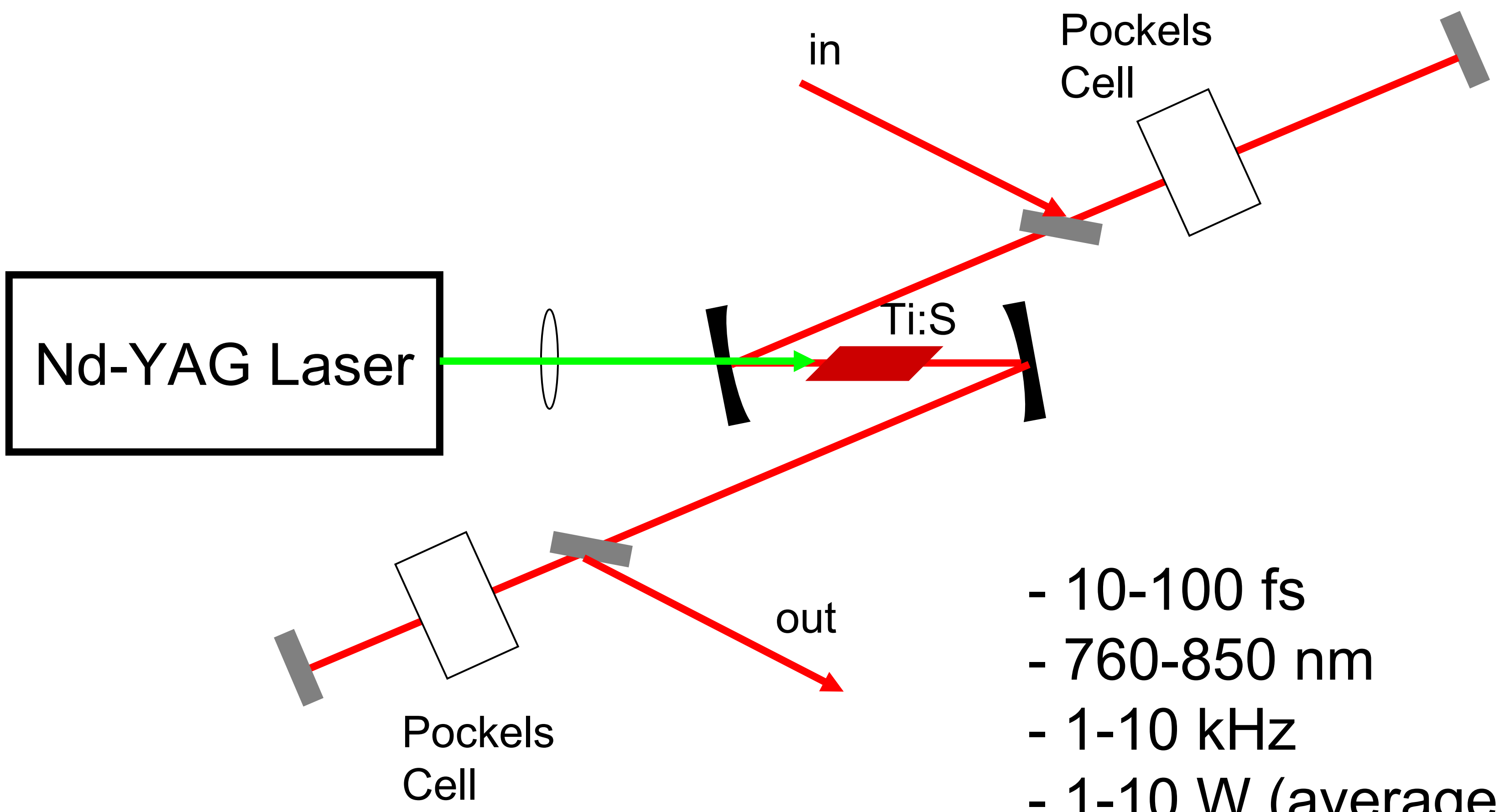
Pump-Probe Spectroscopy



The Laser Lab

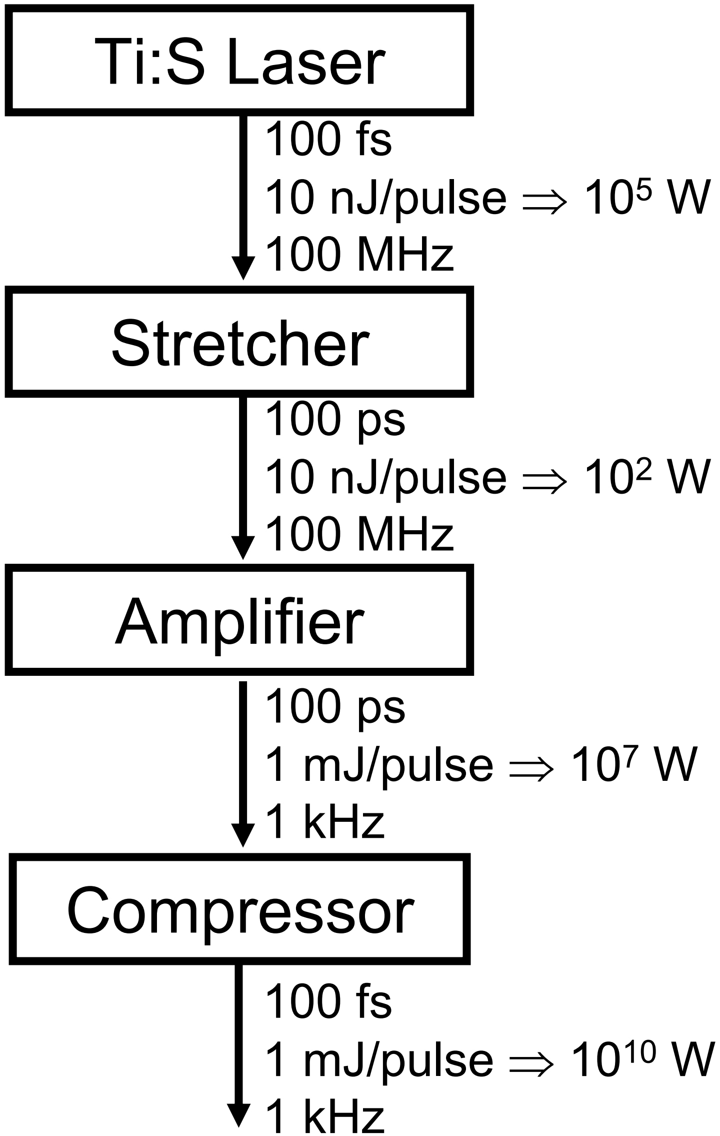


Regenerative Amplifier

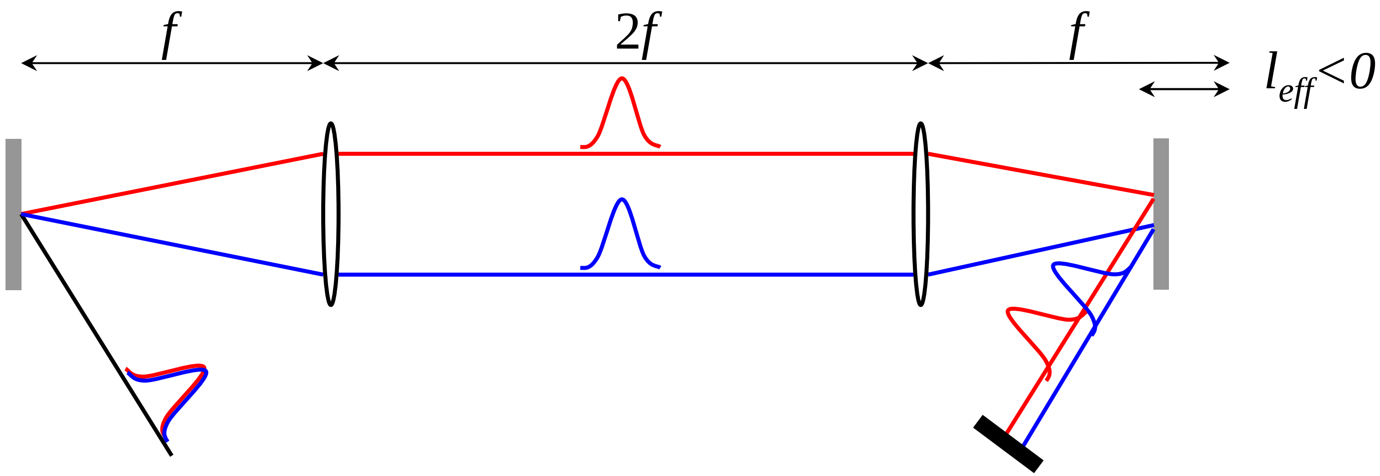


- 10-100 fs
- 760-850 nm
- 1-10 kHz
- 1-10 W (average)
- 1-10 mJ/pulse

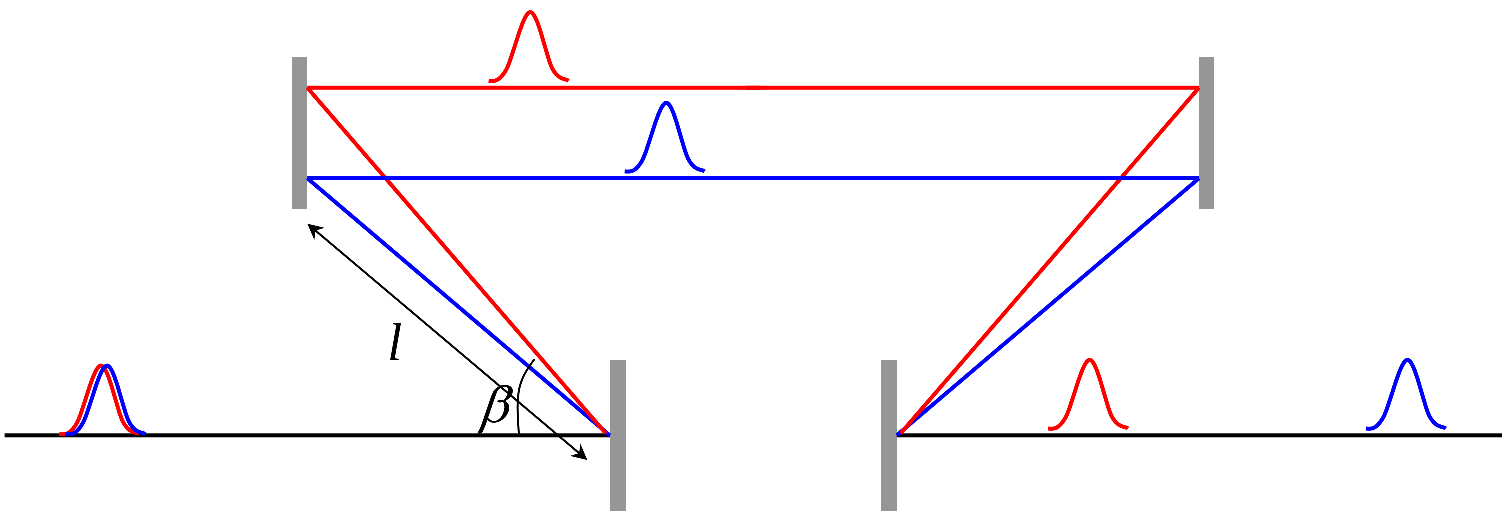
Chirped Pulse Amplification

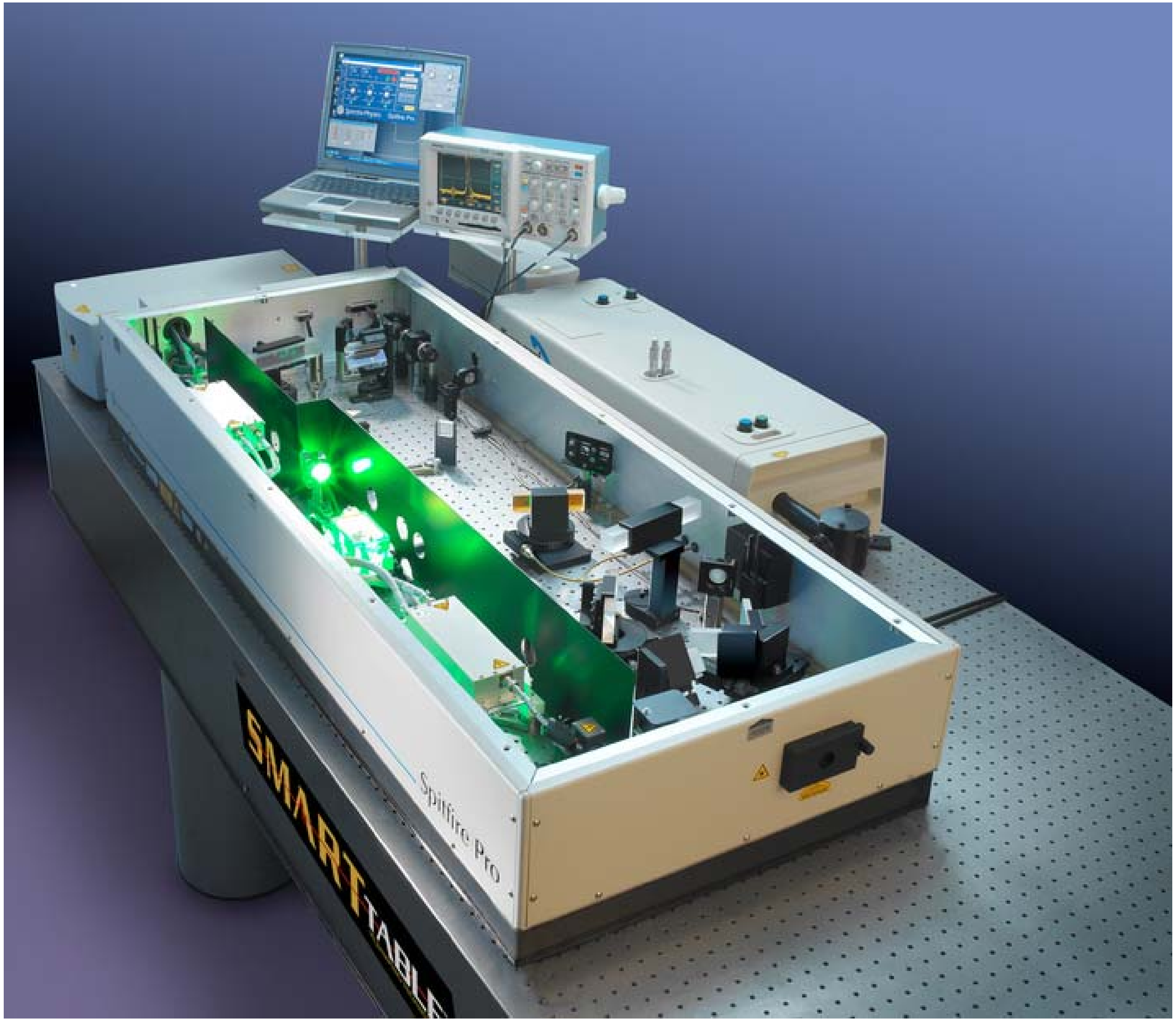


Grating-Stretcher

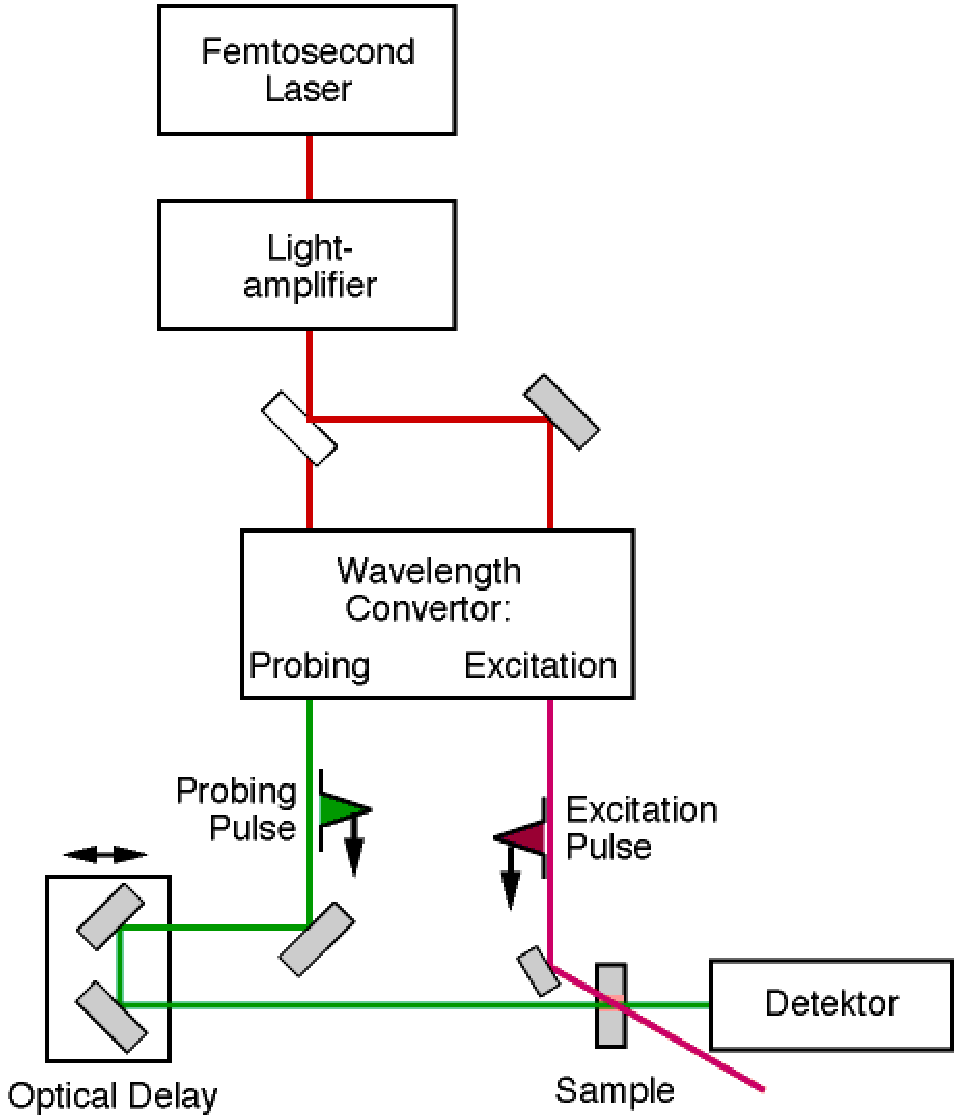


Grating-Compressor

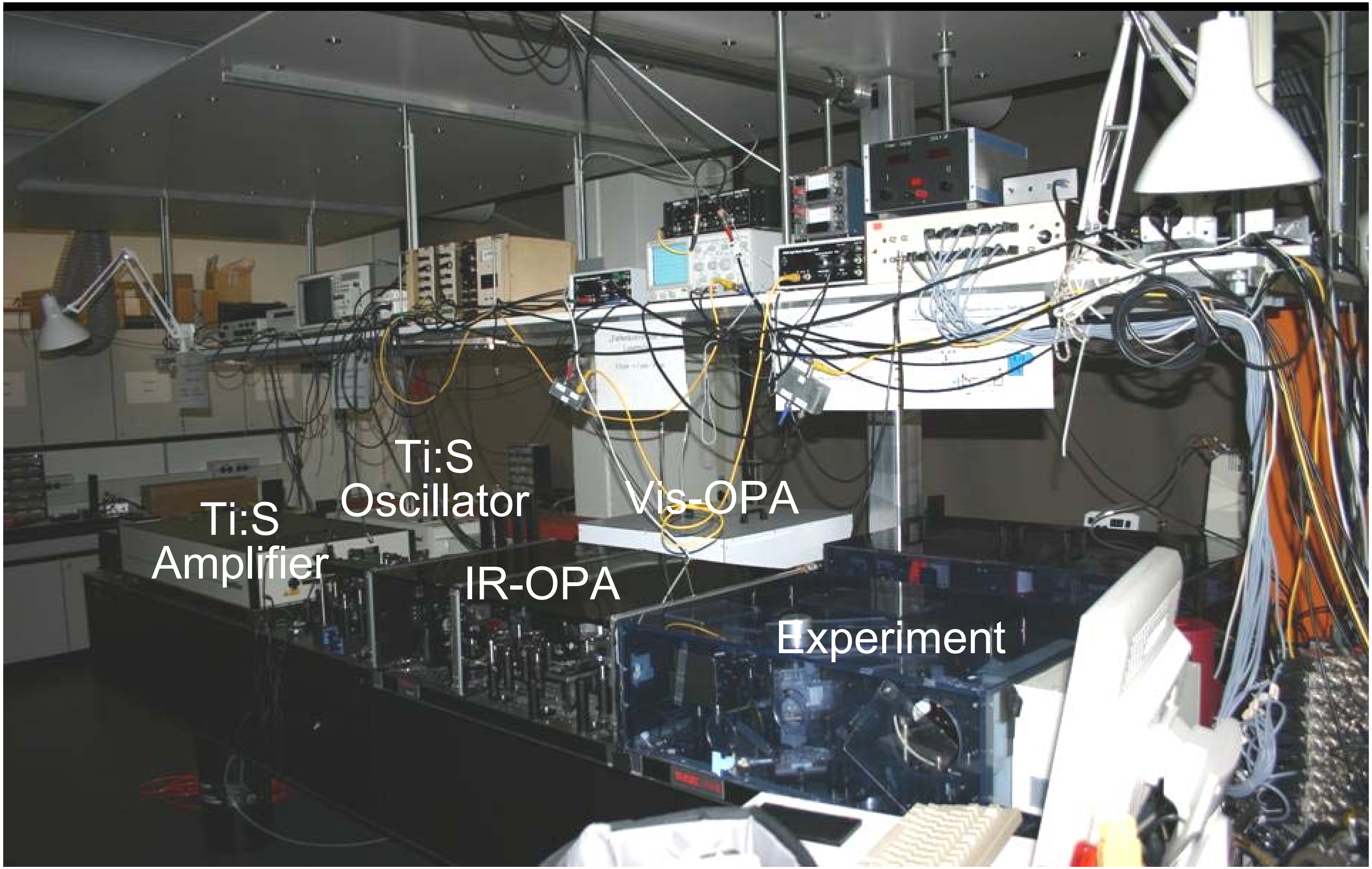



Spitfire Pro
SMARTTABLE

Pump-Probe Spectroscopy



The Laser Lab



Nonlinear Optics

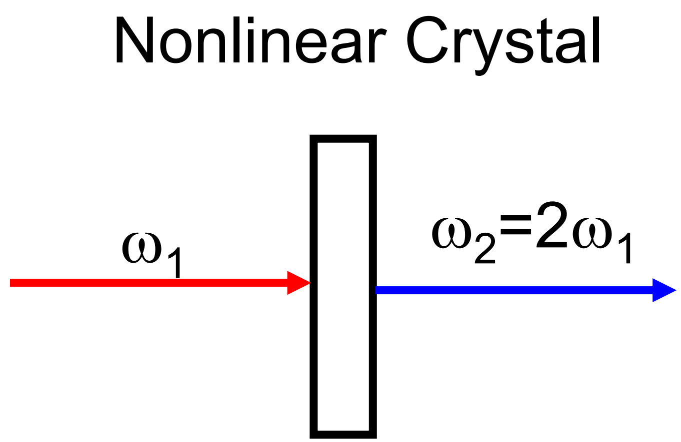
$$P = \chi_1 \cdot E$$

$$E = E_0 \cos \omega t$$

$$P^{(1)} = \chi_1 \cdot E_0 \quad \cdot \cos(\omega t)$$

$$P^{(2)} = \chi_2 \cdot E_0{}^2 \cdot \left(1 + \cos(2\omega t)\right)$$

Second Harmonic Generation



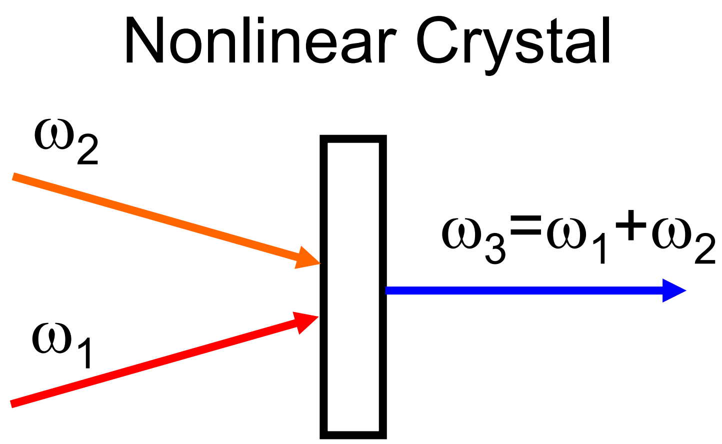
Nonlinear Optics

$$P = \chi_1 \cdot E + \chi_2 \cdot E \cdot E + \dots$$

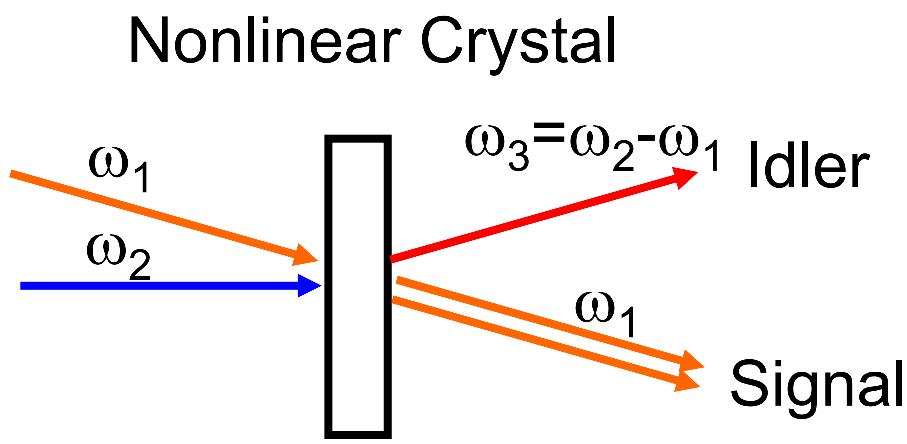
$$E = E_0 \cos \omega_1 t + E_0 \cos \omega_2 t$$

$$P^{(2)} = \chi_2 \cdot E_0{}^2 \cdot \left(\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t \right)$$

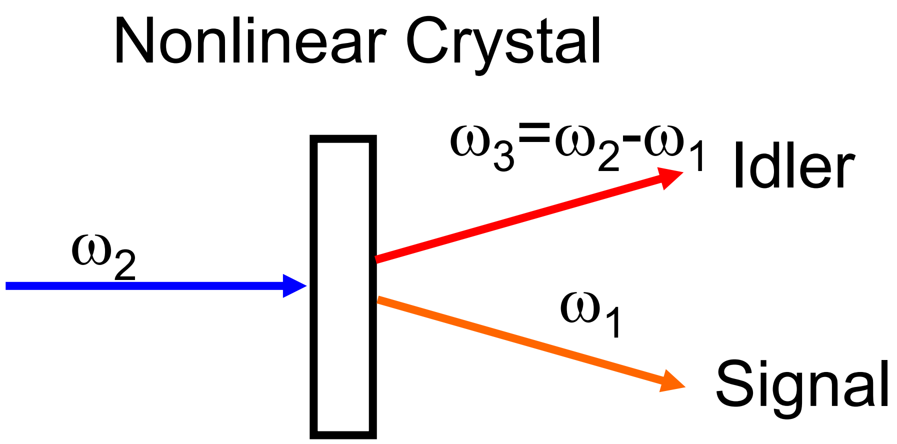
Sum Frequency Generation



Difference Frequency Mixing

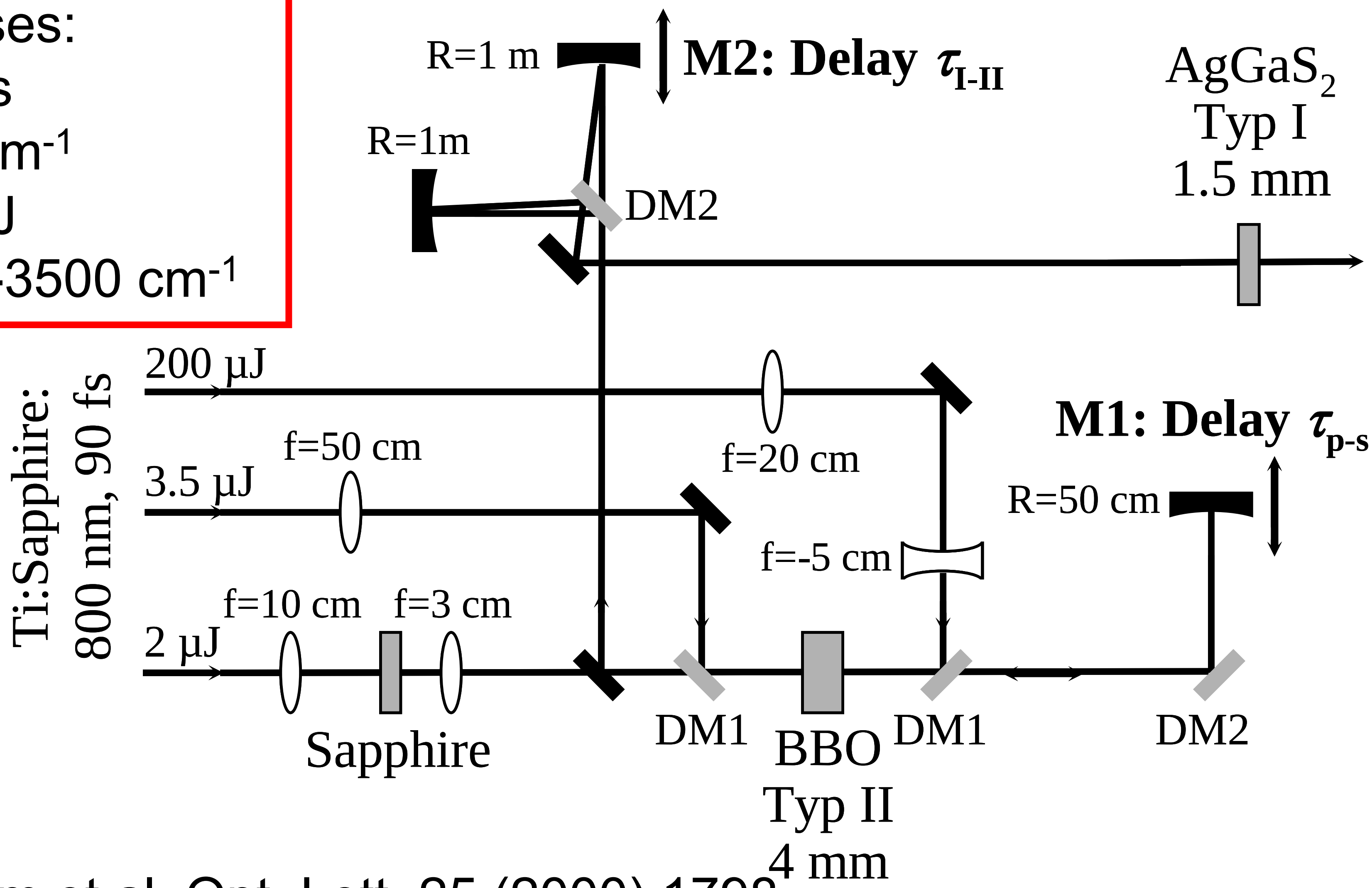


Optical Parametrical Process



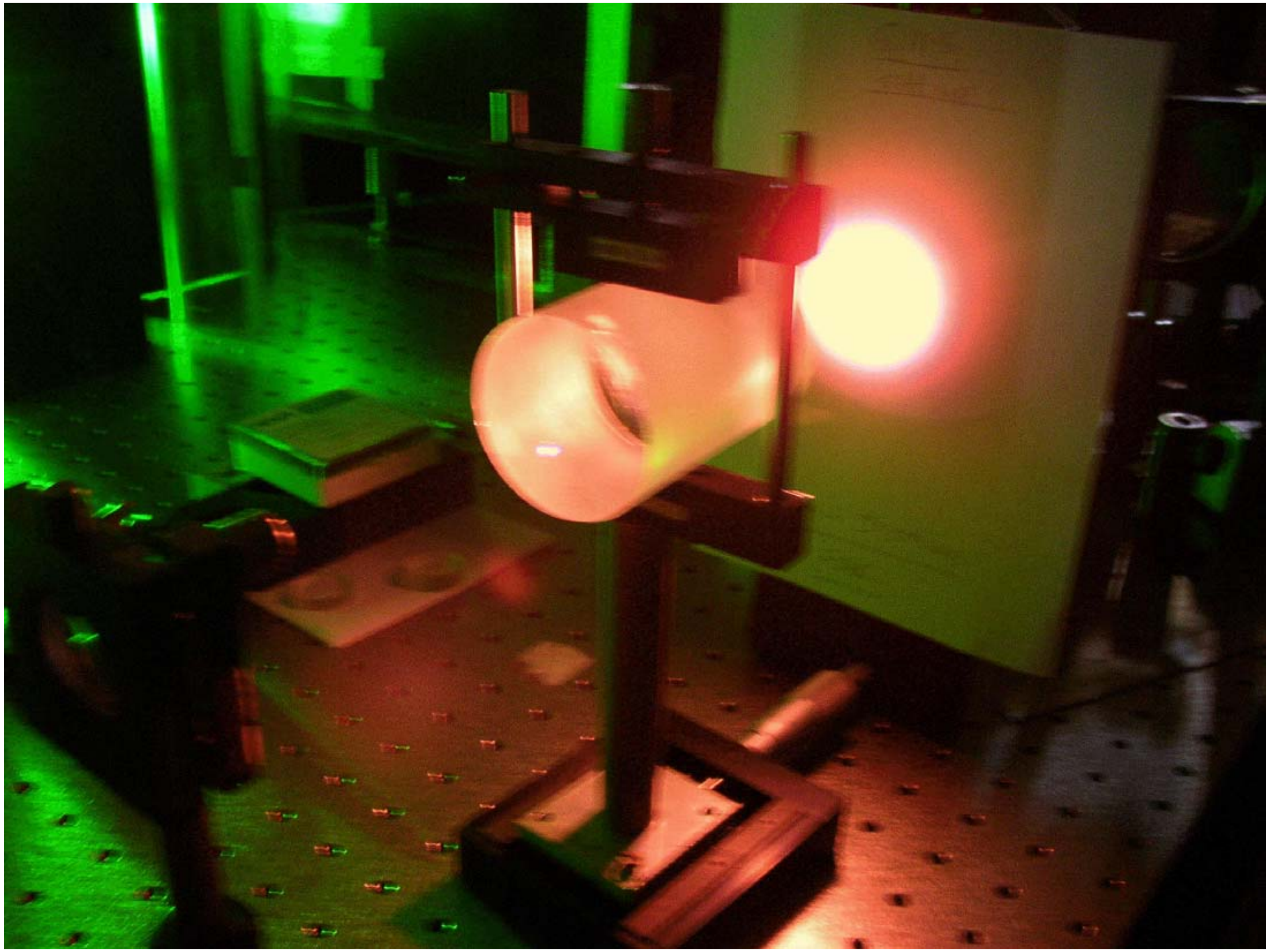
IR Light Source

IR Pulses:
- 100 fs
- 200 cm^{-1}
- 1-2 μJ
- 1000-3500 cm^{-1}

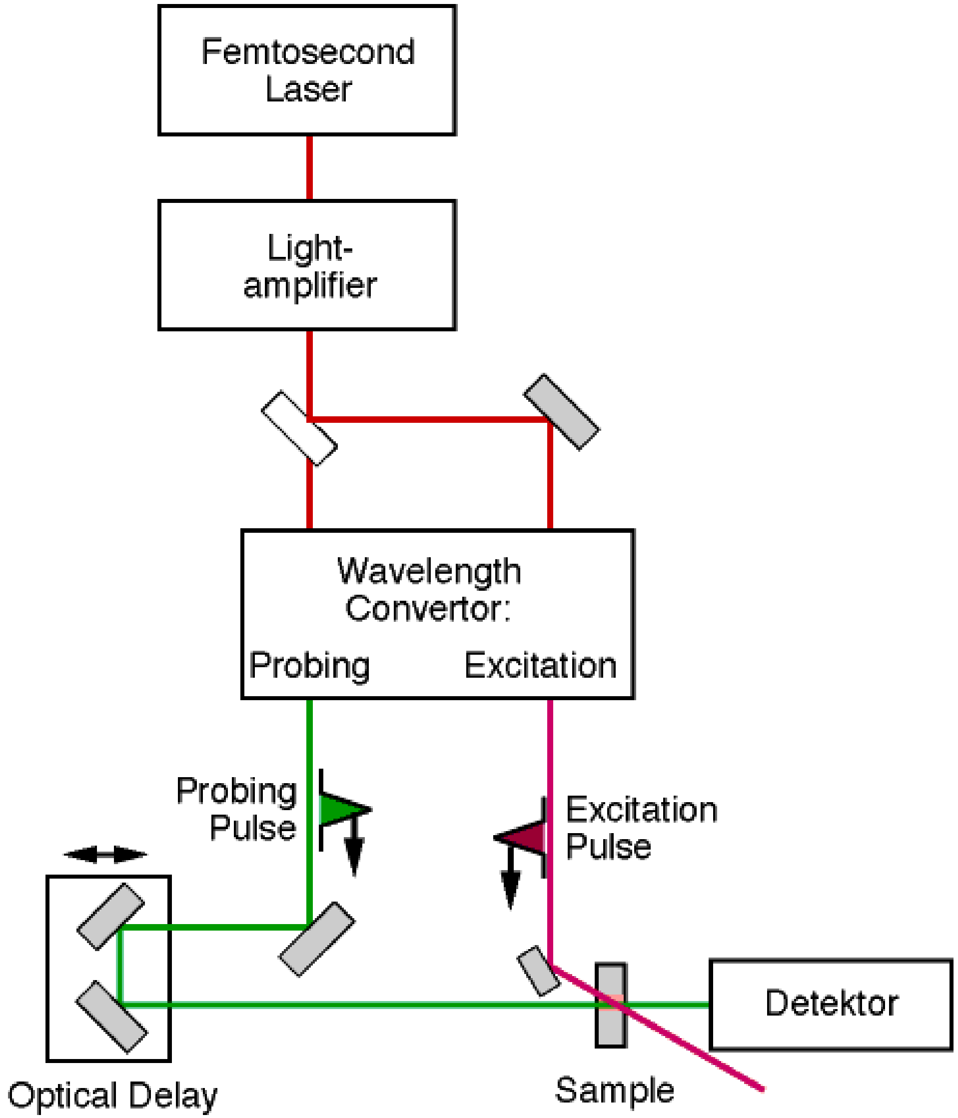


P. Hamm et al. Opt. Lett. 25 (2000) 1798

White-light Generation



Pump-Probe Spectroscopy



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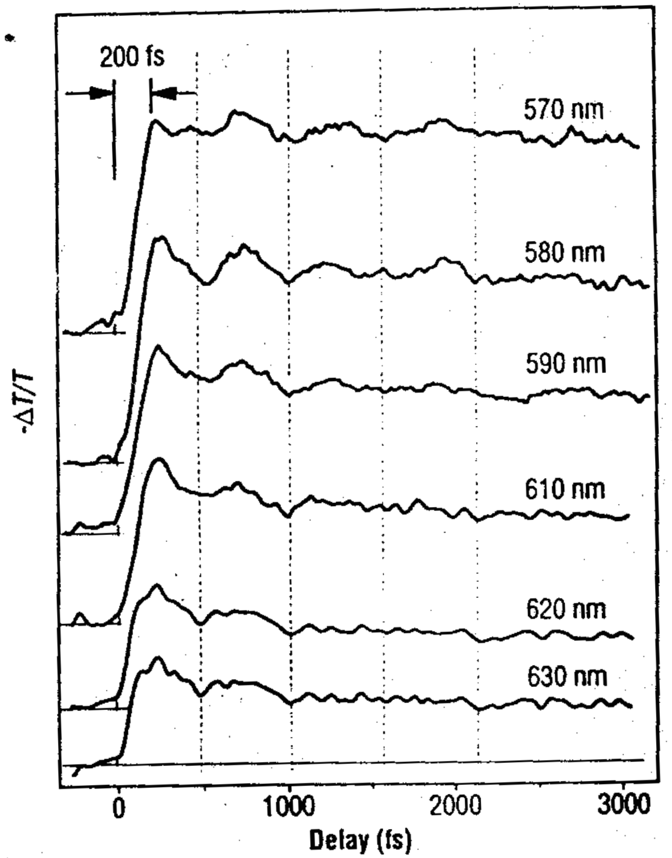
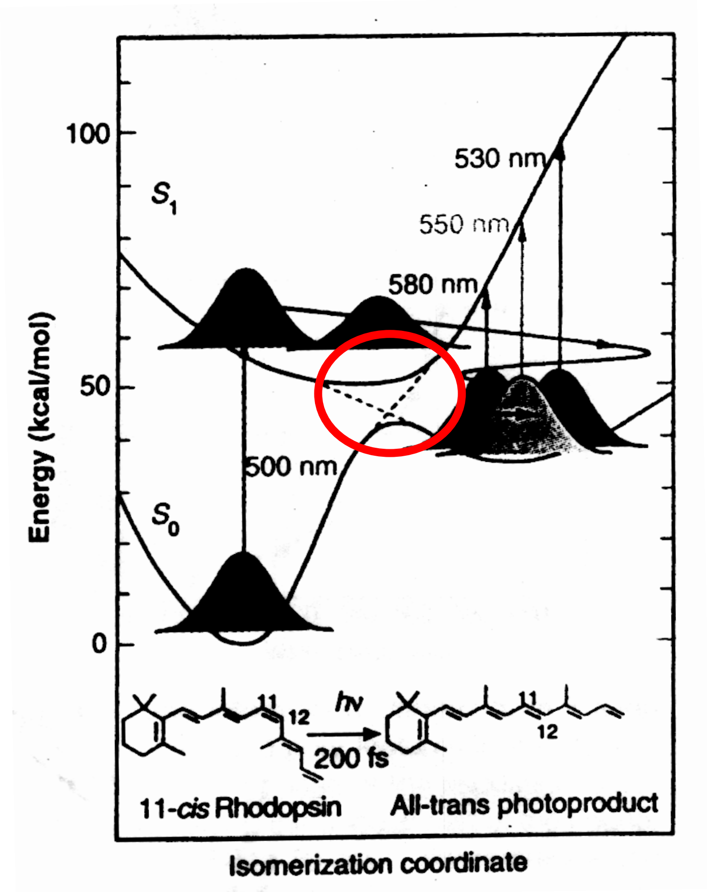
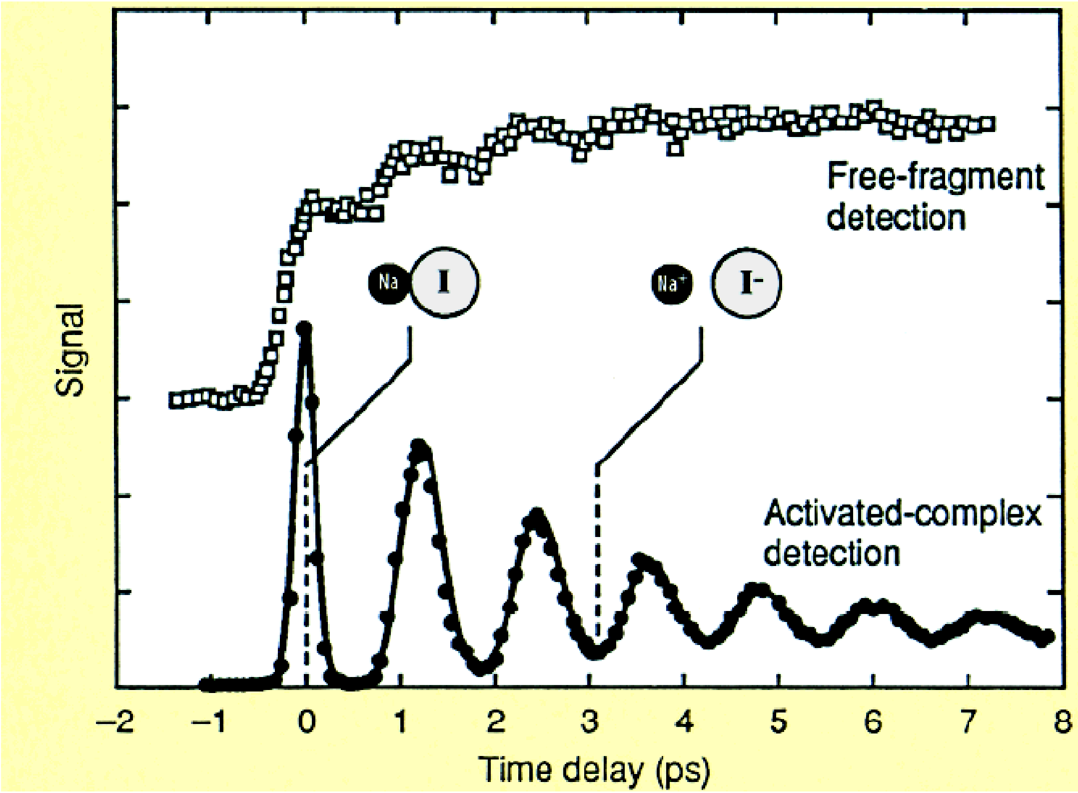
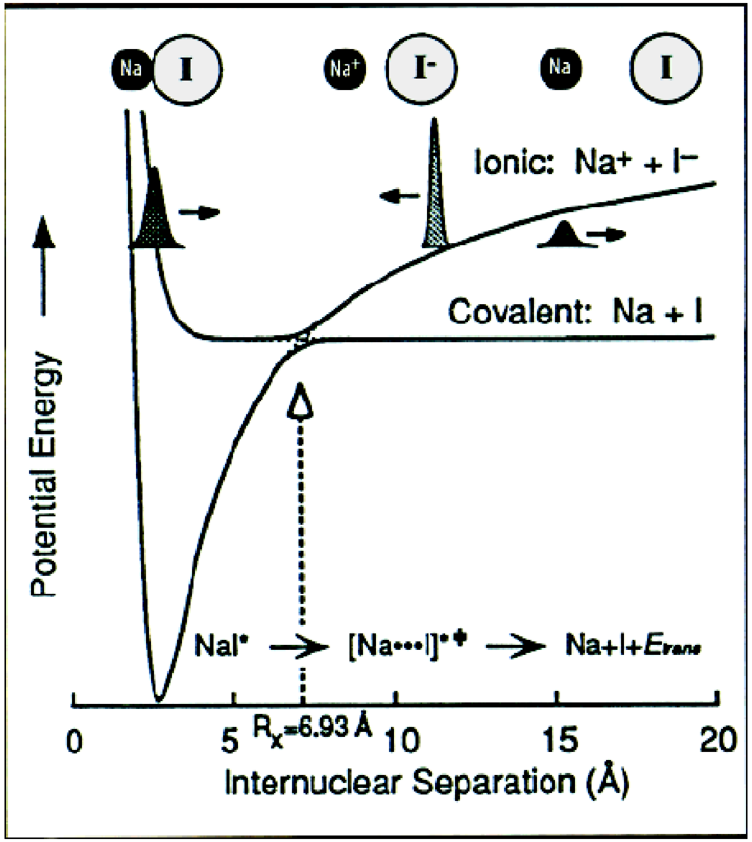




Q. Wang, R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank, Science 266 (1994) 422

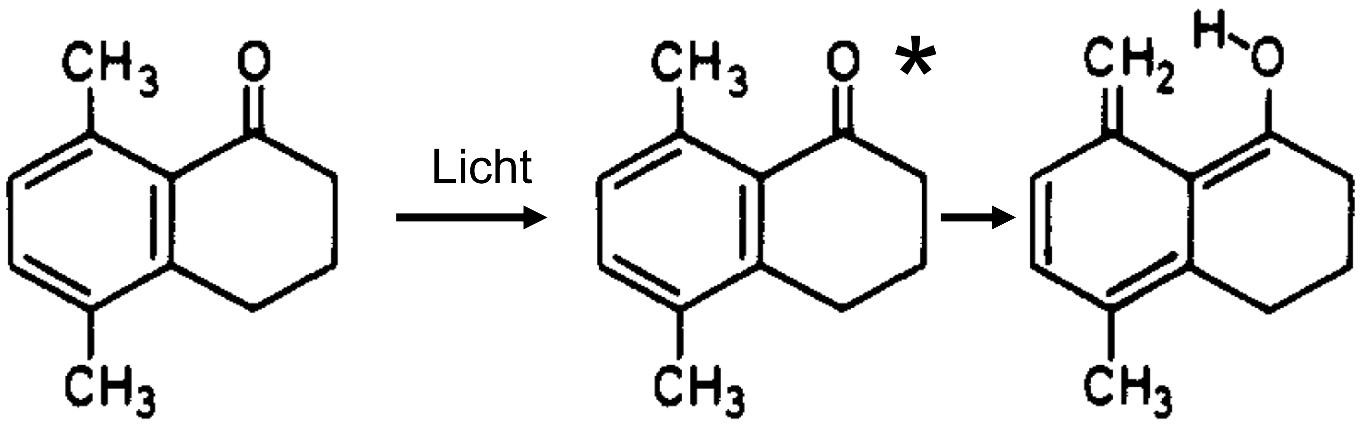
Prototype Photochemical Reaction: NaI

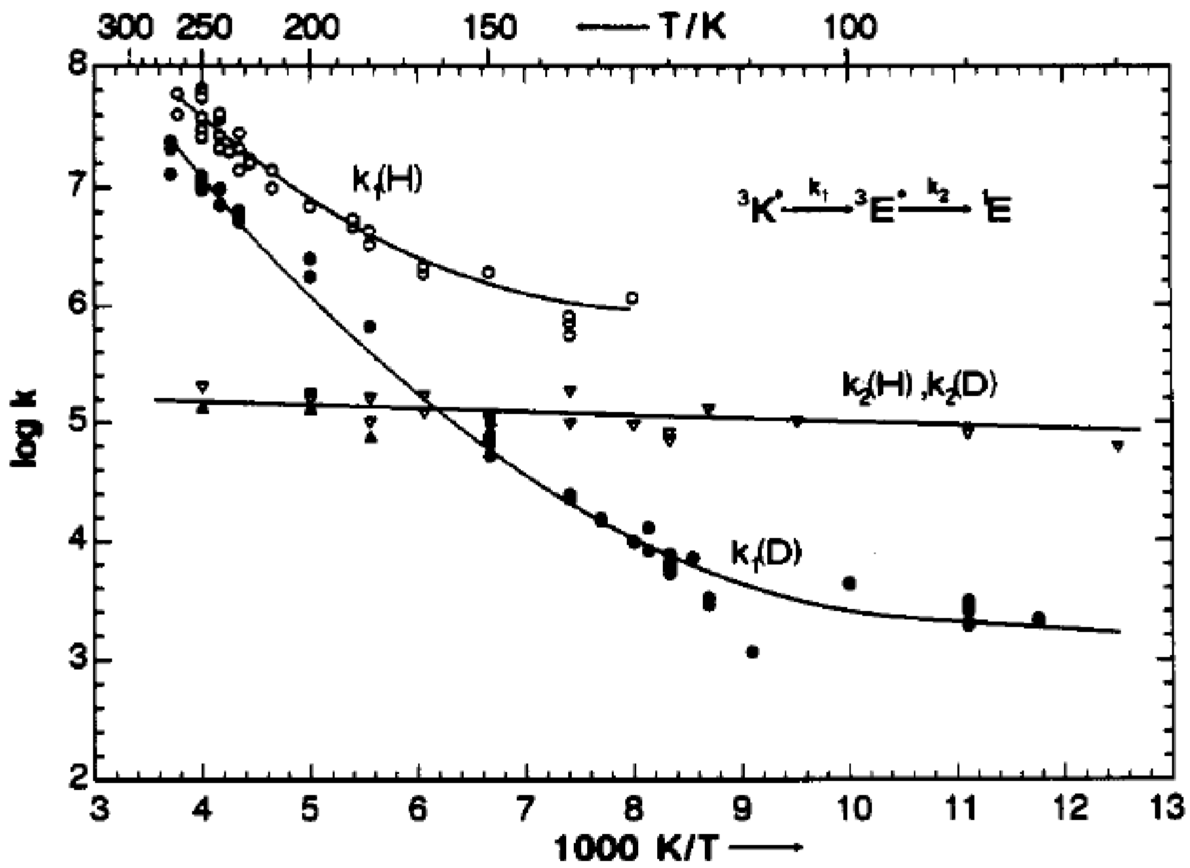




T. S. Rose, M. J. Rosker, A. H. Zewail, J. Chem. Phys. 91 (1989) 7415

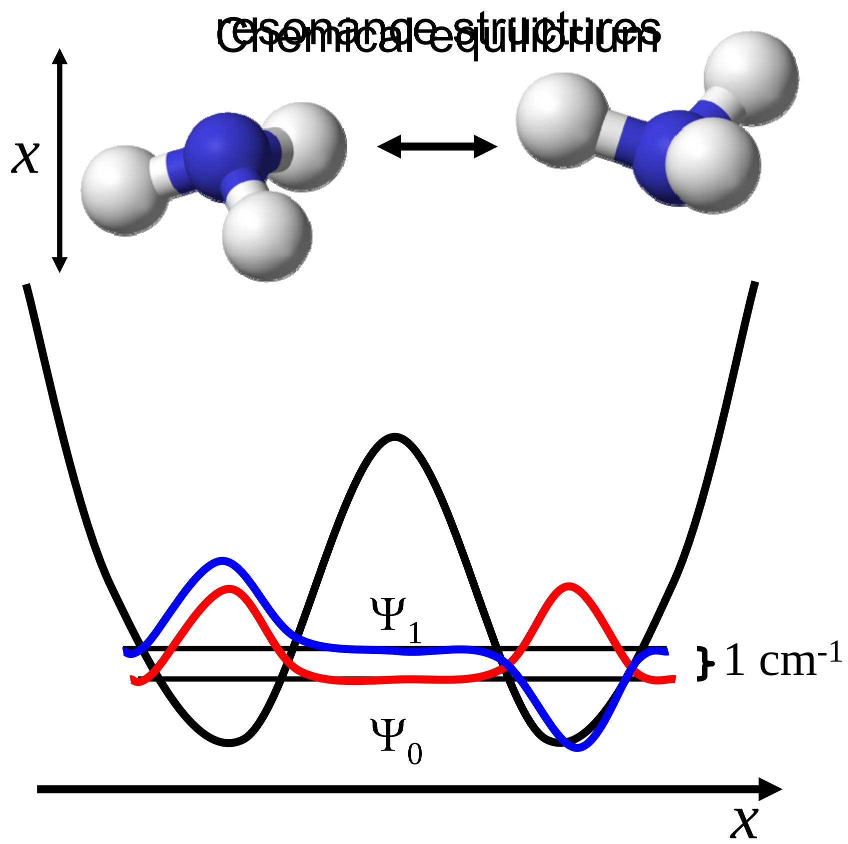
A. H. Zewail, J. Phys. Chem. A 104 (2000) 5660

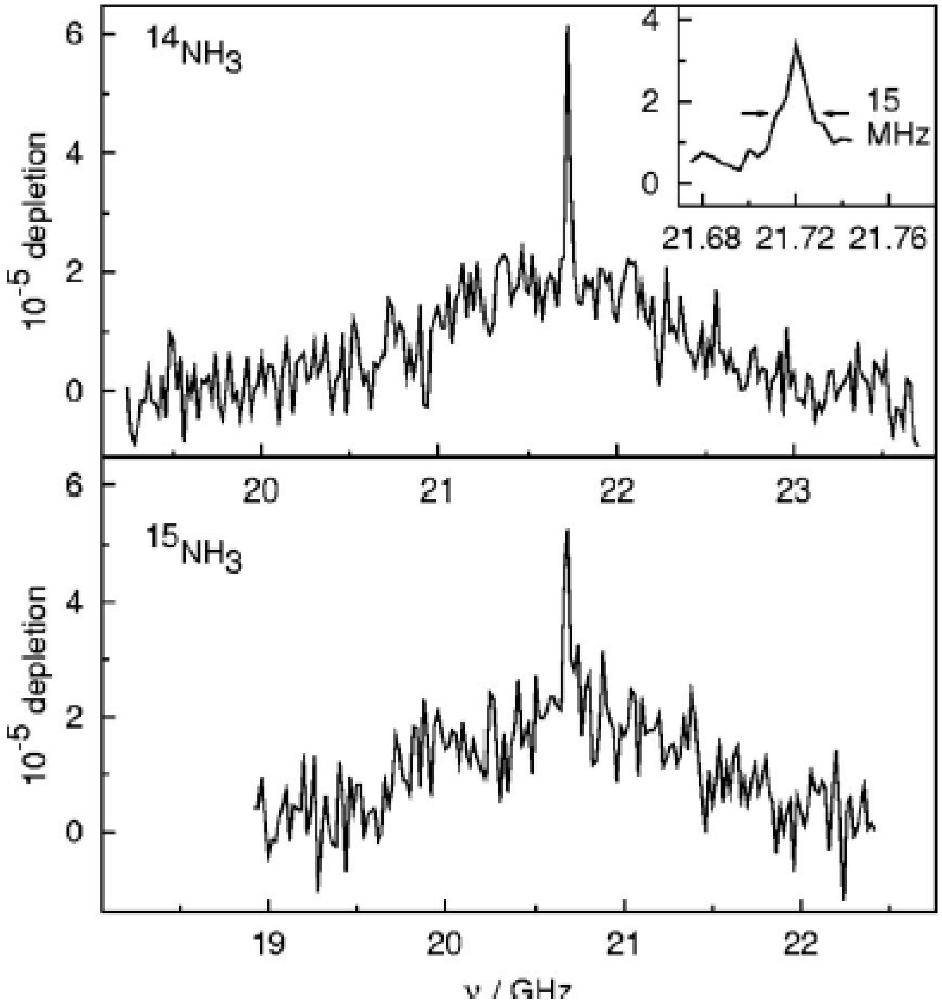




J. Phys. Chem.; **1991**; *95*; 2022.

Inversion Tunneling in Ammonia (in He droplets)





J. Chem. Phys. ***127****, 241101 (2007)*

Time-propagating Wavepackets

- in an eigenstate basis:

$$\Psi(t) = \sum \left\langle \Psi(t=0) \middle| \varphi_i \right\rangle \varphi_i e^{-i\frac{E_i}{\hbar}t}$$

- direct propagation

$$\Psi(t) = e^{-i\frac{\hat{H}}{\hbar}t}\Psi(t=0)$$

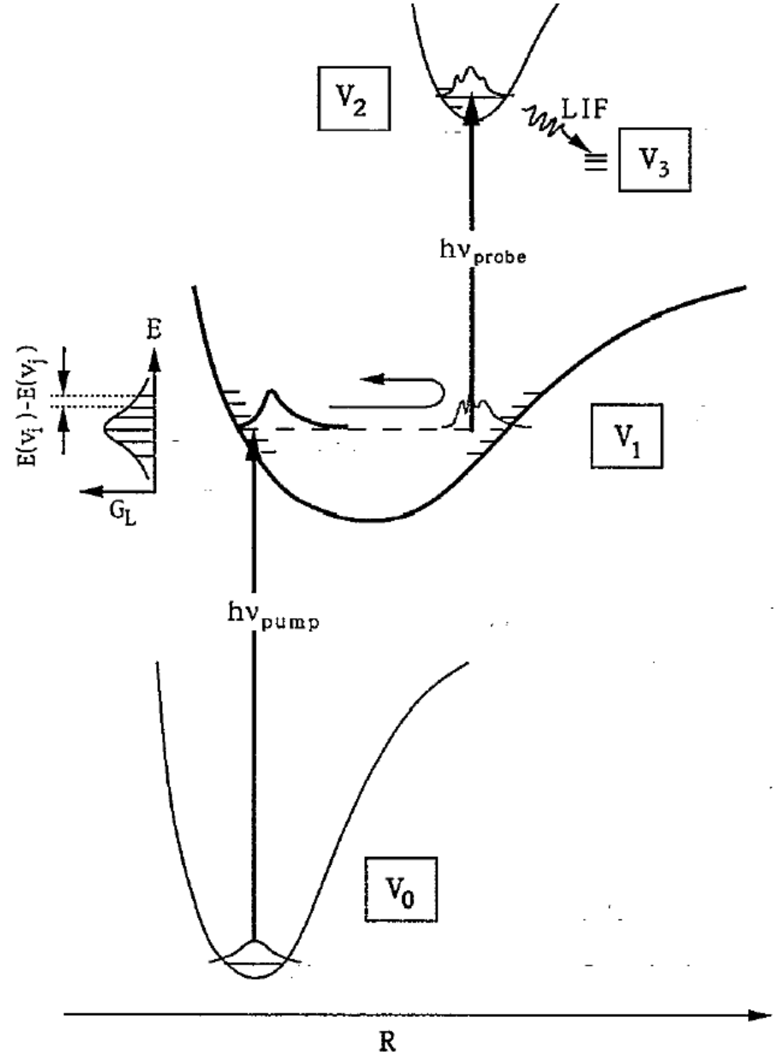
with

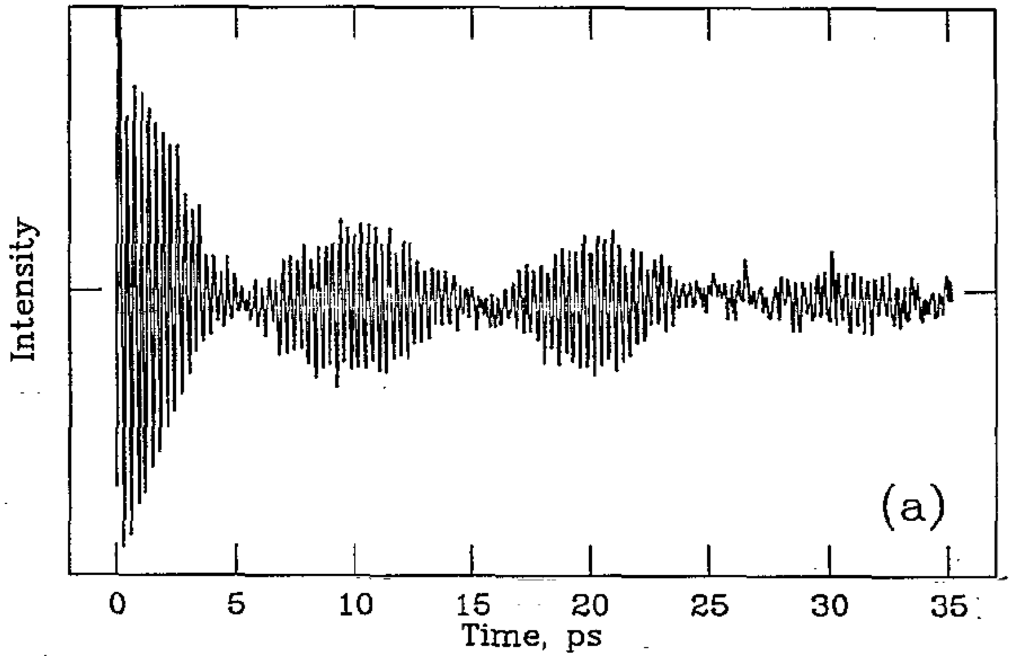
$$e^{-i\frac{\hat{H}}{\hbar}t} \equiv 1 - i\frac{\hat{H}}{\hbar}t - \frac{\hat{H}^2}{\hbar^2}t^2 + \dots$$

- simple numerical scheme by discretizing time

$$\Psi(t+\Delta t) = \Psi(t-\Delta t) - 2i\frac{\hat{H}}{\hbar}\Psi(t)\cdot\Delta t$$

Motion in Quantum Mechanics: I_2

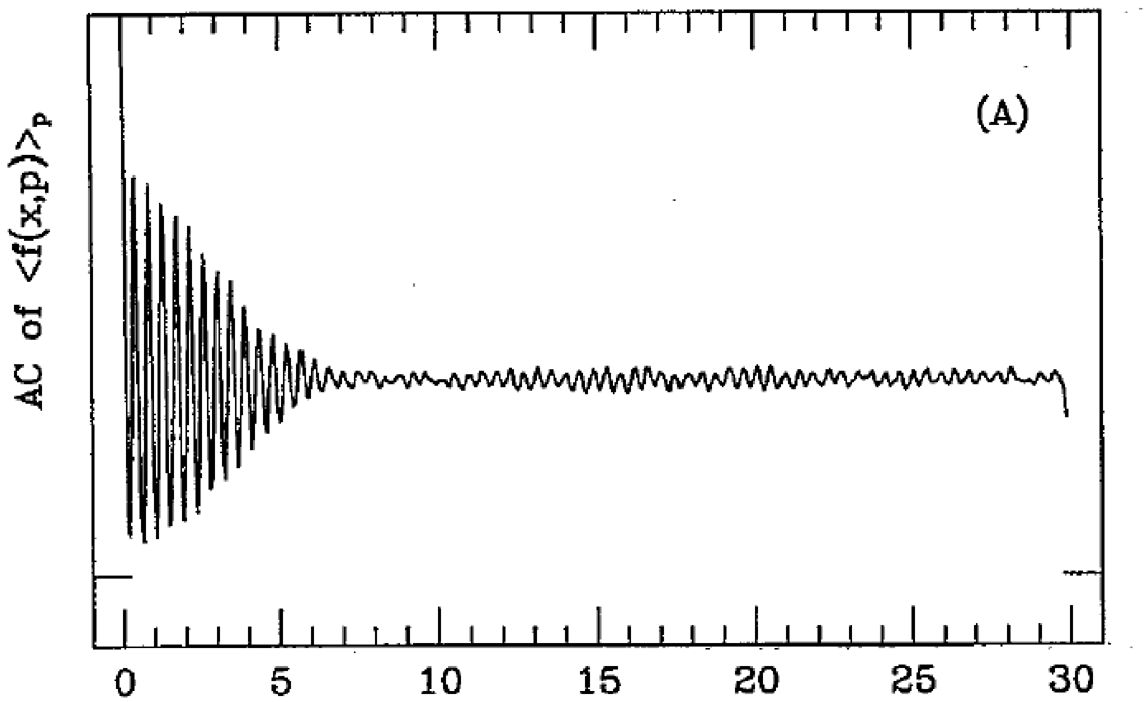




M. Gruebele, A. H. Zewail, J. Chem. Phys. 98 (1993) 883

Wavepackets: I_2

Classical Wavepacket



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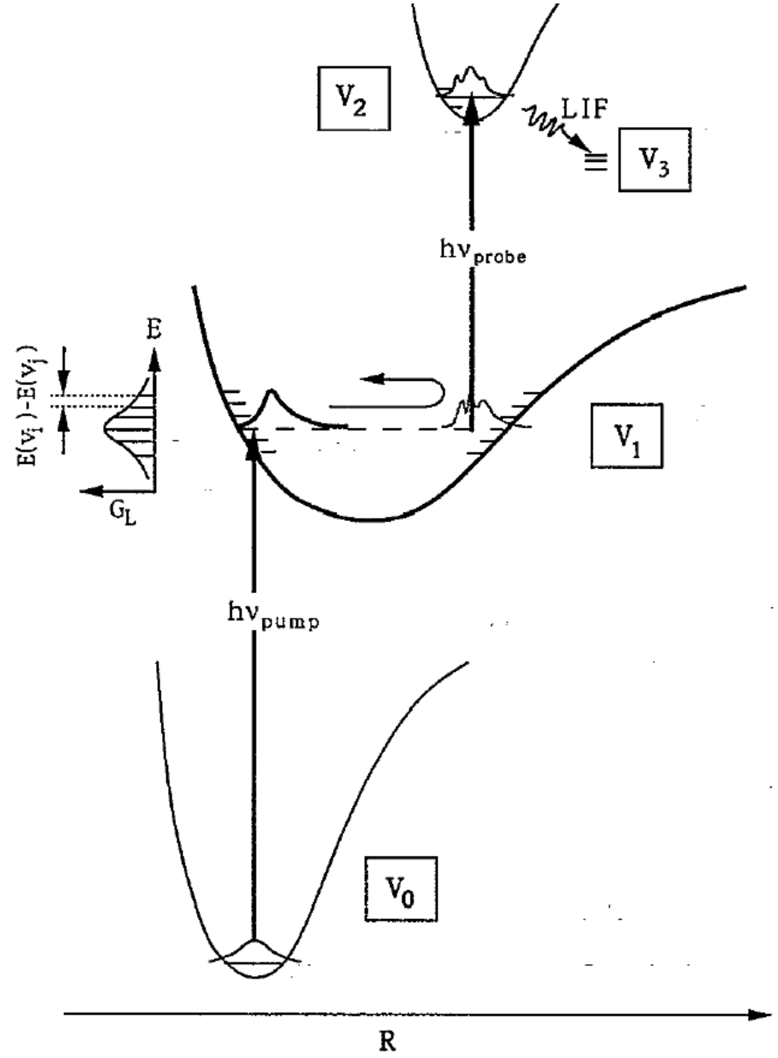
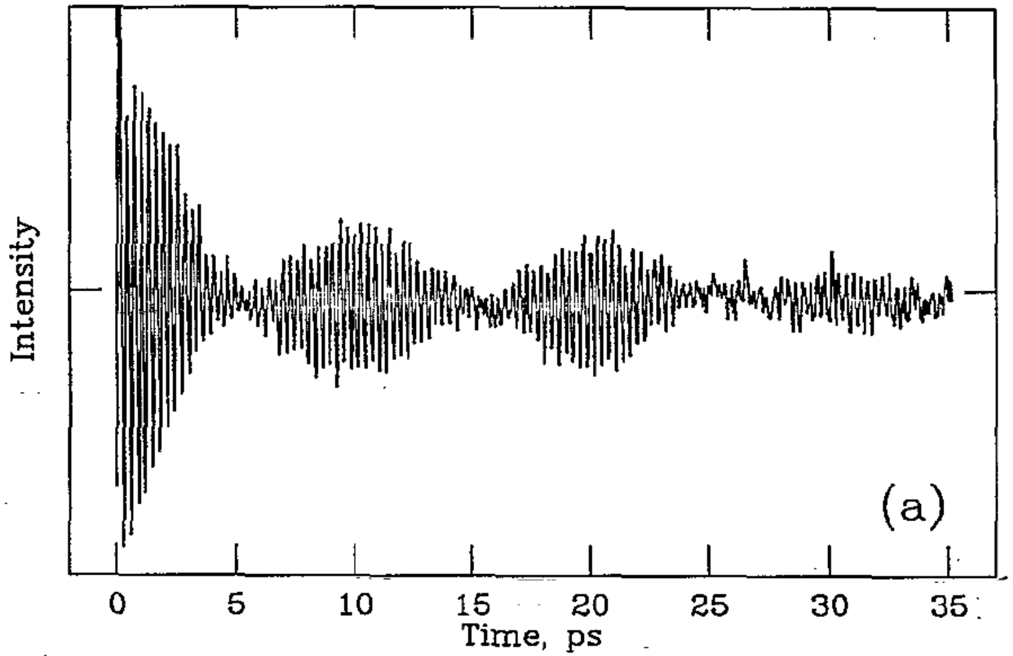
Motion in Quantum Mechanics: I_2





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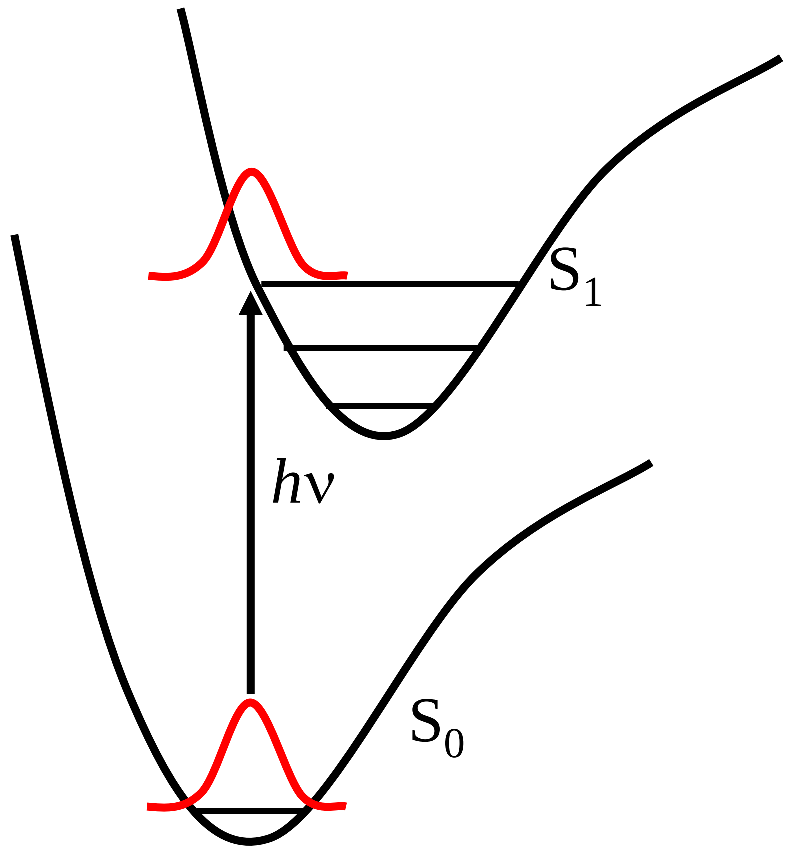
Vertical Franck Condon Transition



$$\Psi(t=0) = \sum_i \langle \phi_0^{(S_0)} | \phi_i^{(S_1)} \rangle \phi_i^{(S_1)}$$

$$\Psi(t=0) = \phi_0^{(S_0)}$$

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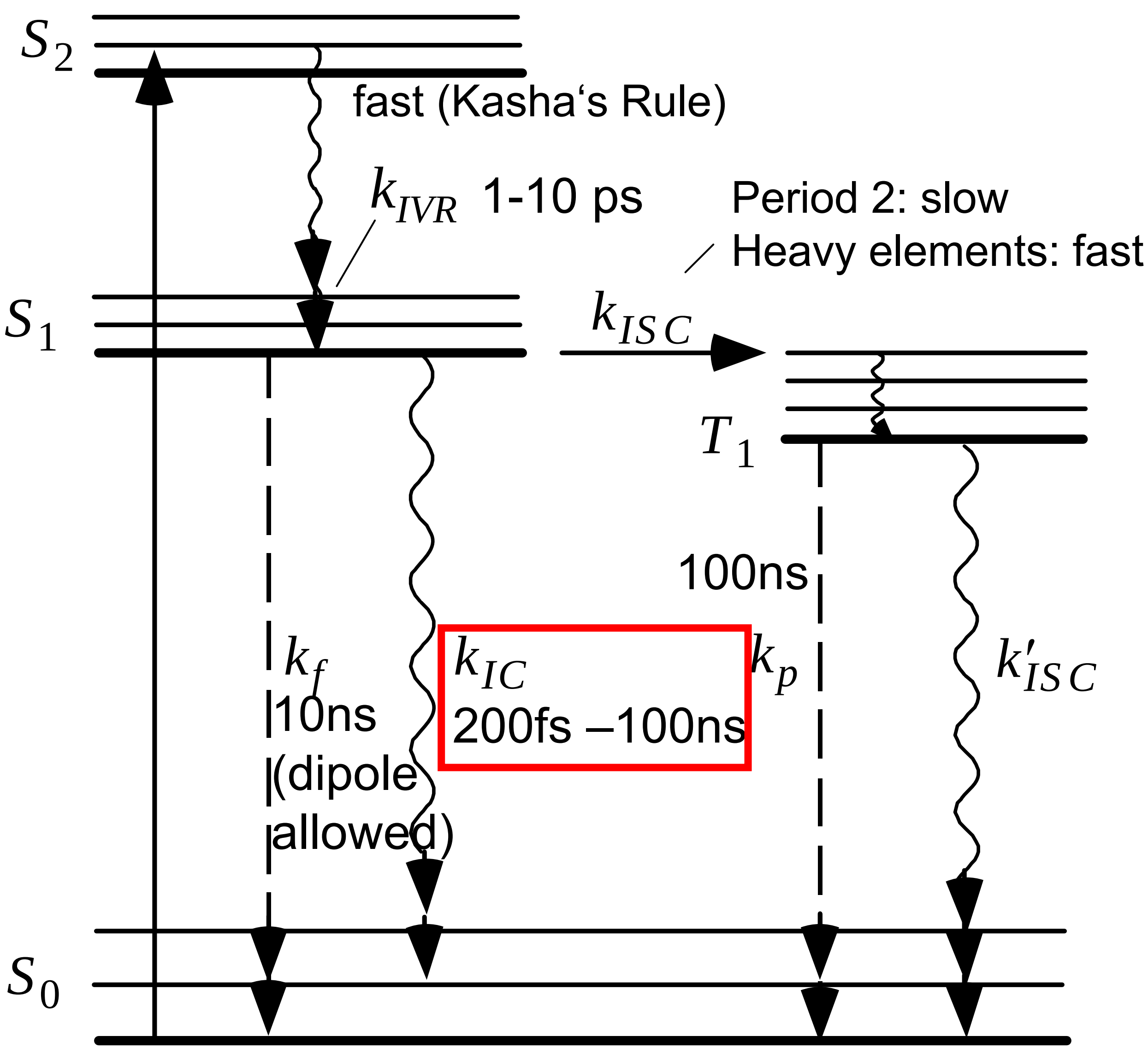
Jablonski Diagram



k_{IVR}: Intramolecular Vibrational Energy Relaxation

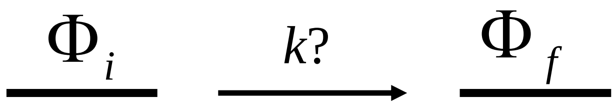
k_f: Fluorescence

k_p: Phosphorescence

k_{IC}: Internal conversion (non-radiadive decay)

k_{ISC}: Intersystem Crossing

Fermi Golden Rule: Derivation



$$H = \begin{pmatrix} E_i & V \\ V & E_f \end{pmatrix} \quad \text{with} \quad V = \langle \Phi_i | \hat{V} | \Phi_f \rangle$$

propagating the time-dependent SEQ:

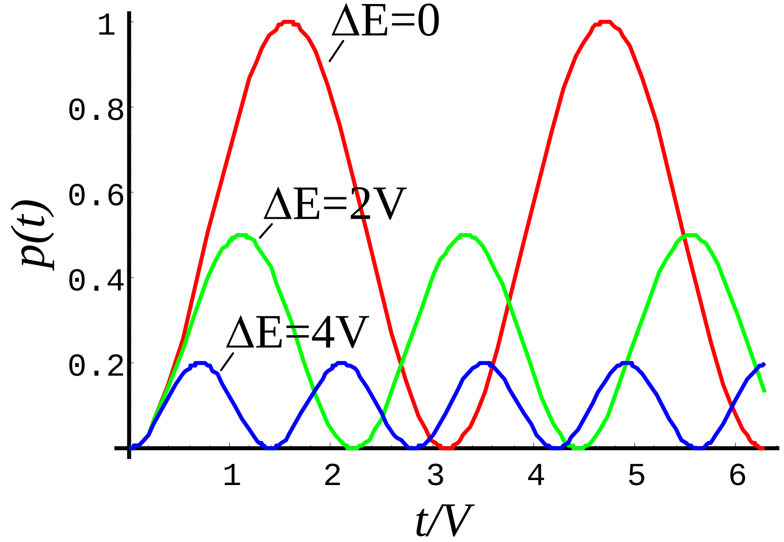
$$p(t) \equiv |\langle \Psi(t) | \Phi_i \rangle|^2 = c_f^2 = \sin^2\left(\frac{V}{\hbar} t\right)$$

same for non-resonant states:

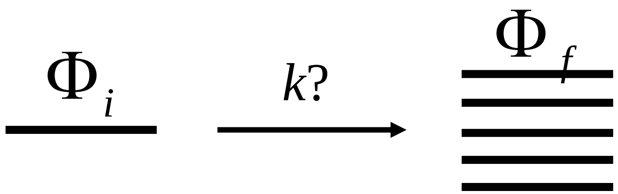
$$p(t) = \frac{4V^2}{\Delta E^2 + 4V^2} \sin^2\left(\frac{\sqrt{\Delta E^2 + 4V^2}}{2\hbar} t\right)$$

with V<<ΔE

$$p(t) = \frac{4V^2}{\Delta E^2} \sin^2\left(\frac{\Delta E}{2\hbar} t\right)$$



Fermi Golden Rule: Derivation

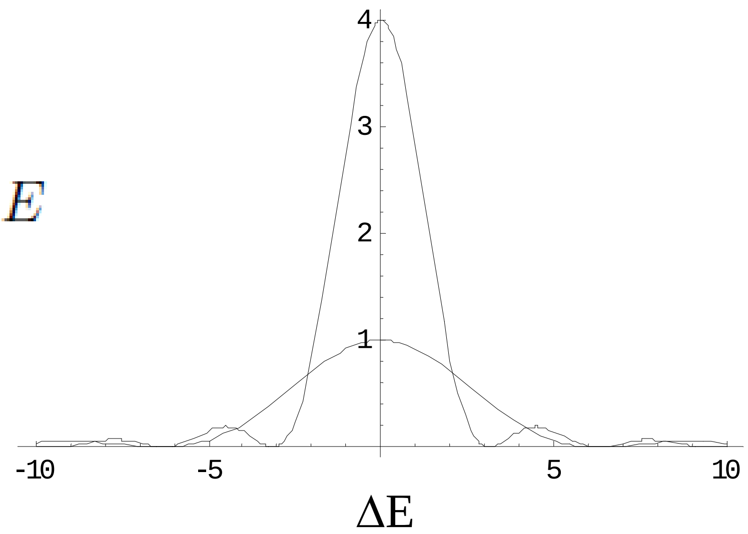


relaxation into a continuum of states:

$$P(t) = \int_{-\infty}^{\infty} p(t)\rho(E)d\Delta E$$

$$P(t) = \rho(E)V^2 \int_{-\infty}^{\infty} \frac{4\sin^2 \Delta E/(2\hbar)t}{\Delta E^2} d\Delta E$$

$$P(t) = \frac{2\pi}{\hbar}\rho(E)V^2 t$$



Fermi Golden Rule

$$k_{if} = \frac{2\pi}{\hbar} V_{if}{}^{2} \delta(\Delta E)$$

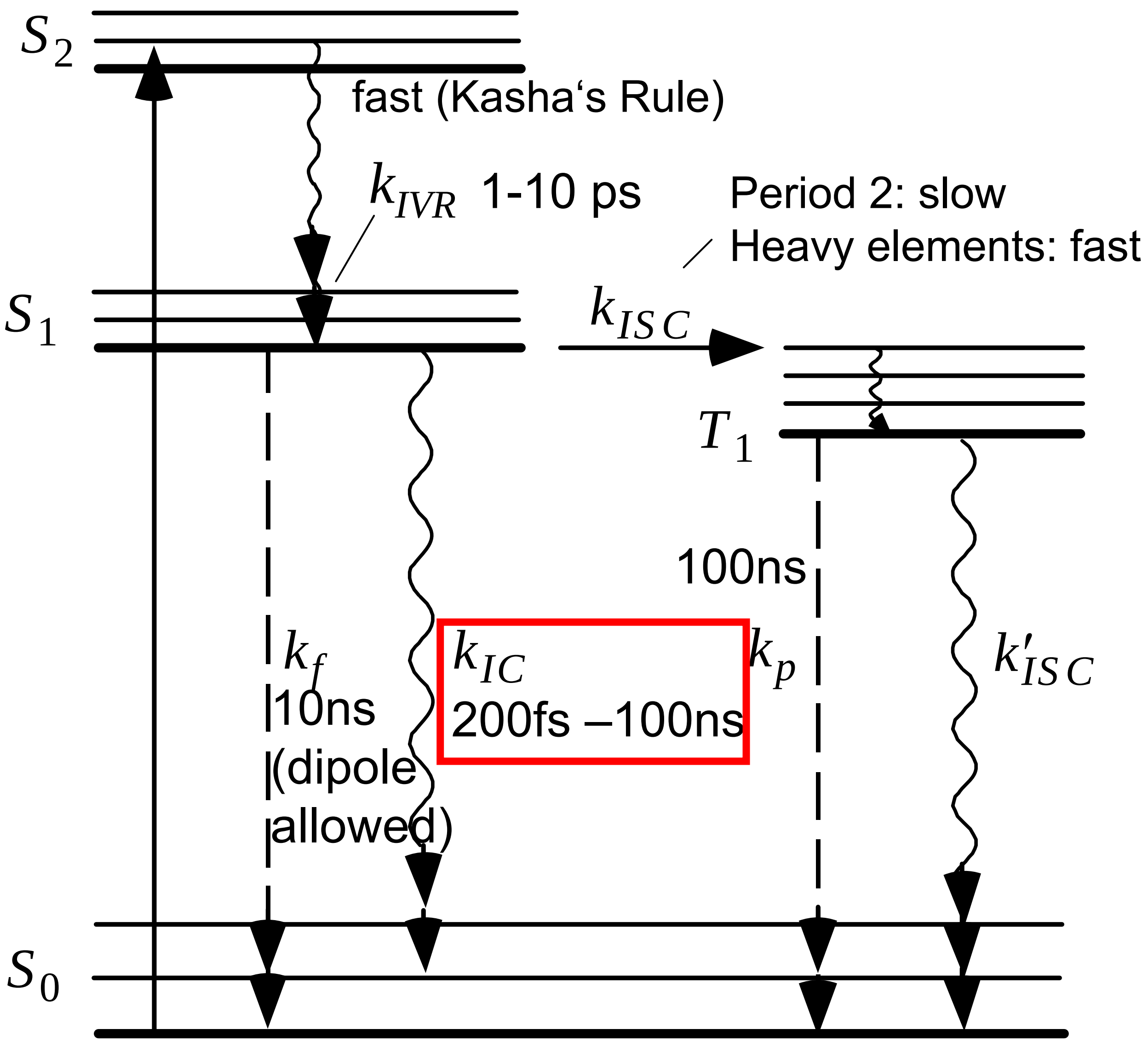
or

$$k_{if} = \frac{2\pi}{\hbar} V_{if}{}^{2} \rho(E)$$

with

$$V_{if} = \langle \Phi_i | V | \Phi_f \rangle$$

Jablonski Diagram



k_{IVR}: Intramolecular Vibrational Energy Relaxation

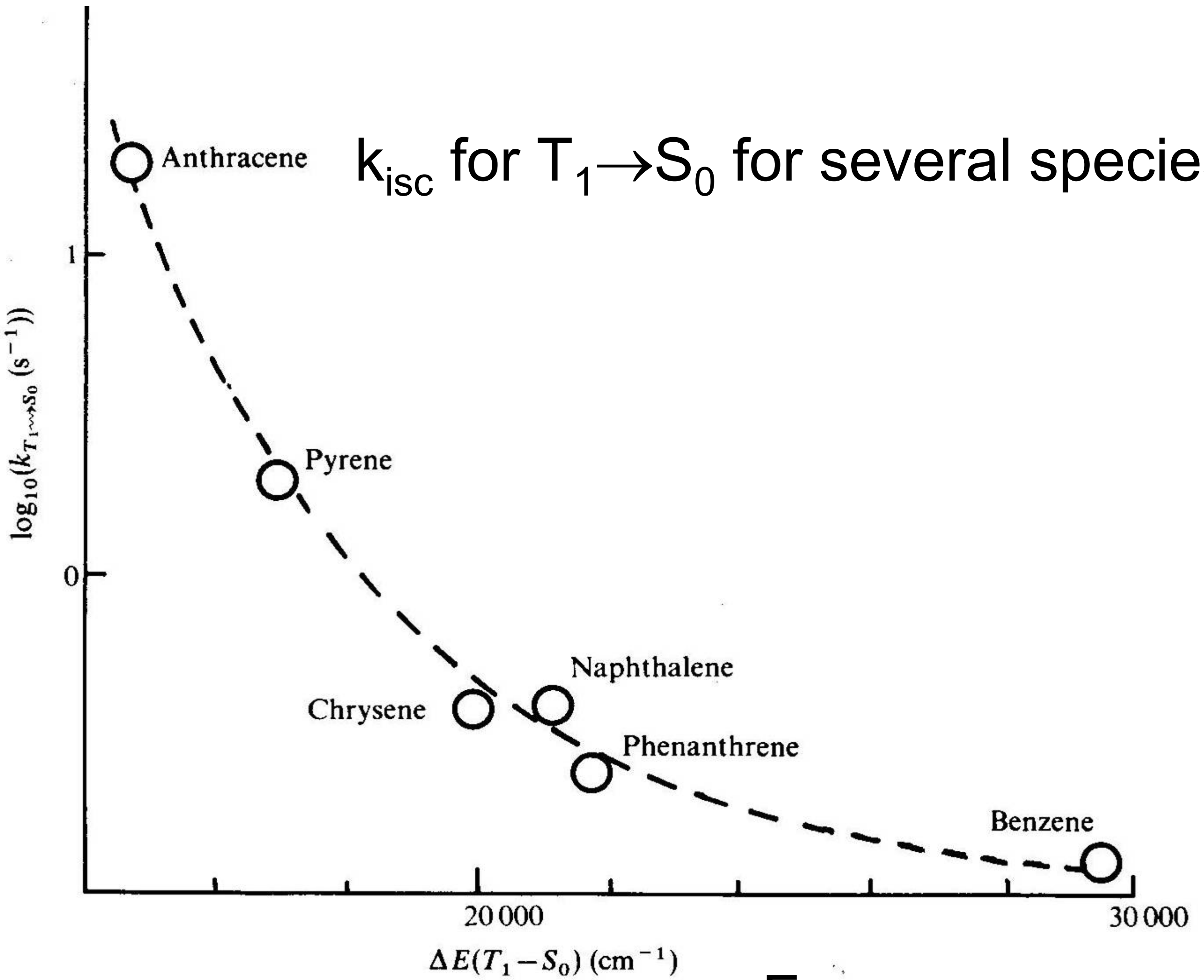
k_f: Fluorescence

k_p: Phosphorescence

k_{IC}: Internal conversion (non-radiadive decay)

k_{ISC}: Intersystem Crossing

Energy Gap Law



k_{isc} for $T_1 \rightarrow S_0$ for several species

Energy gap

Internal Conversion or Non-Radiative Decay

$$k_{if} = \frac{2\pi}{\hbar} V_{if}^{\ 2} \delta(\Delta E)$$

$$V_{if} = \left\langle \Phi_i \middle| V \middle| \Phi_f \right\rangle$$

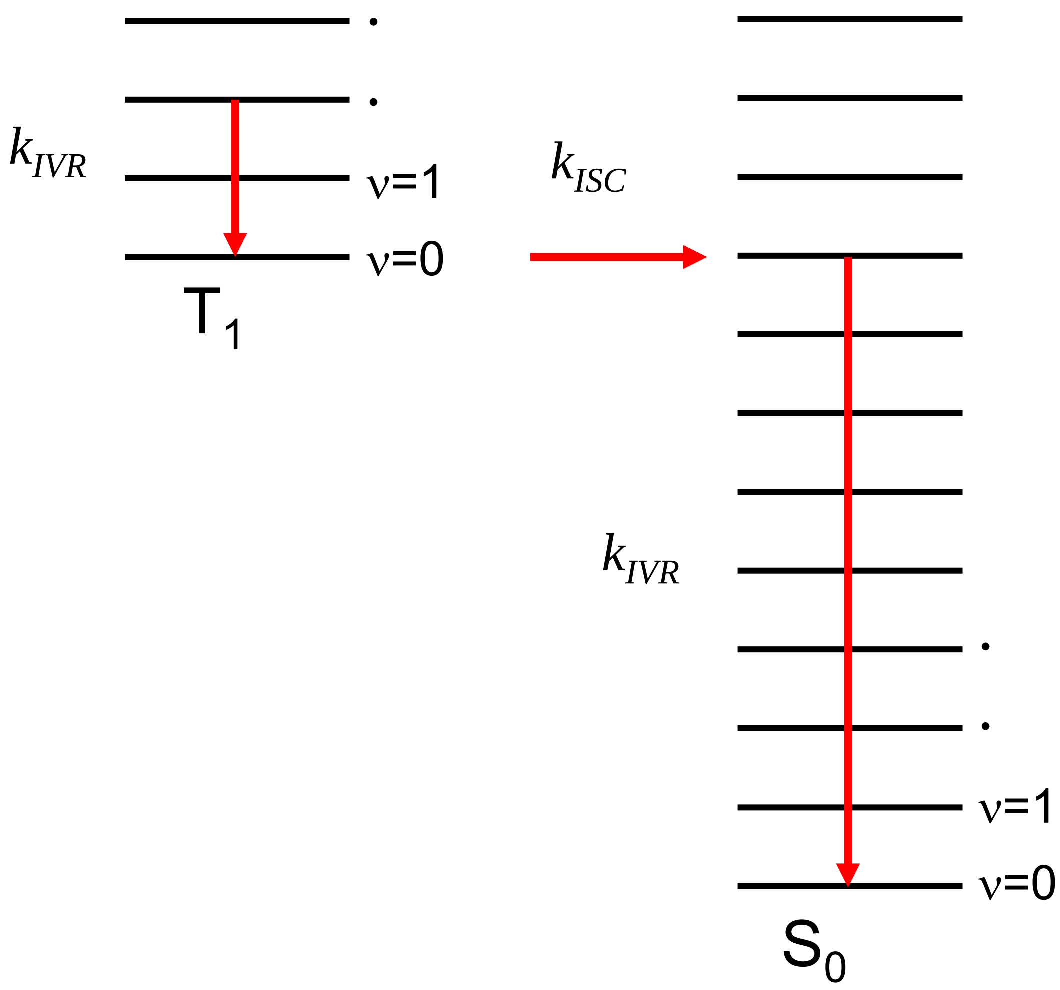
$$\Phi(R, r) = \Psi_{el}(r; R)\chi_{nuc}(R)$$

electronic nuclear

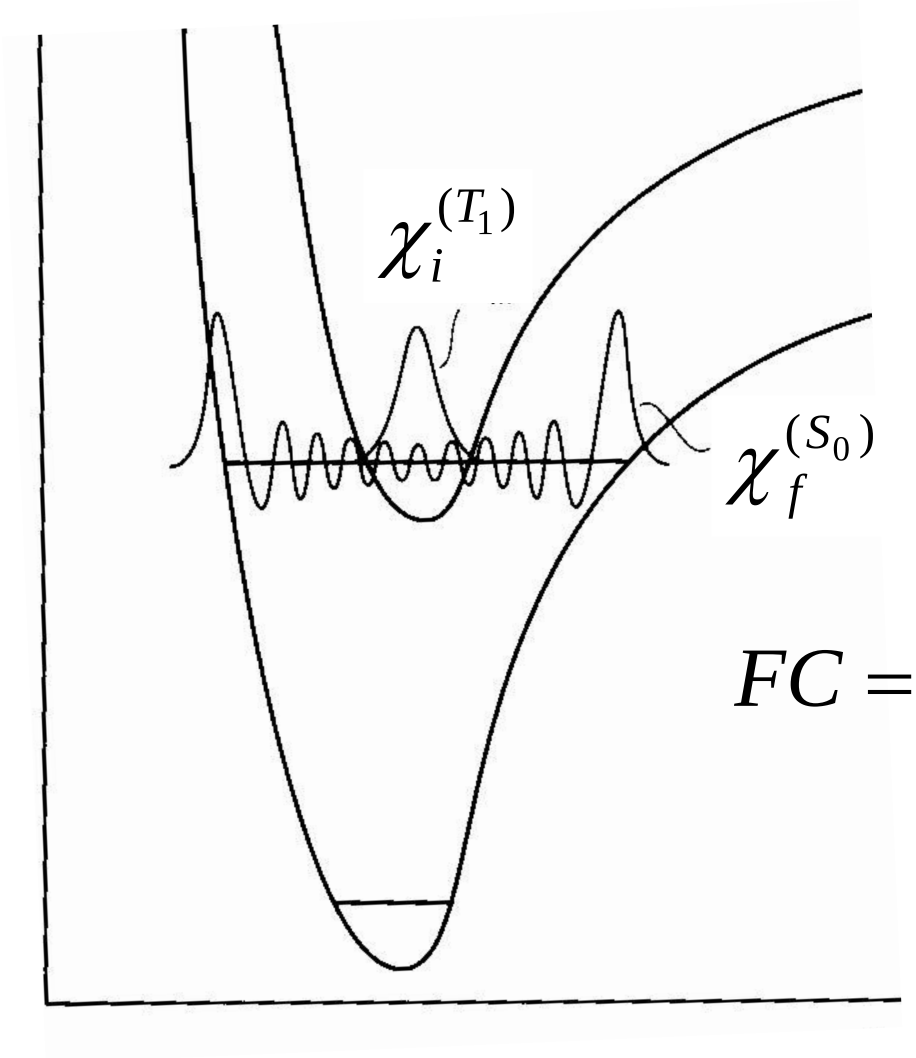
$$V_{if} = \left\langle \Psi_i \middle| V_{el} \middle| \Psi_f \right\rangle \left\langle \chi_i \middle| \chi_f \right\rangle$$

Franck-Condon Factor

Internal Conversion or Non-Radiative Decay



Internal Conversion or Non-Radiative Decay

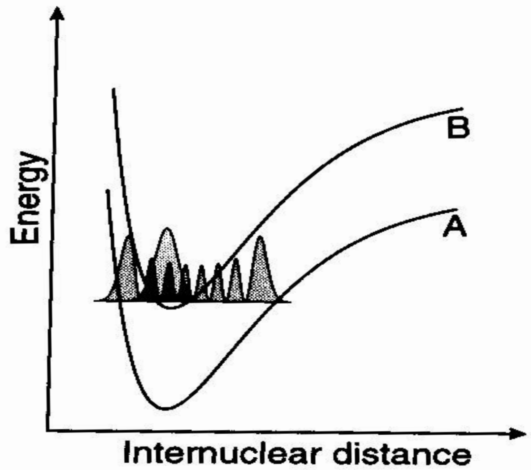


$$FC = \left\langle \chi_i^{(T_1)} \middle| \chi_f^{(S_0)} \right\rangle$$

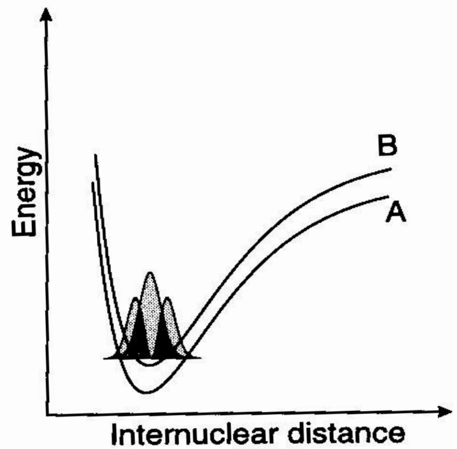
Internal Conversion or Non-Radiative Decay

Poor overlap

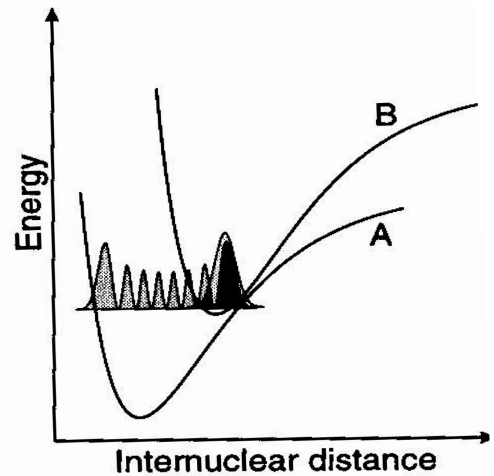
Better overlap



(a) Similar geometry, with large energy separation.



(b) Similar geometry, with small energy separation.



(c) Different geometry, with large energy separation.

Energy Gap Law

Rates of $T_1 - S_0$ intersystem crossing

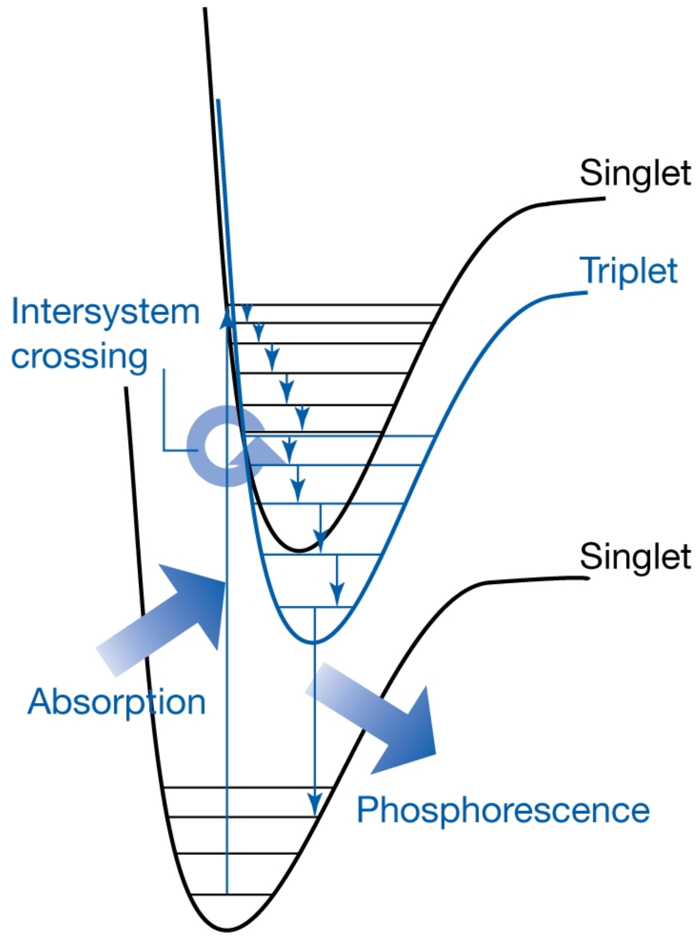
M	$10^{-4} k''_{ISC}/s^{-1}$	τ_p/s
Benzene	17.6	4.75
Benzene-d_1	16.0	5.15
Benzene-d_5	7.1	9.50
Benzene-d_6	3.7	14.1

The vibrational frequency of deuterium substituted compounds is lower than unsubstituted

Thus higher quantum numbers (more nodes) involved in final state for same energy gap – poorer overlap.

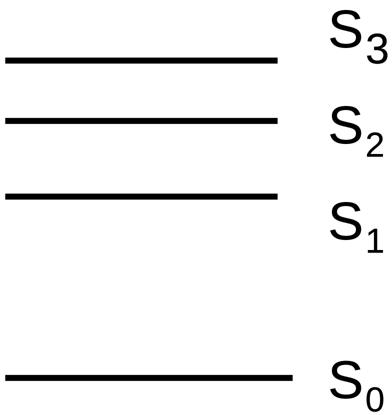
Energy Gap Law

- Rate of intramolecular energy transfer decreases with increasing energy gap
- Usually S1-T1 < T1-S0 < S1-S0
- Thus this factor tends to make ISC faster than IC



Kasha's Rule

- Emission from the lowest excited state S_1.
- Consequence of energy gap law (FC factor)
- In general $E(S_2)-E(S_1) << E(S_1)-E(S_0)$



Thus fast internal conversion between higher singlet states

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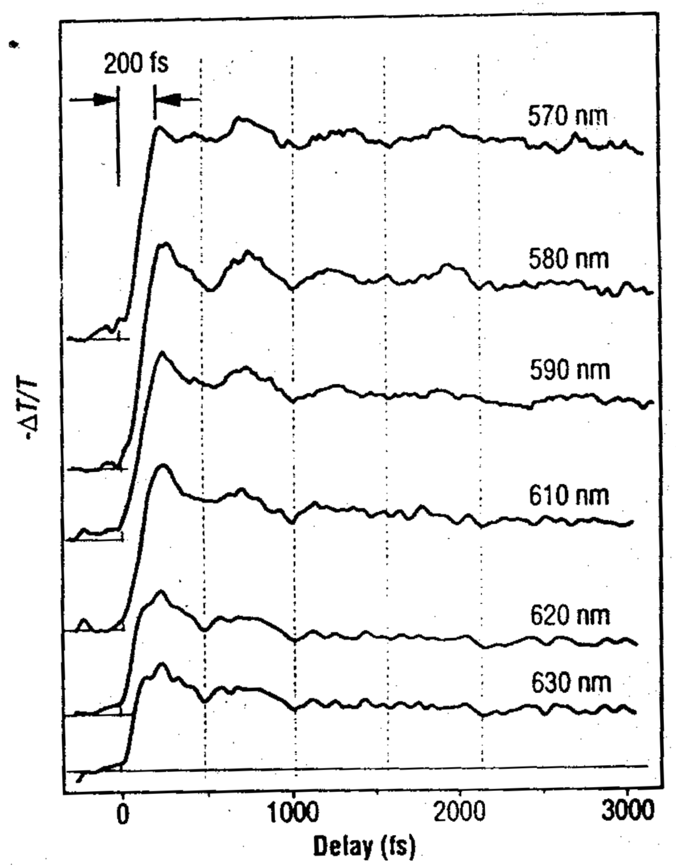
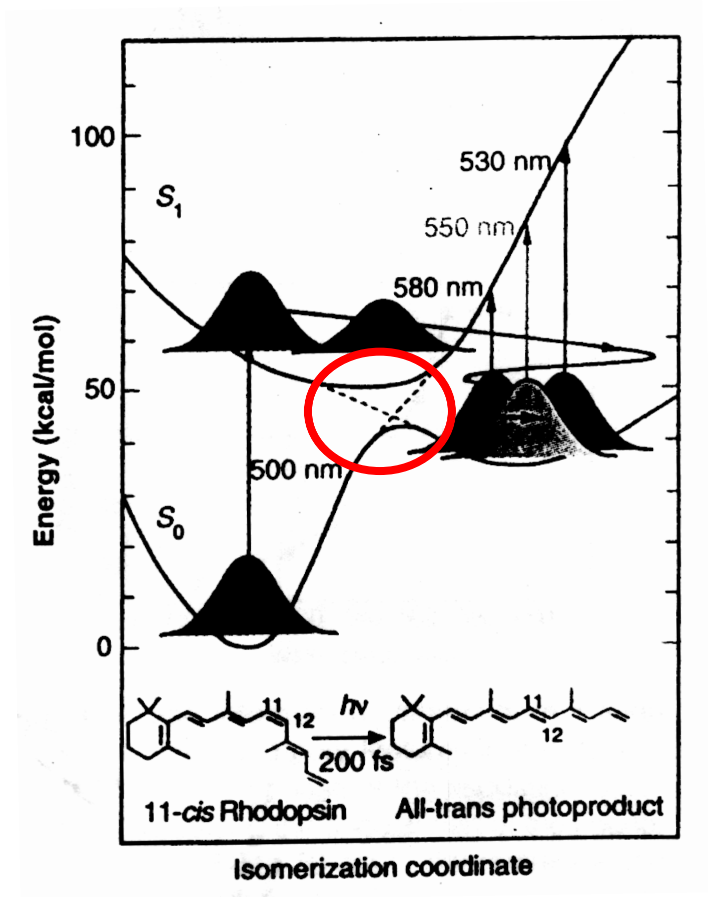
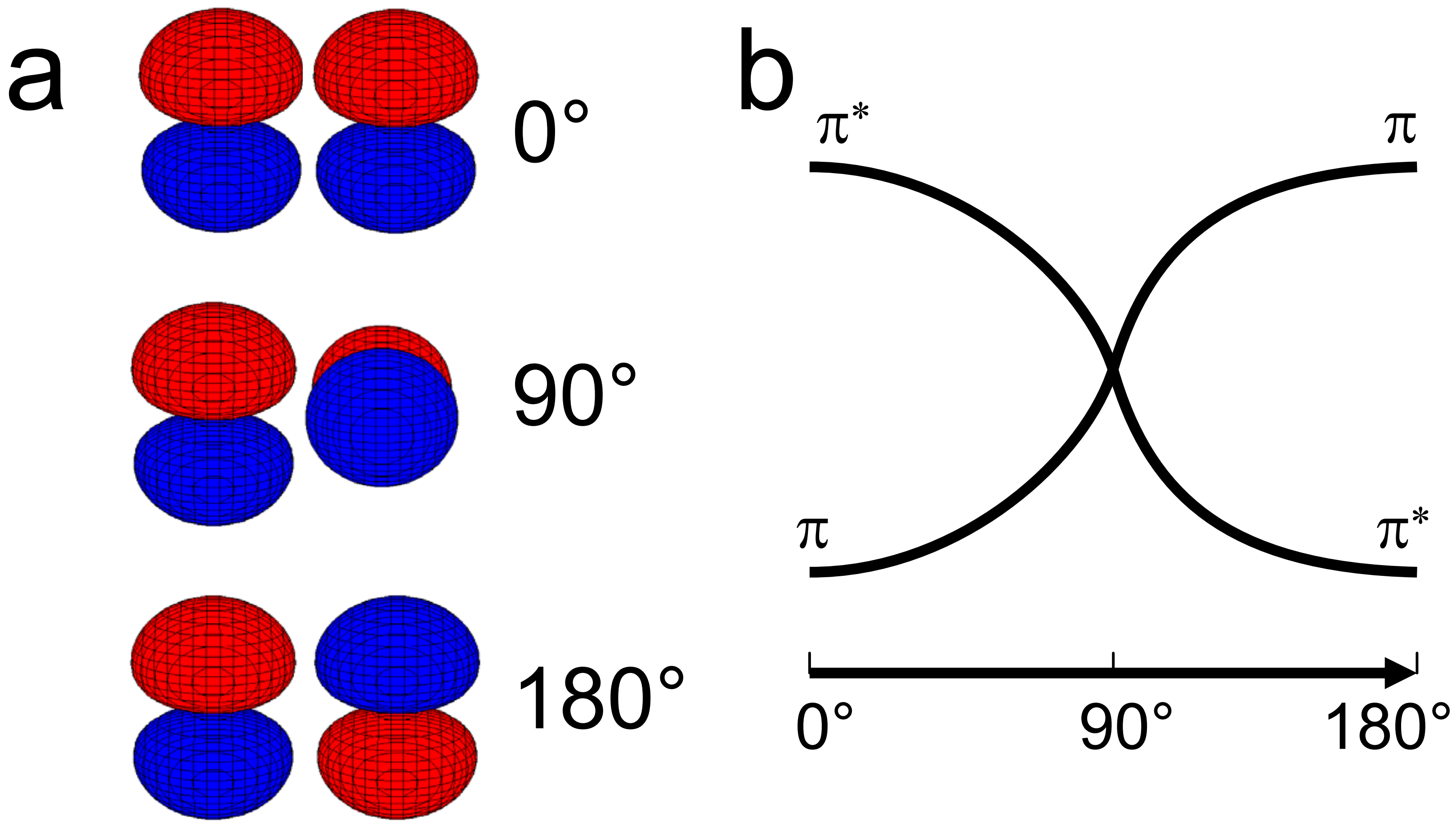


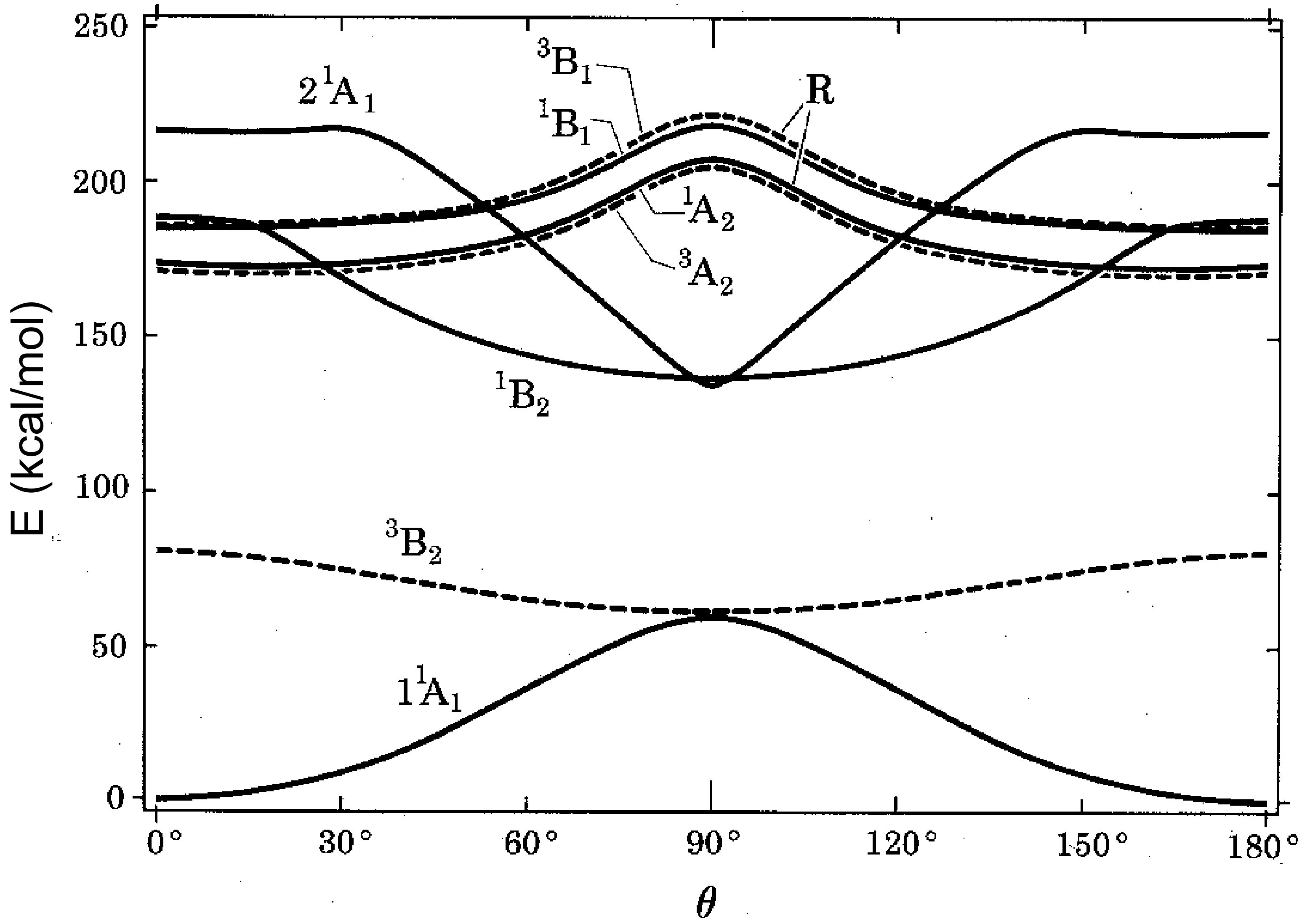


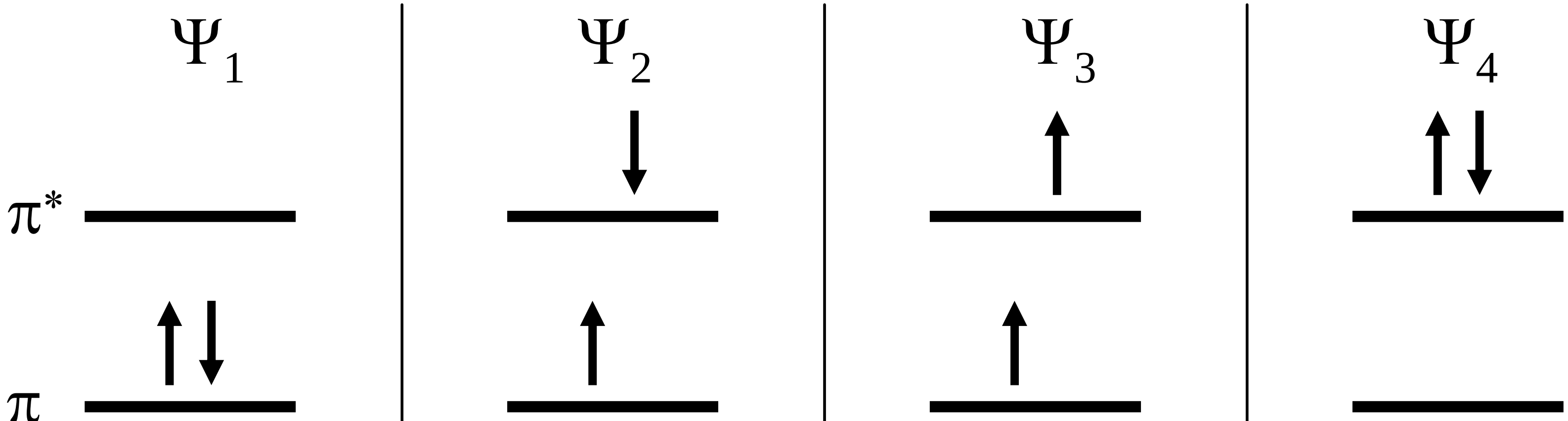
Q. Wang, R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank, Science 266 (1994) 422

Ethylene: MO picture



Ethylene: Large Scale CI



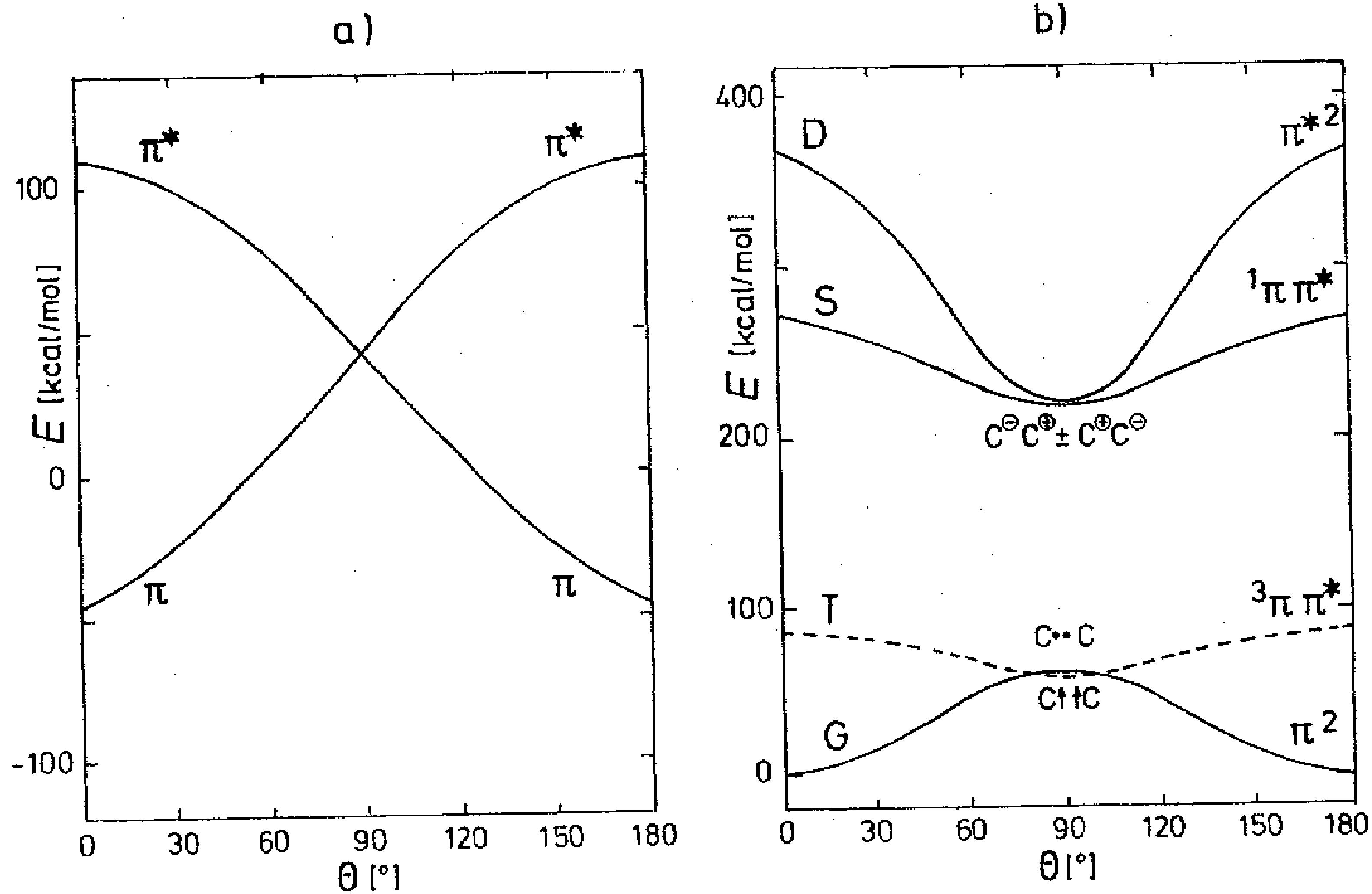


	Ψ_1	Ψ_2	Ψ_3	Ψ_4
spatial part	$\pi(1)\pi(2)$ symmetric under particle exchange	$\pi(1)\pi^*(2)+\pi(2)\pi^*(1)$ symmetric	$\pi(1)\pi^*(2)-\pi(2)\pi^*(1)$ antisymmetric	$\pi^*(1)\pi^*(2)$ symmetric
spin part	$\alpha(1)\beta(2)-\alpha(2)\beta(1)$	$\alpha(1)\beta(2)-\alpha(2)\beta(1)$	$\alpha(1)\alpha(2)$ $b(1)b(2)$ $\alpha(1)\beta(2)+\alpha(2)\beta(1)$	$\alpha(1)\beta(2)-\alpha(2)\beta(1)$
	Singlet $^1A_1$	Singlet $^1B_2$	Triplet $^3B_2$	Singlet $^1A_1$

Symmetric case: $\{\Psi_1,\Psi_4\}$ couple

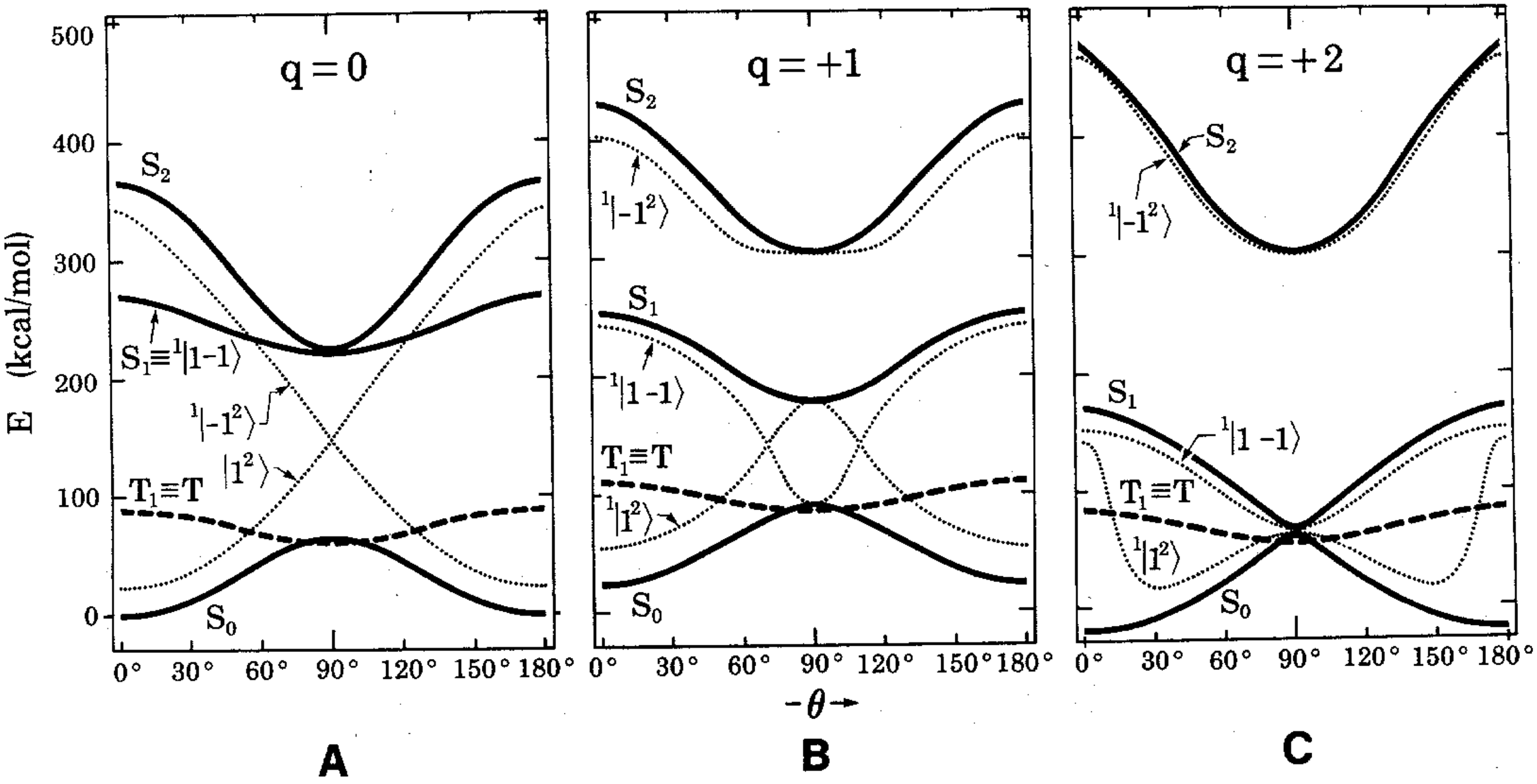
Asymmetric case: $\{\Psi_1, \Psi_2, \Psi_4\}$ couple ⇨ 3×3 CI Model

Prototype Isomerization: Ethylene

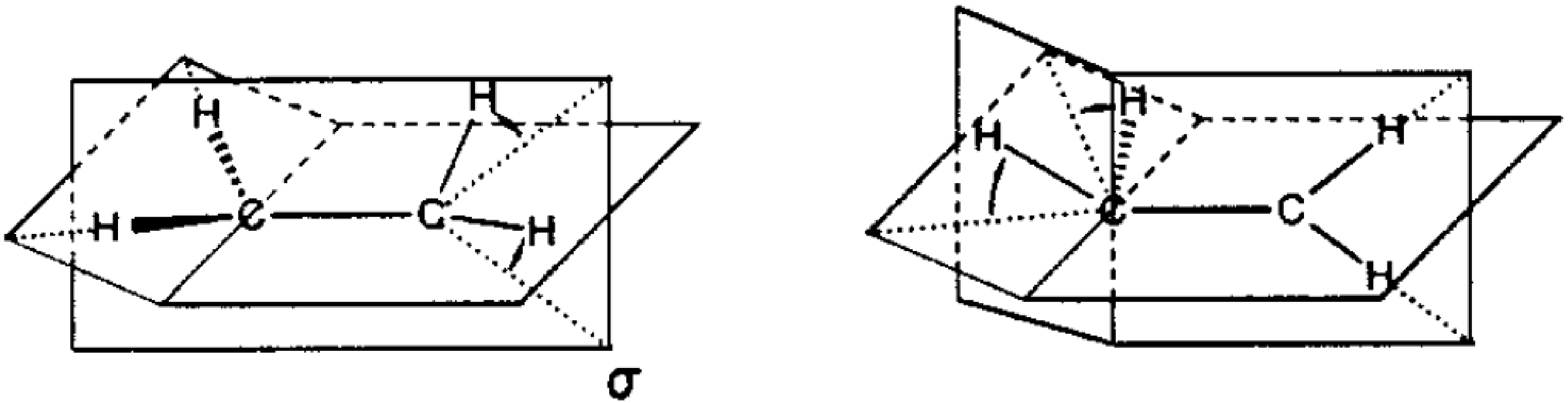


Breaking the Symmetry

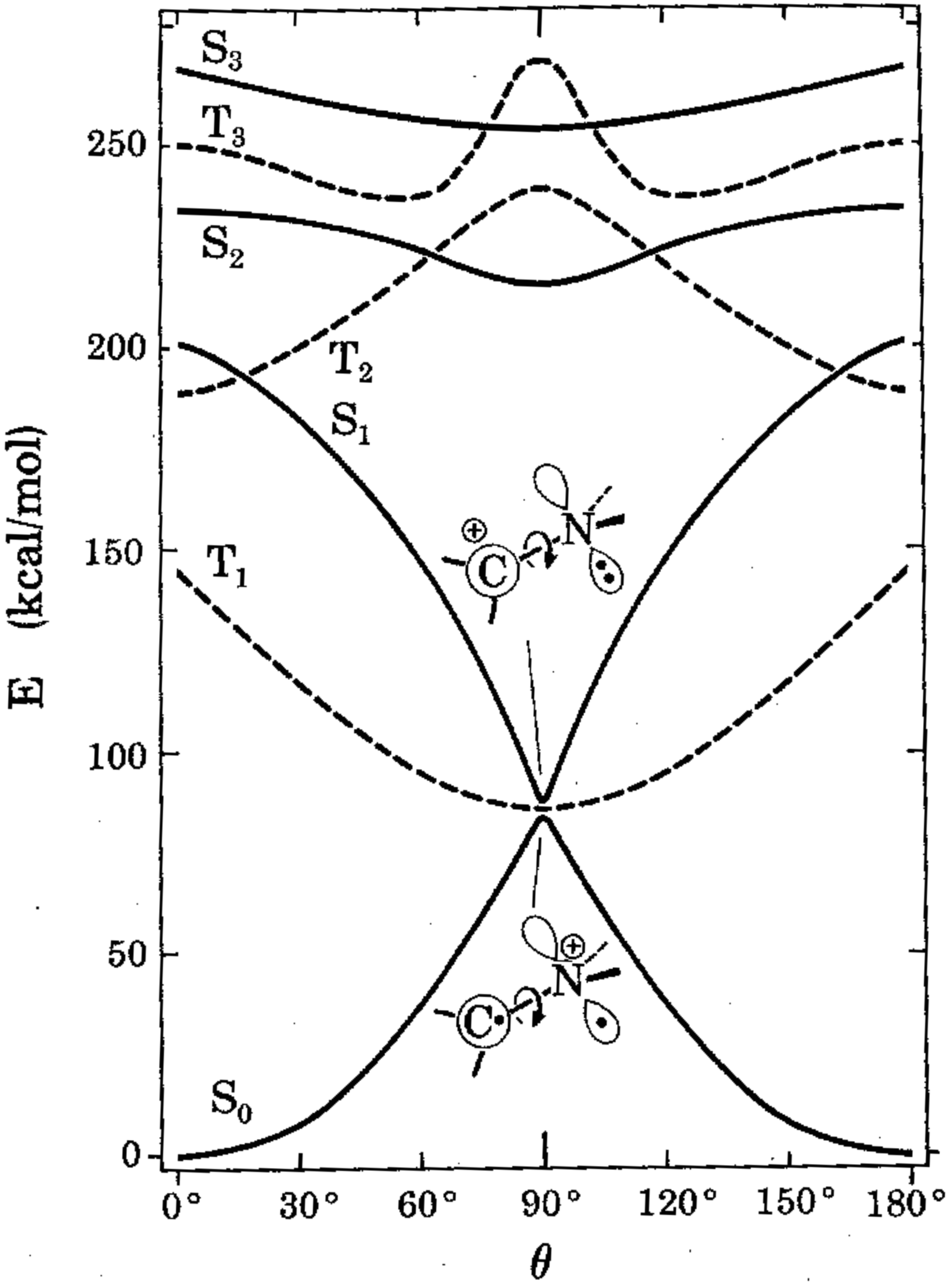
Charge 1.85 Å away along the C=C axis



Prototype Isomerization: Ethylene



$CH_2{=}NH_2^+$



S3
T3
S2
T2
S1
T1
S0
C
N
E (kcal/mol)
0
50
100
150
200
250
0°
30°
60°
90°
120°
150°
180°
θ

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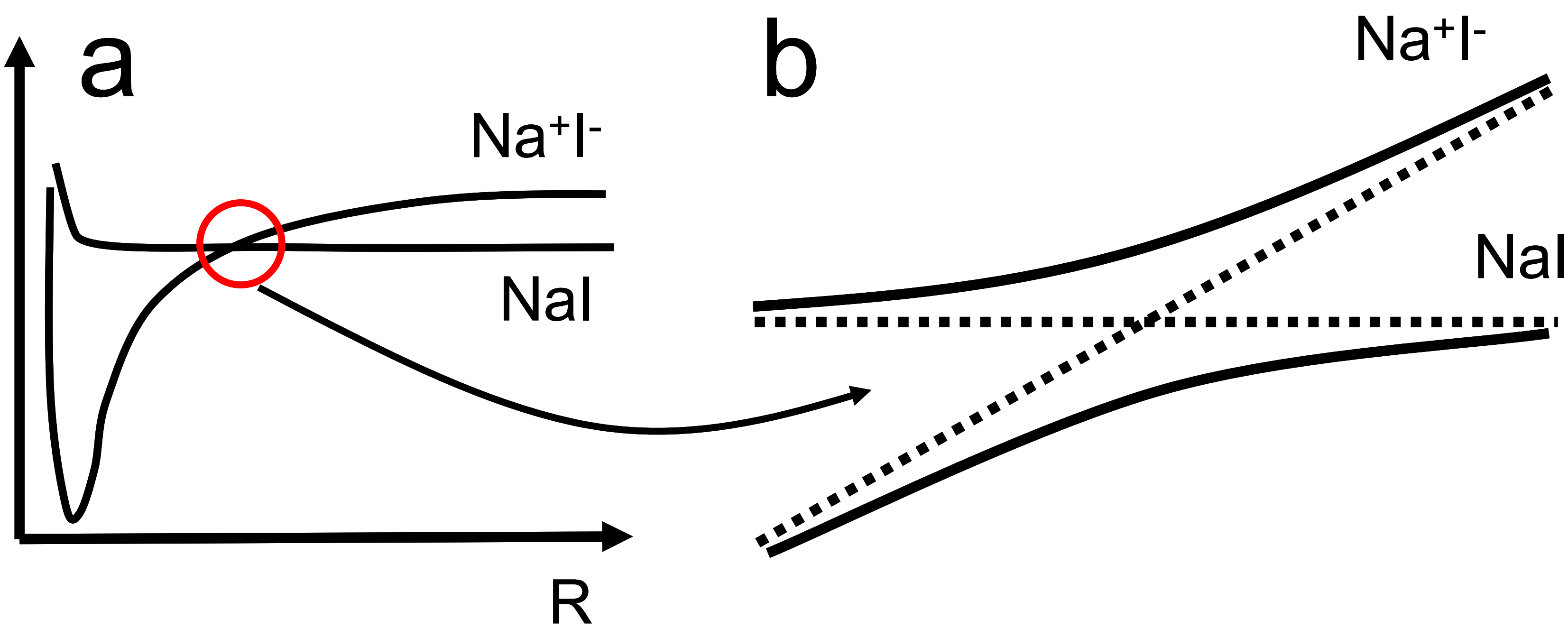
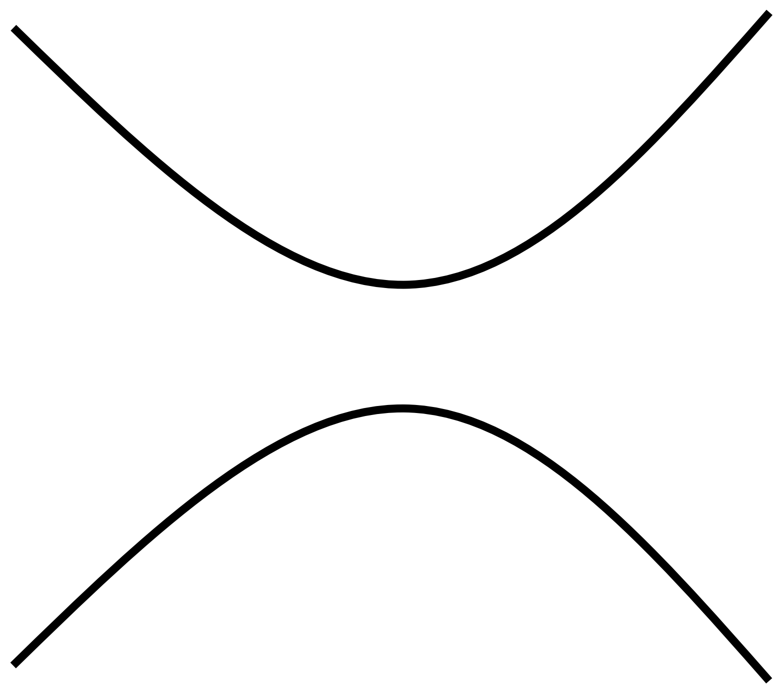
Ionic Bond



Avoided Crossing, Non-crossing Rule

$$H(R) = \begin{pmatrix} H_{11}(R) & H_{12}(R) \\ H_{21}(R) & H_{22}(R) \end{pmatrix}$$

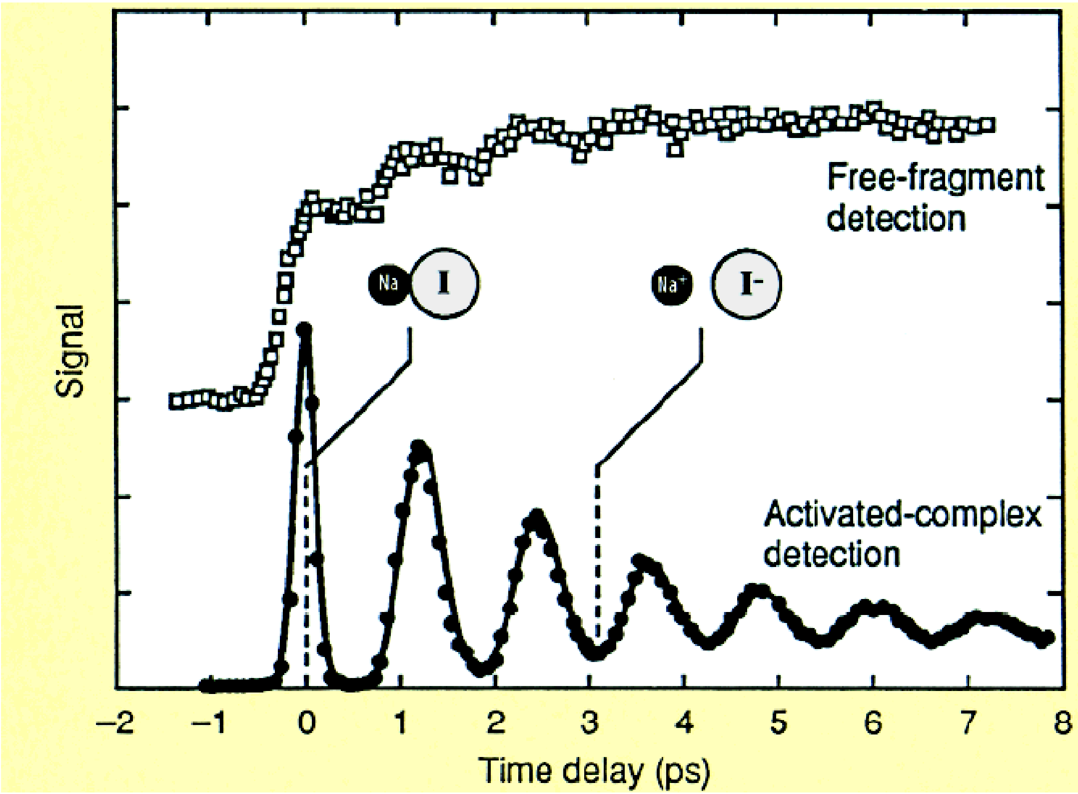


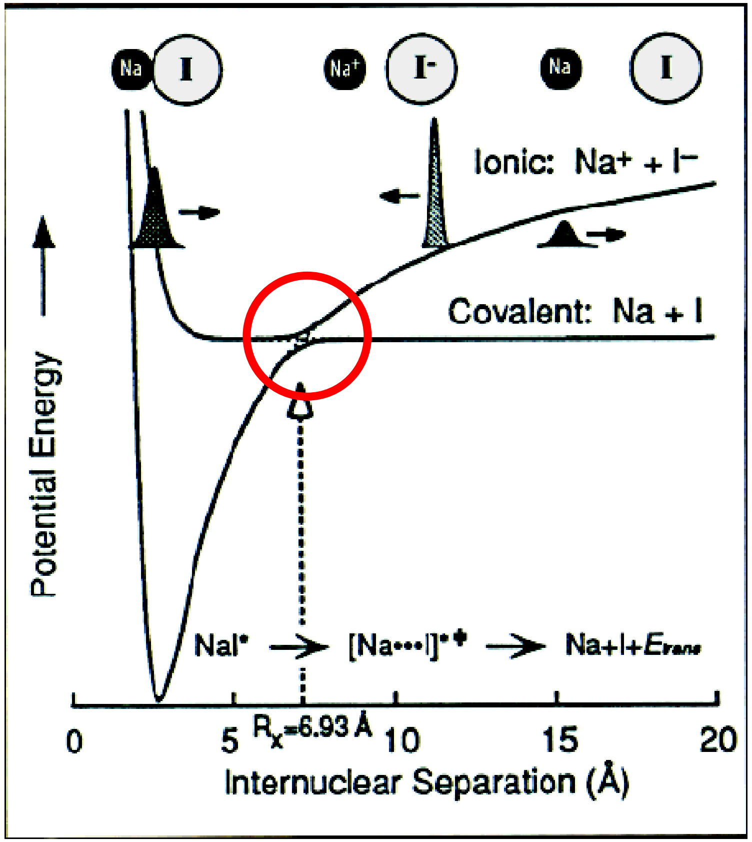
Two surfaces cross when:

$$H_{11}(R) = H_{22}(R)$$
$$H_{12}(R) = 0$$

In 1D: Avoided Crossing

Avoided Crossing in NaI





T. S. Rose, M. J. Rosker, A. H. Zewail, J. Chem. Phys. 91 (1989) 7415
A. H. Zewail, J. Phys. Chem. A 104 (2000) 5660

Avoided Crossing, Non-crossing Rule

S_1 and S_2 in pyrazine in the Q_{6a} and Q_{10a} subspace

$$H(R) = \begin{pmatrix} H_{11}(R) & H_{12}(R) \\ H_{21}(R) & H_{22}(R) \end{pmatrix}$$

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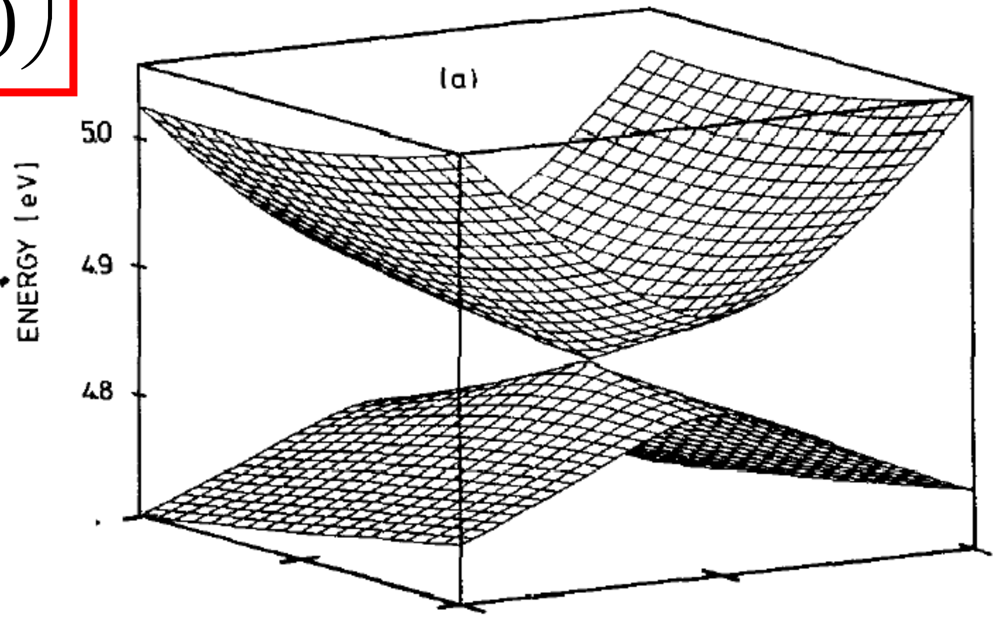

In 2D: 0D-Conical Intersection

C. Woywod, W. Domcke, A. L. Sobolewski, H.-J. Werner J. Chem. Phys. 100, 1400 (1994)

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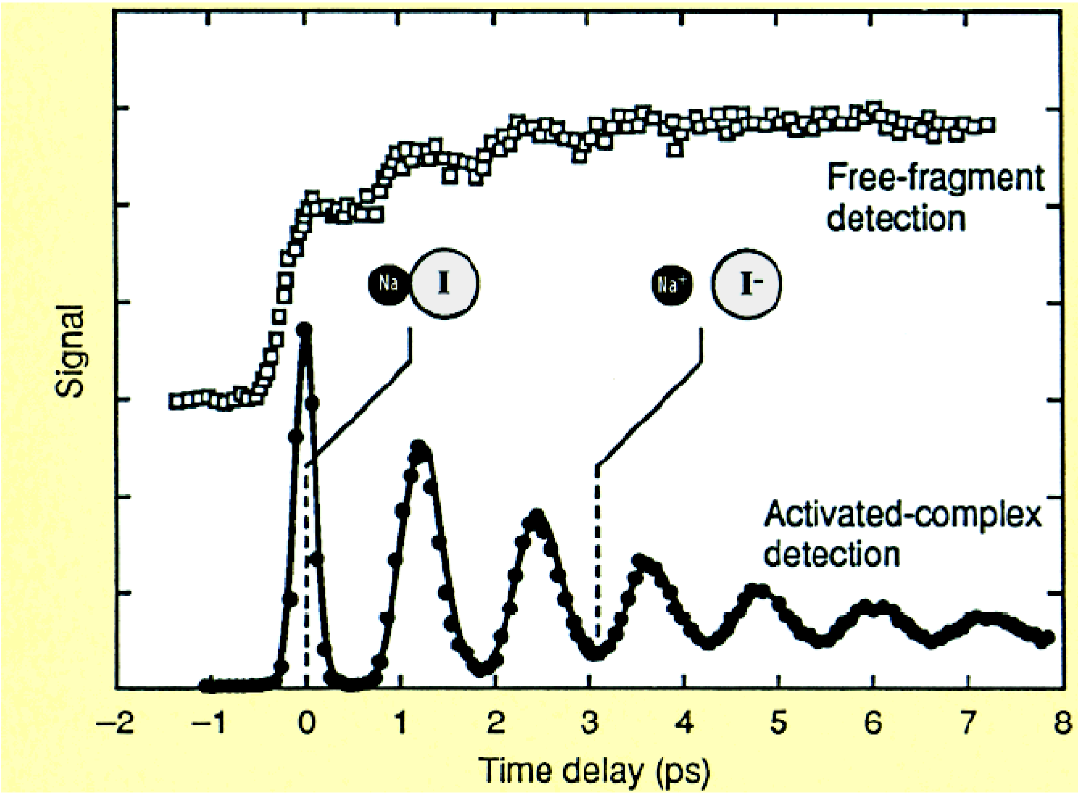
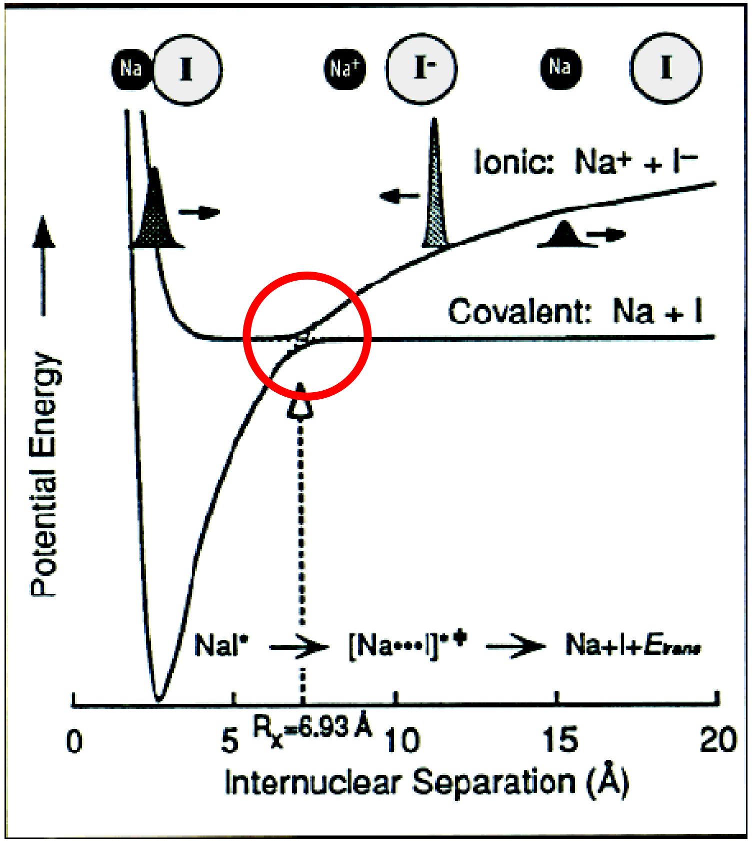
Avoided Crossing in NaI





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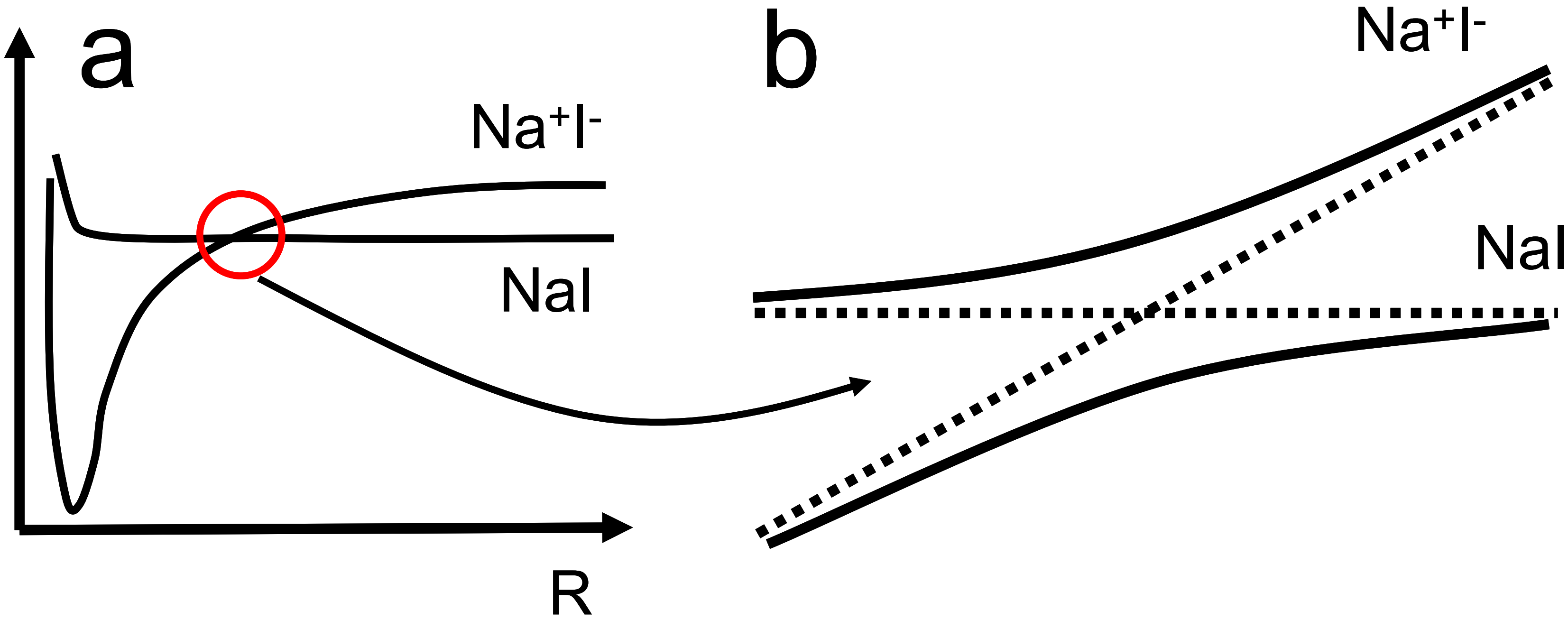
Born Oppenheimer Expansion

$$E_j(R)\chi_j(R) + \sum_i \langle\Psi_j|\hat{T}_{nuc}|\Psi_i\rangle\chi_i = \epsilon\chi_j(R)$$

$$\begin{aligned}
\langle\Psi_j|\hat{T}_{nuc}|\Psi_i\rangle\chi_i &= -\frac{\hbar^2}{2M}\left\langle\Psi_j\left|\frac{\partial^2}{\partial R^2}\right|\Psi_i\right\rangle\chi_i \\
&\quad -\frac{\hbar^2}{M}\left\langle\Psi_j\left|\frac{\partial}{\partial R}\right|\Psi_i\right\rangle\left(\frac{\partial}{\partial R}\chi_i\right) \\
&\quad -\frac{\hbar^2}{2M}\langle\Psi_j|\Psi_i\rangle\left(\frac{\partial^2}{\partial R^2}\chi_i\right) \\
&\equiv -\frac{\hbar^2}{2M}\left(G_{ij}\chi_i + 2F_{ij}\frac{\partial\chi_i}{\partial R}\right) - \delta_{ij}\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}\chi_i
\end{aligned}$$

Ionic Bond



Adiabatic Representation

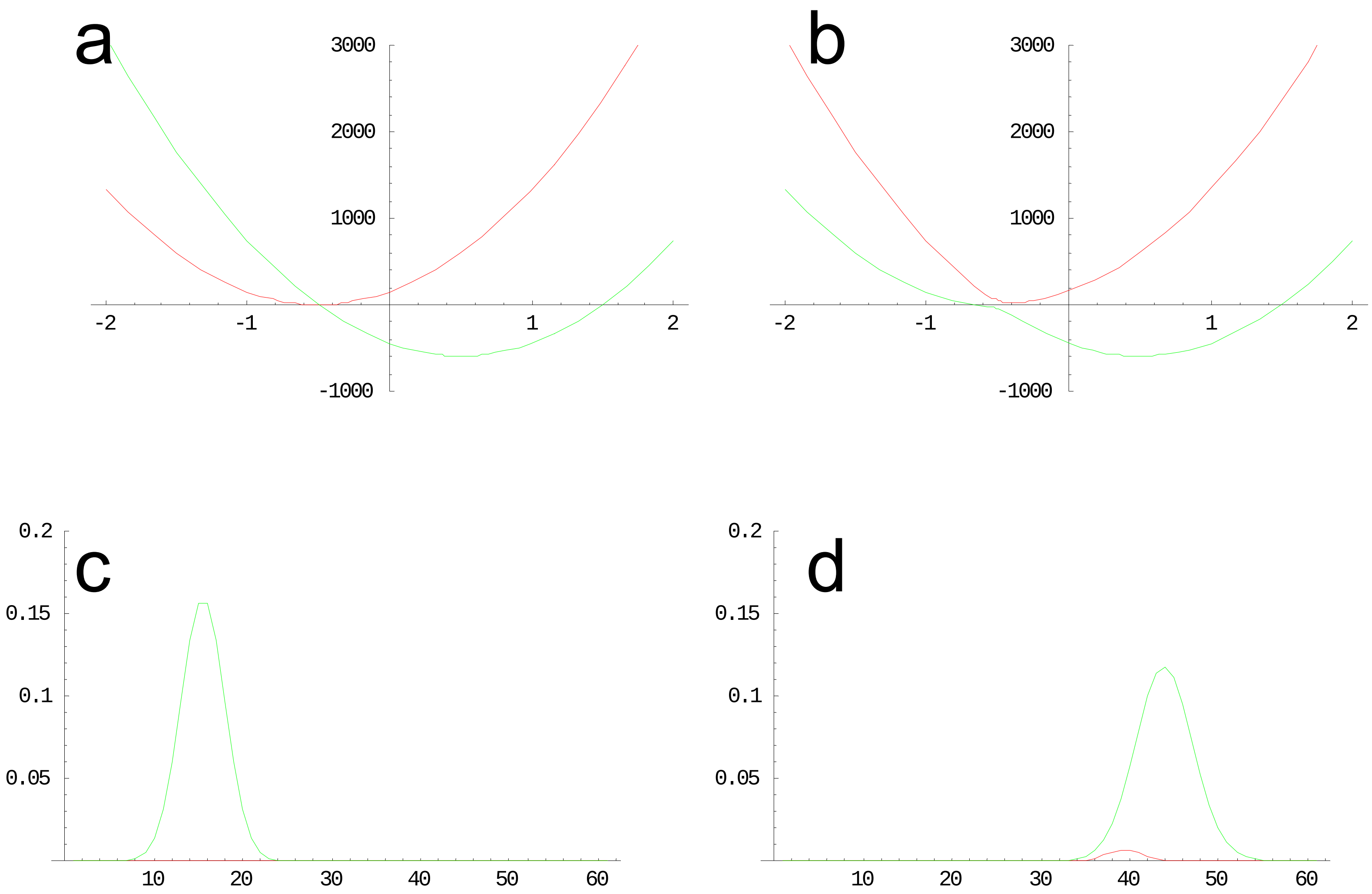
$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}=\left[\begin{pmatrix}T_{nuc} & F_{12}\\ F_{12} & T_{nuc}\end{pmatrix}+\begin{pmatrix}E_1^{(ad)} & 0\\ 0 & E_2^{(ad)}\end{pmatrix}\right]\begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}$$

with: $F_{12}=\left\langle \Psi_1\left|\frac{\partial}{\partial R}\right|\Psi_2\right\rangle$

Diabatic Representation

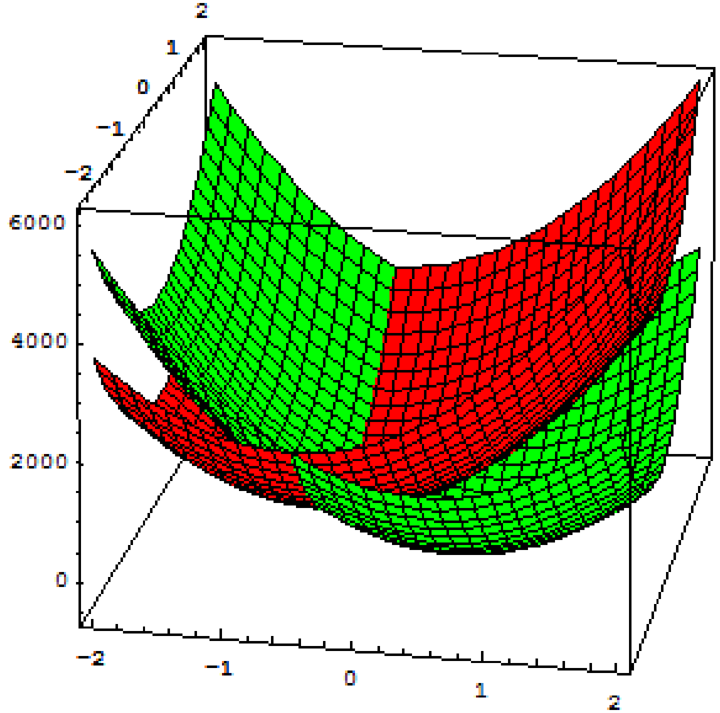
$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}=\left[\begin{pmatrix}T_{nuc} & 0\\ 0 & T_{nuc}\end{pmatrix}+\begin{pmatrix}E_1^{(dia)} & E_{12}^{(dia)}\\ E_{12}^{(dia)} & E_2^{(dia)}\end{pmatrix}\right]\begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}$$

Wavepacket on Coupled Surfaces



Adiabatic Representation	Diabatic Representation
+ Output of quantum chemistry programs	+ renders $\partial / \partial R \Psi^{(el)} = 0$ or small
+ Born Oppenheimer approximation	+ closer to chemical intuition
- Discontinuous at CI	+ continuous even in CI
- Breaks down in avoided crossing	+ Better description in avoided crossing region
- Useless for numerical wavepacket propagation	+ Useful for numerical purposes
	- Requires additional coupling surface E_{12}
	- Not calculated by quantum chemistry programs
	- Not unique in more than 1D

$V_1,\ V_2$



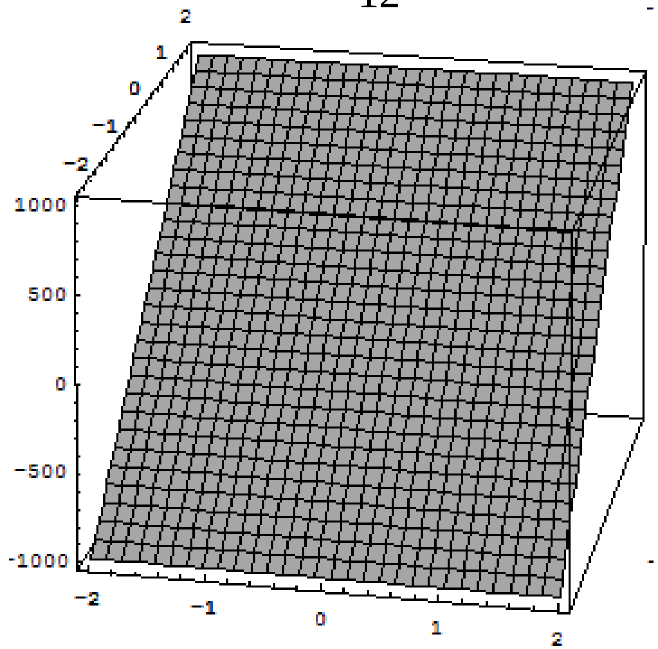
$$V_1 = k_1(x_1 - 0.5)^2 + k_2 {x_2}^2$$

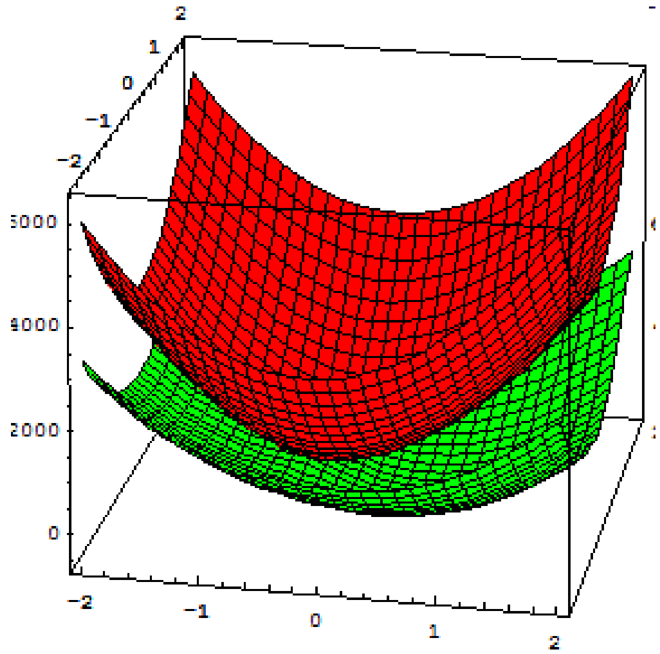
$$V_2 = k_1(x_1 + 0.5)^2 + k_2 {x_2}^2$$

$$V_{12} = k_{12} x_2$$

$$H = \begin{pmatrix} V_1 & V_{12} \\ V_{12} & V_2 \end{pmatrix}$$

V_{12}





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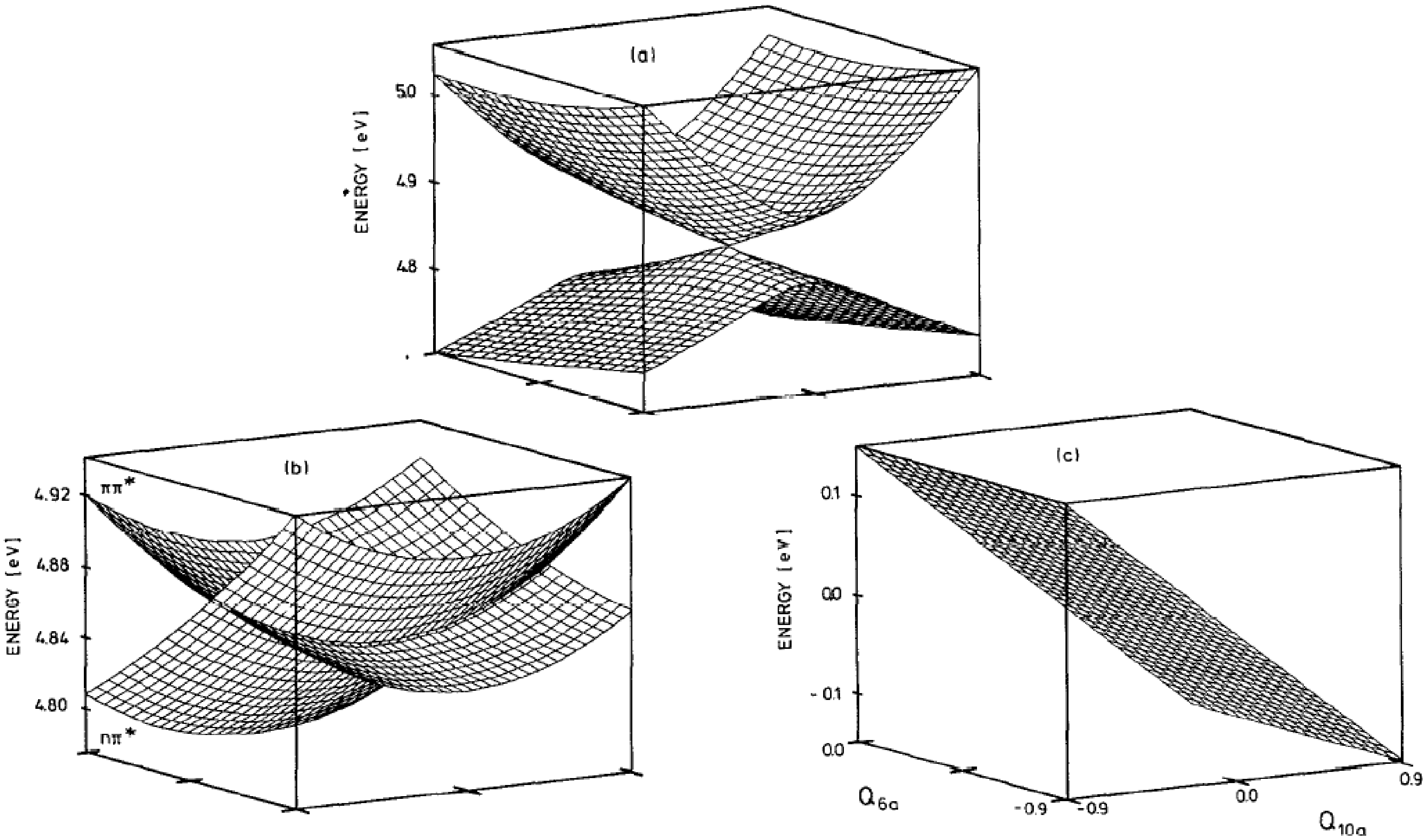
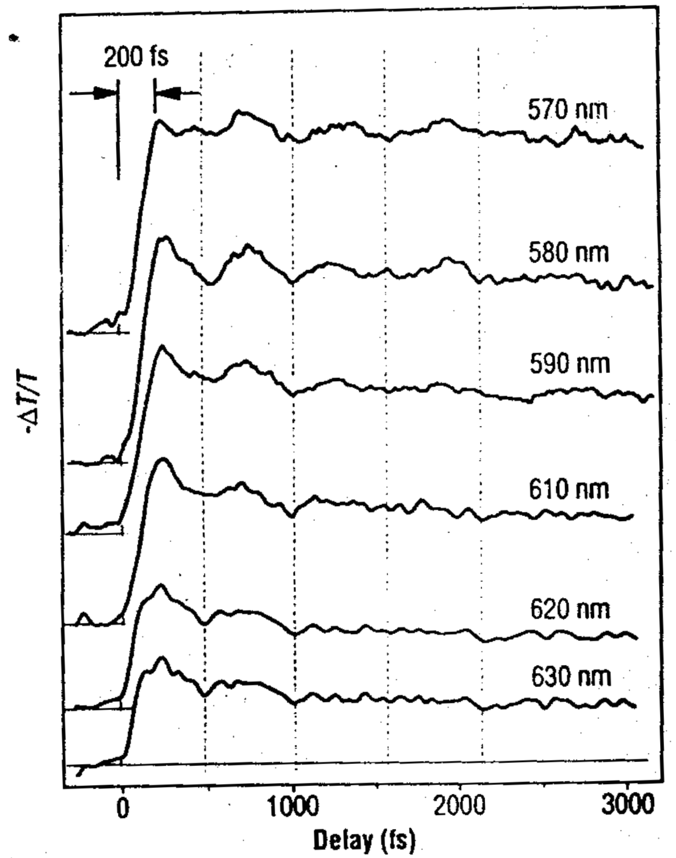
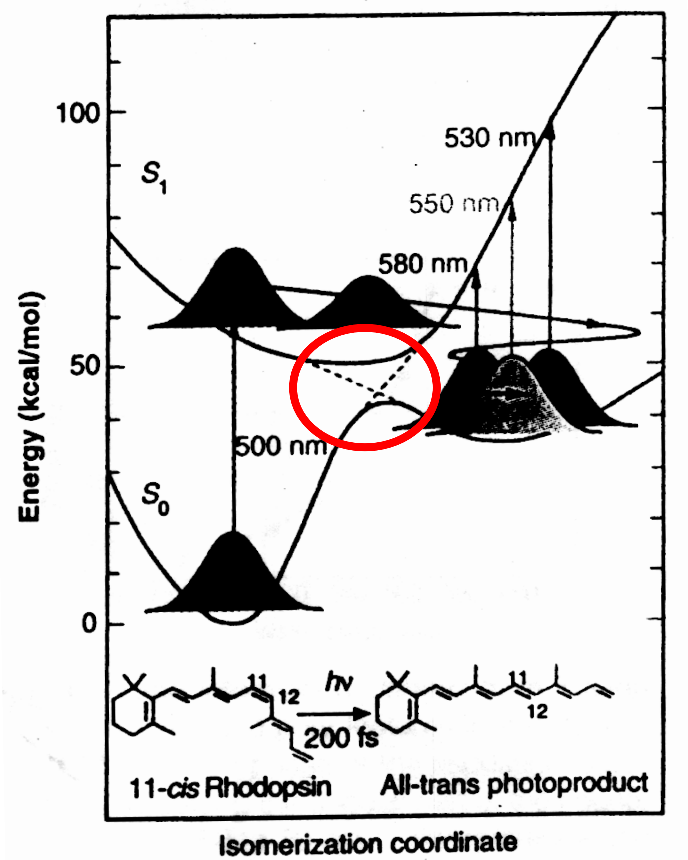


Domcke et al. JCP 100 (1994) 1400

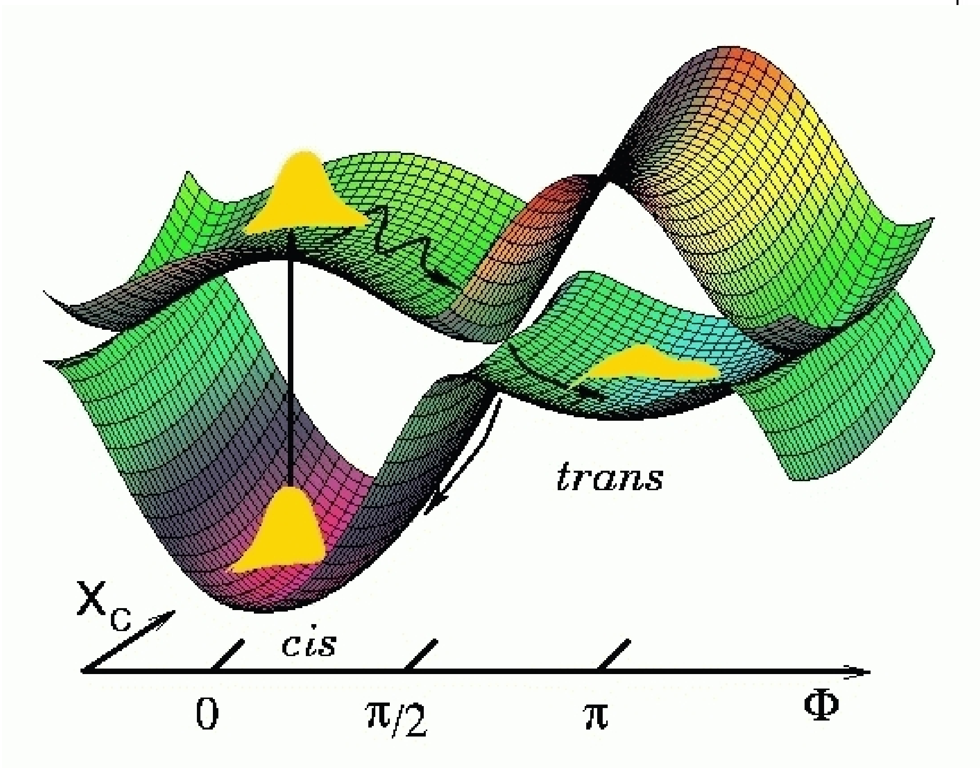
Photochemical Reactions in Nature: Isomerization of Rhodopsin

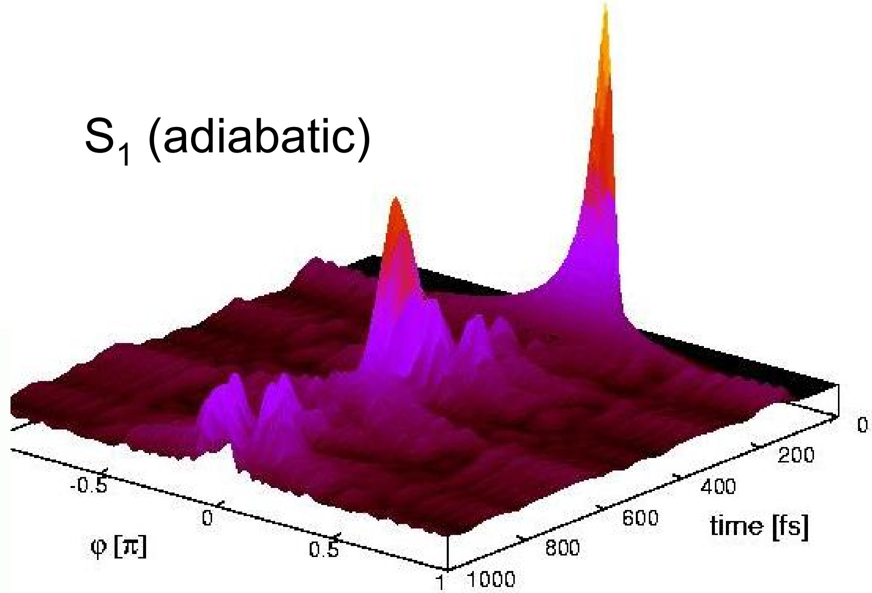


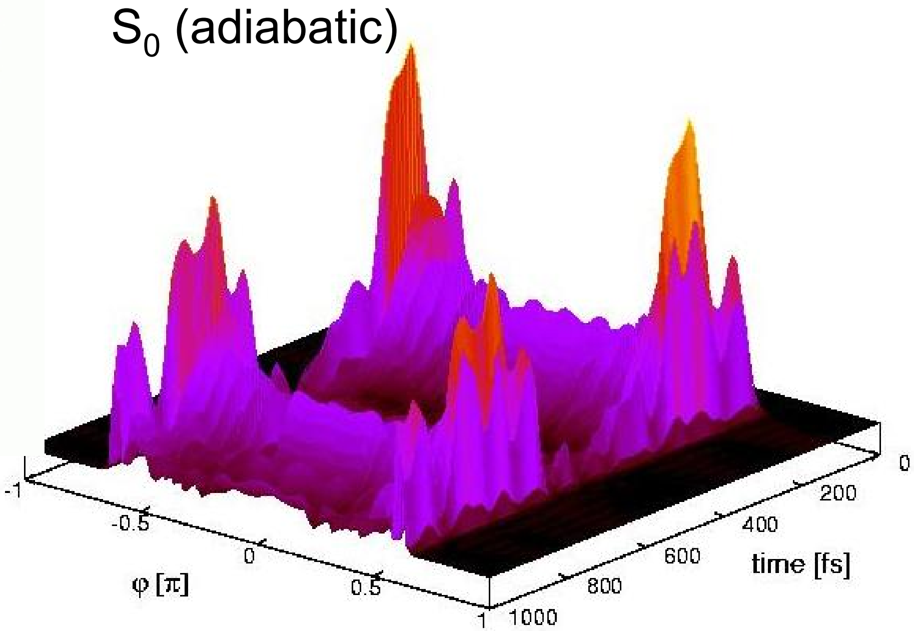


Q. Wang, R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank,
Science 266 (1994) 422

Model Rhodopsin







S. Hahn, G. Stock, J. Phys. Chem. B, Vol. 104, 2000, 1146

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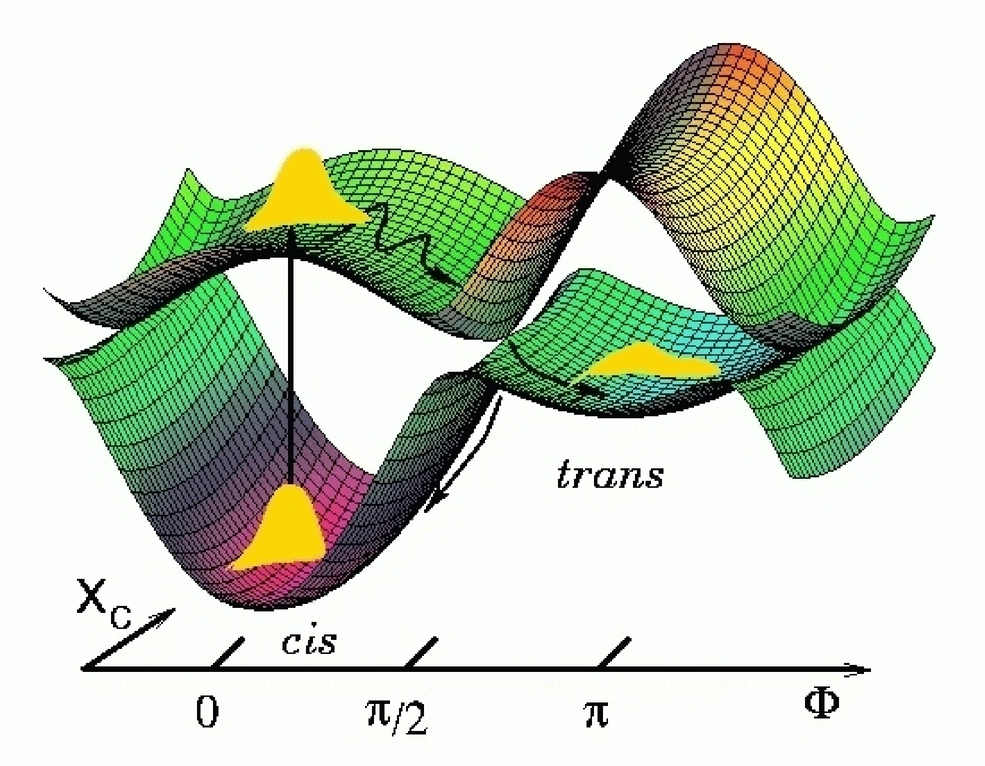

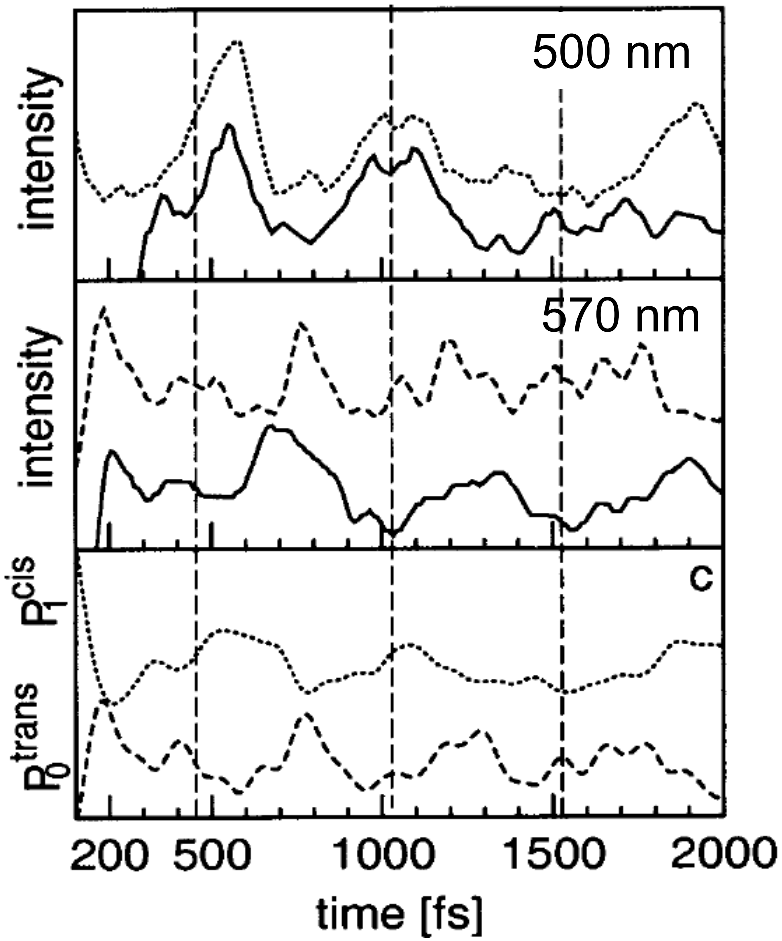

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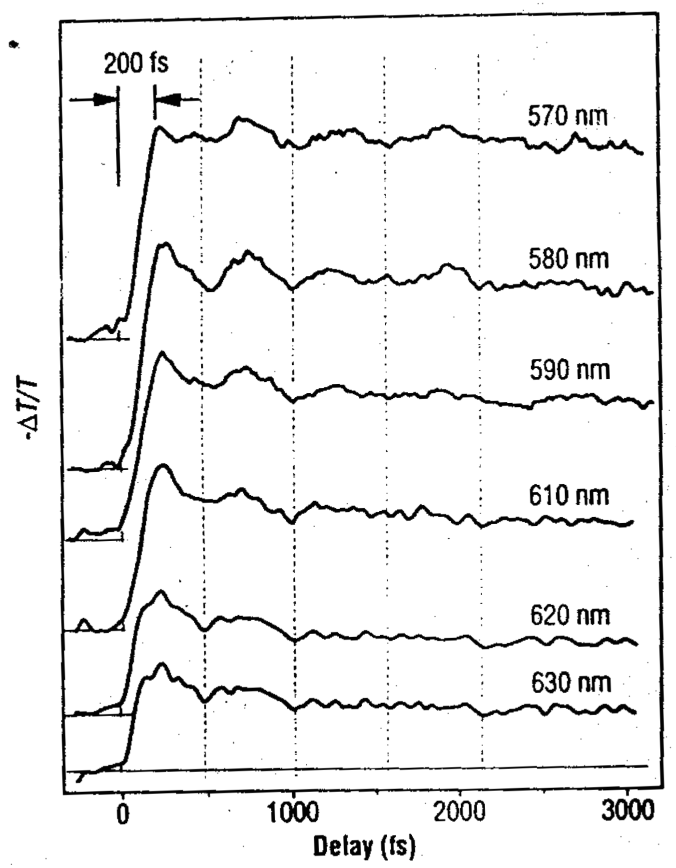

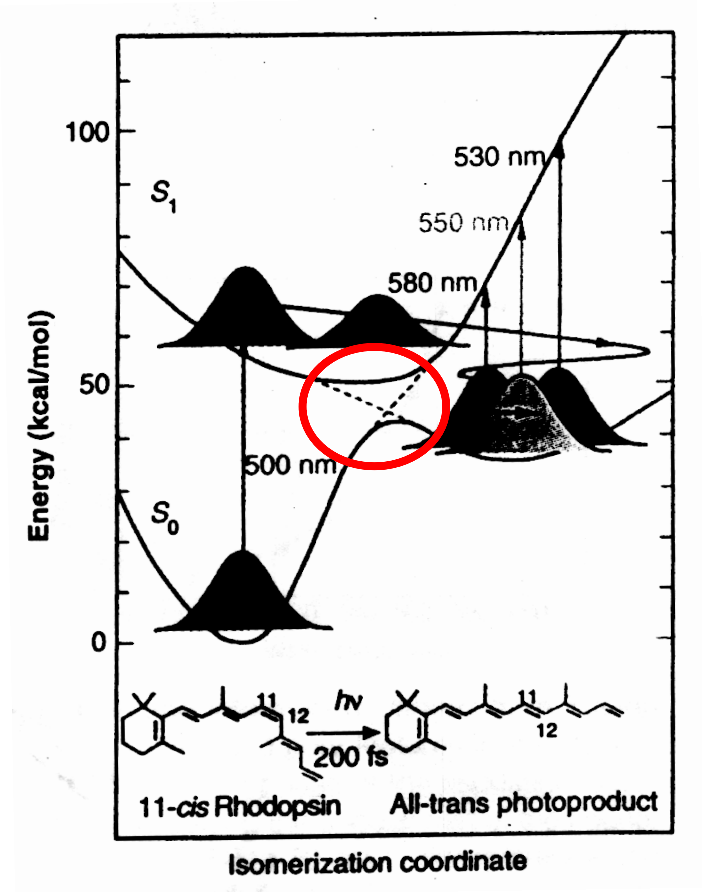

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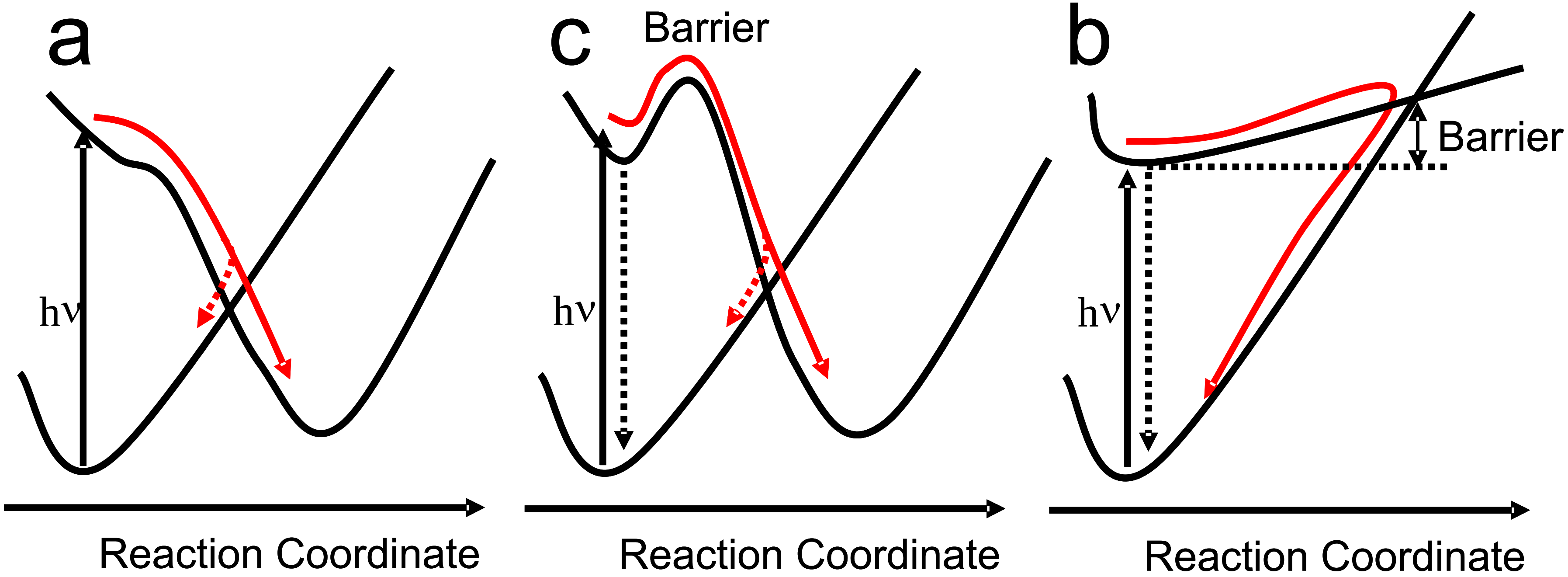
a
hν
Reaction Coordinate
c
Barrier
hν
Reaction Coordinate
b
Barrier
hν
Reaction Coordinate

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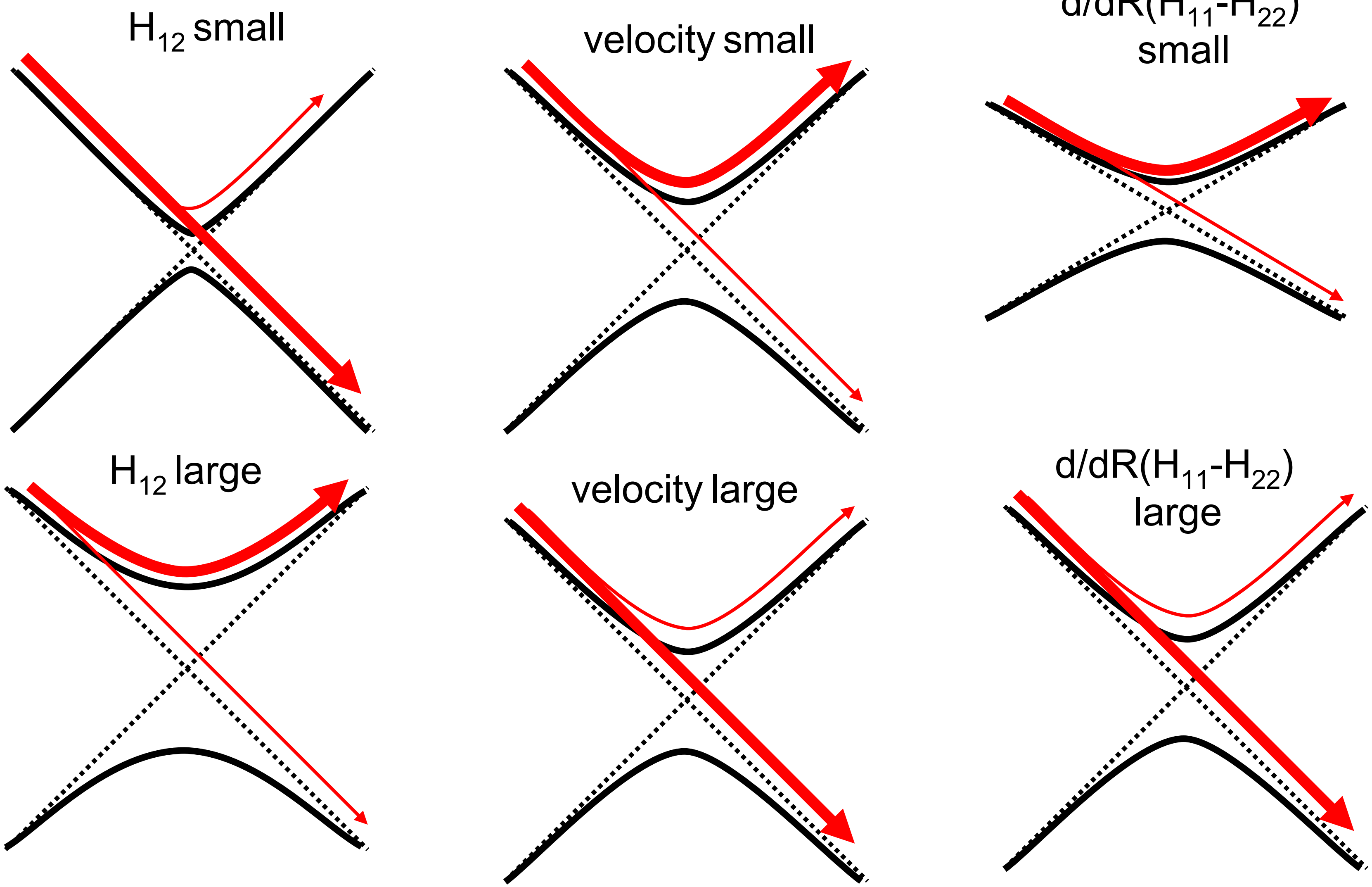
Semiclassical Approximation:

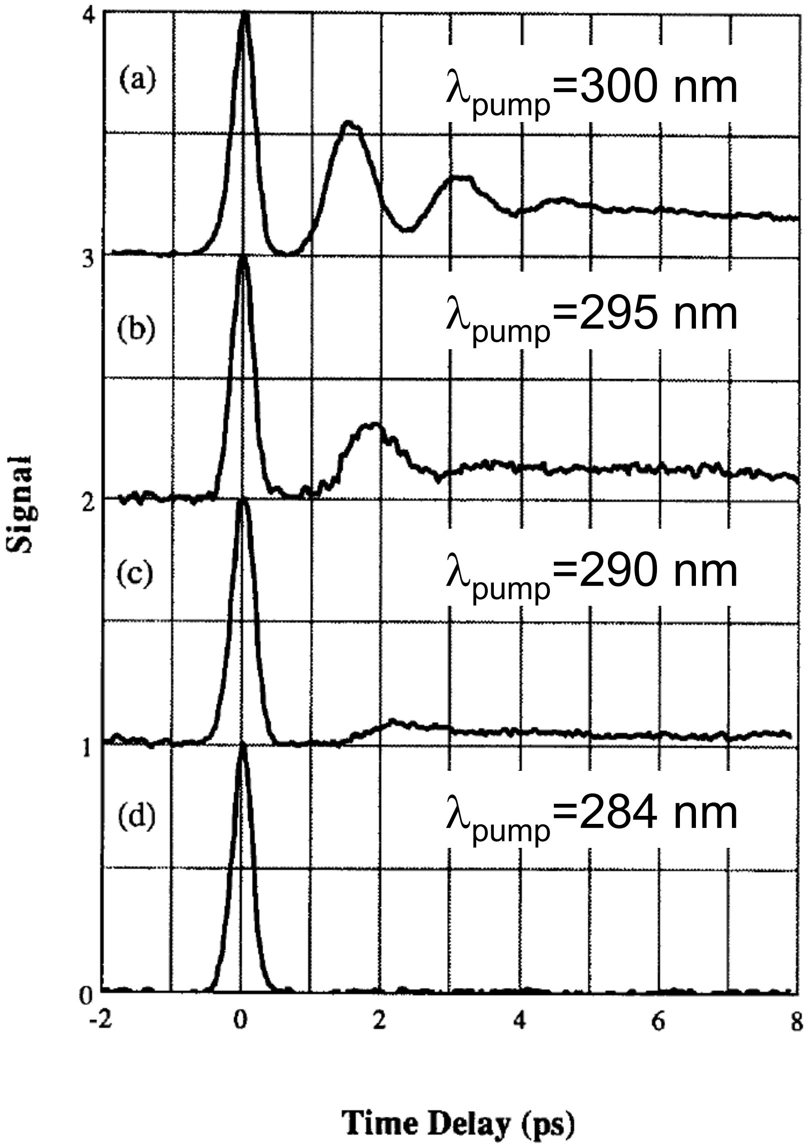
$$R(t)=v\times t$$

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}c_1\\ c_2\end{pmatrix}=\left[\begin{pmatrix}H_1^{(dia)}(R(t)) & H_{12}^{(dia)}(R(t))\\ H_{12}^{(dia)}(R(t)) & H_2^{(dia)}(R(t))\end{pmatrix}\right]\begin{pmatrix}c_1\\ c_2\end{pmatrix}$$

$$P^{(dia)} = 1 - \exp\left[-\frac{4\pi^2}{hv} \frac{H_{12}{}^2}{\left| \partial/\partial R \left(H_{11} - H_{22} \right) \right|} \right]$$



Landau Zener: Velocity Dependence



Mean-Field Approach

$$M\ddot{R}(t) = F^q$$

Equation of motion of classical subsystem

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = H(R)\Psi(t)$$

Equation of motion of quantum subsystem

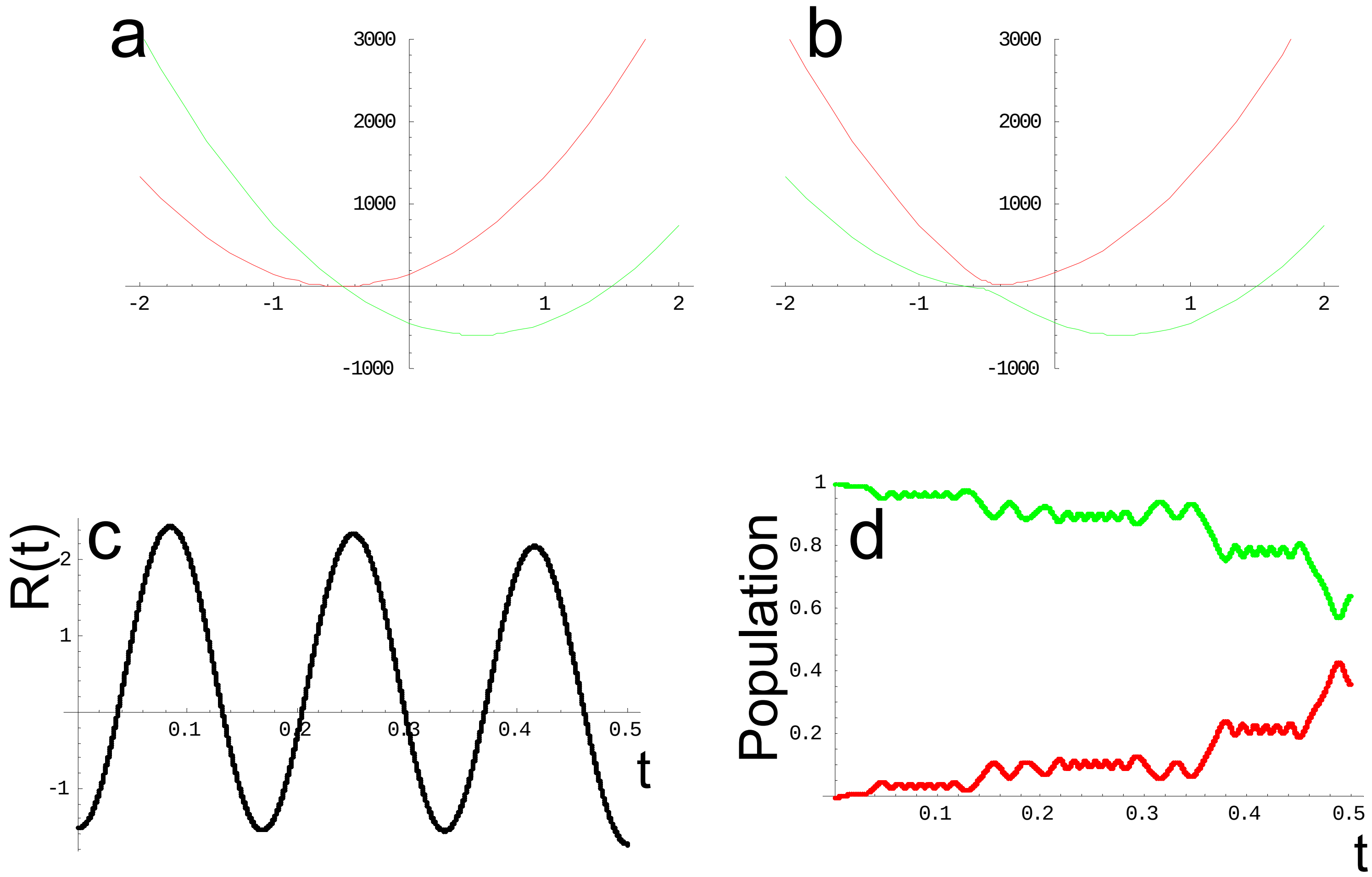
$$F^q = -\frac{\partial}{\partial R}\langle E\rangle = -\frac{\partial}{\partial R}\langle\Psi|H|\Psi\rangle = -\langle\Psi|\frac{\partial}{\partial R}H|\Psi\rangle$$

Hellmann-Feynmann force

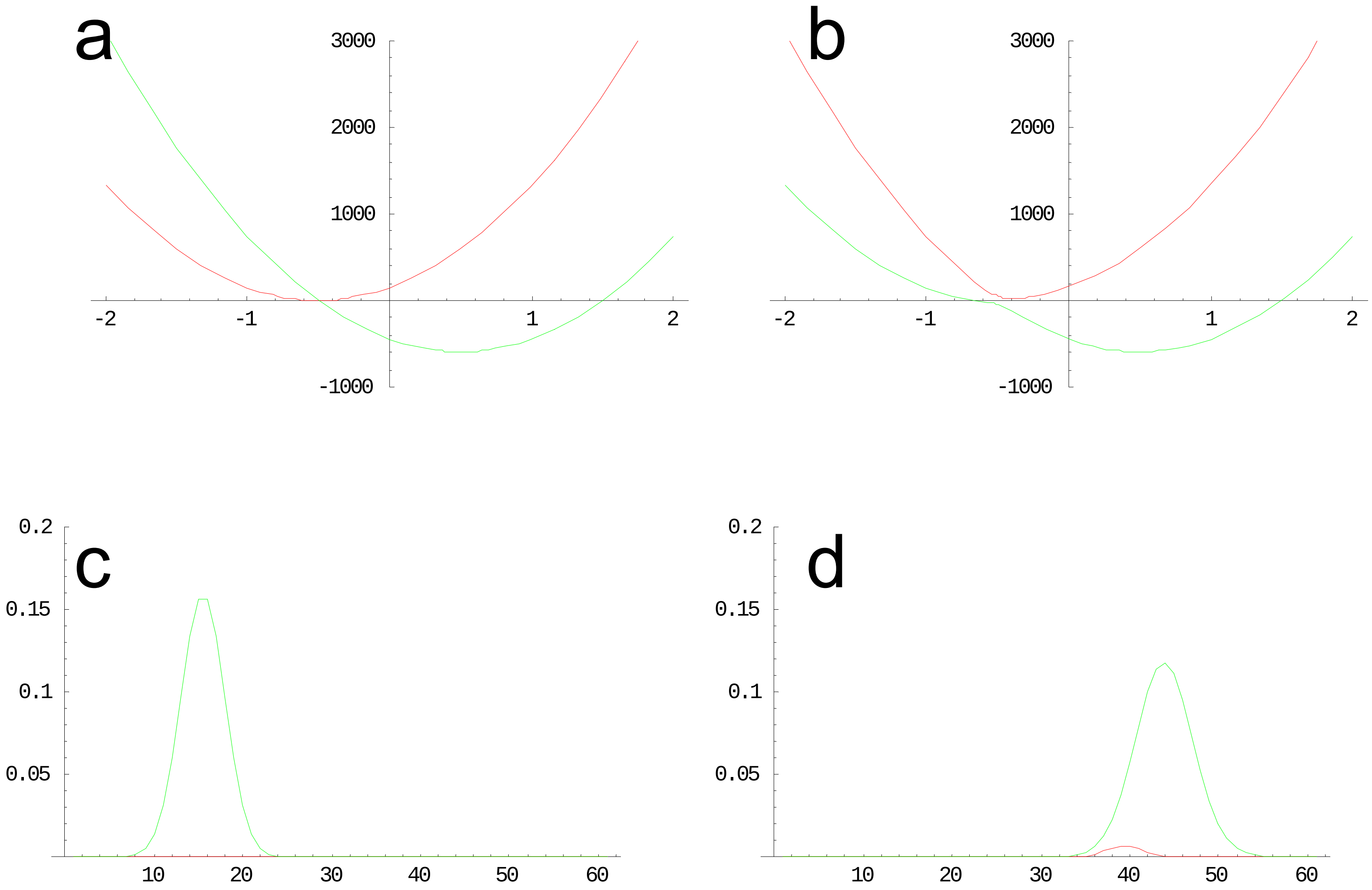
$$E_{tot} = \langle\Psi|H|\Psi\rangle + \frac{1}{2}M\dot{R}^2 = const$$

Energy conservation

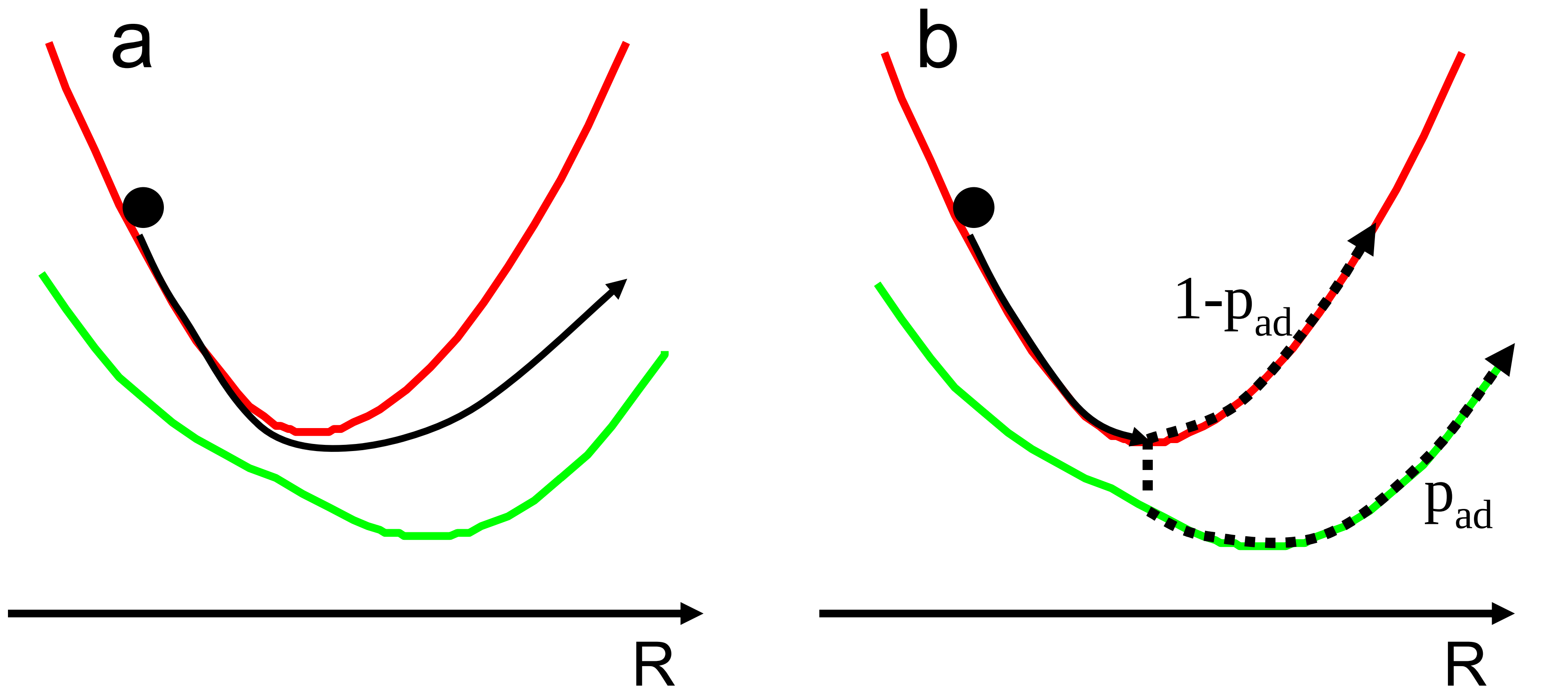
Mean-Field Approach



Wavepacket on Coupled Surfaces



Mean-Field *versus* Surface Hopping



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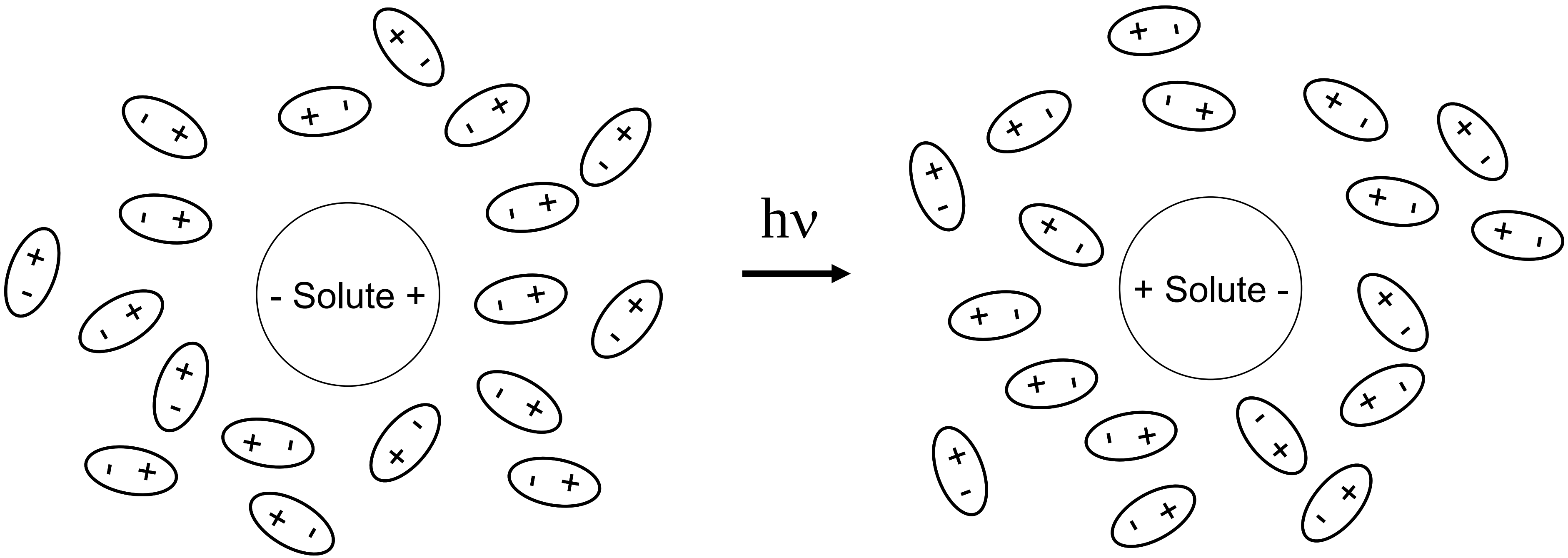
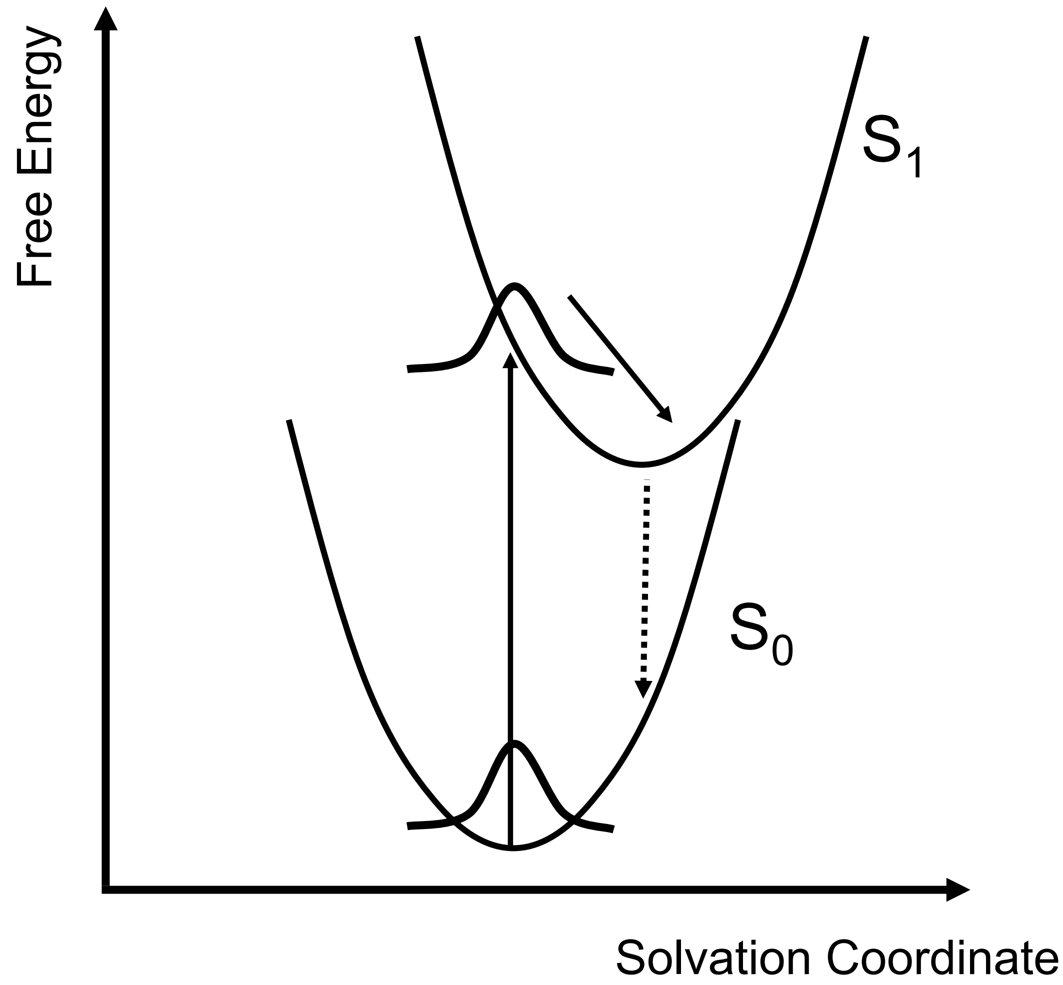
Solvation



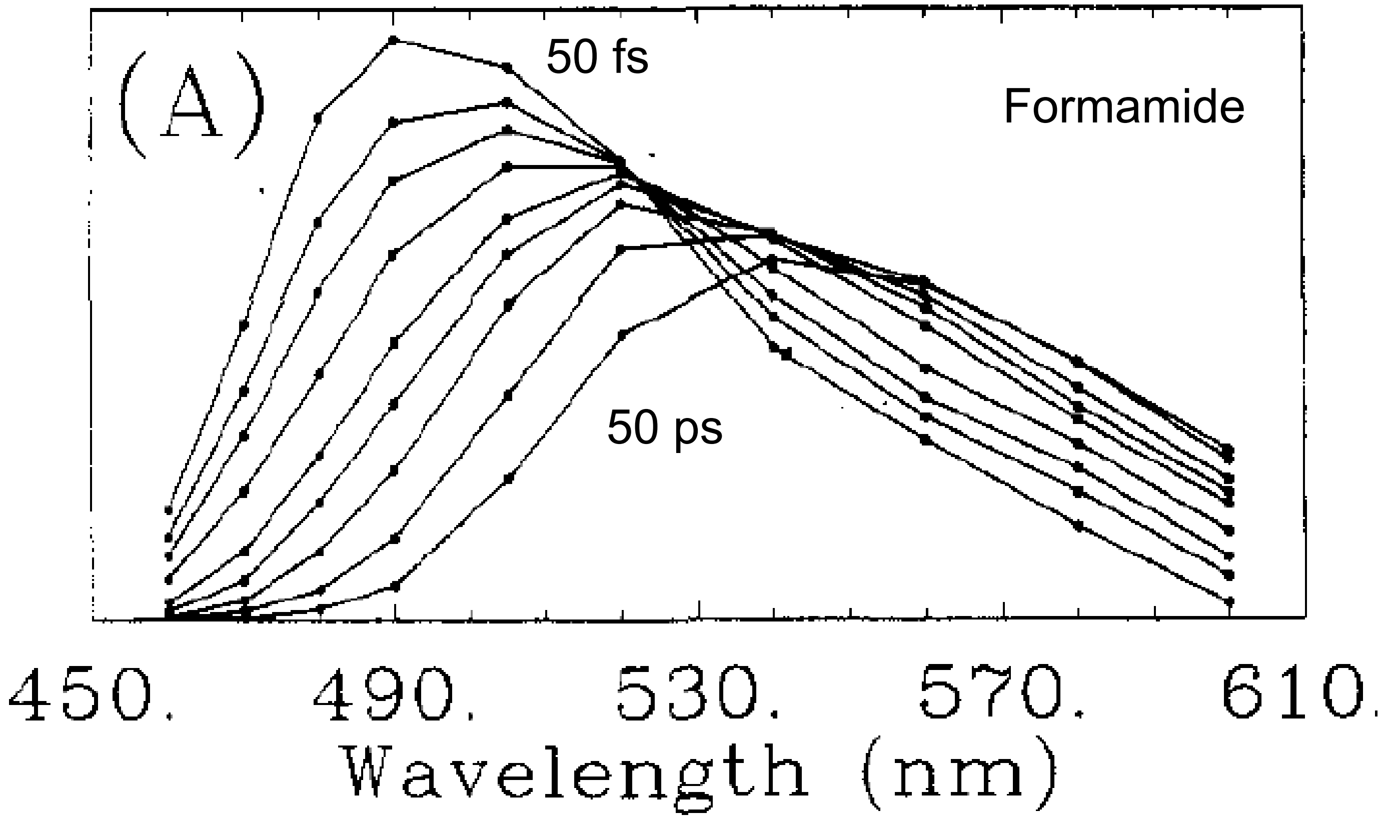
$$\Delta E = \frac{(\varepsilon - 1)}{(2\varepsilon + 1) r^3} \mu^2$$

Onsager‘s Reaction Field Model

Solvation

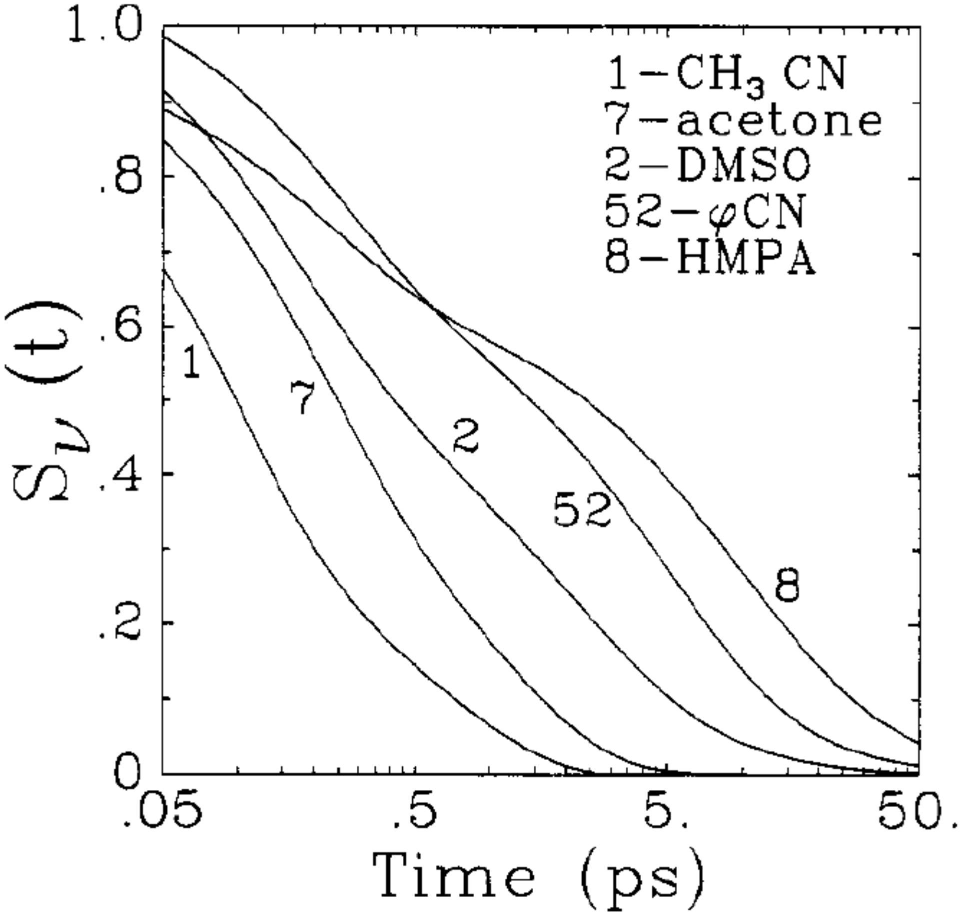


Solvation of Coumarin in Ploar Solvents



M. L. Horng, J. A. Gardecki, A. Papazyan, M. Maroncelli, *Subpicosecond Measurements of Polar Solvation Dynamics: Coumarin 153 Revisited*
J. Phys. Chem.; **1995**; 99(48); 17311-17337.

Solvation of Coumarin in Polar Solvents



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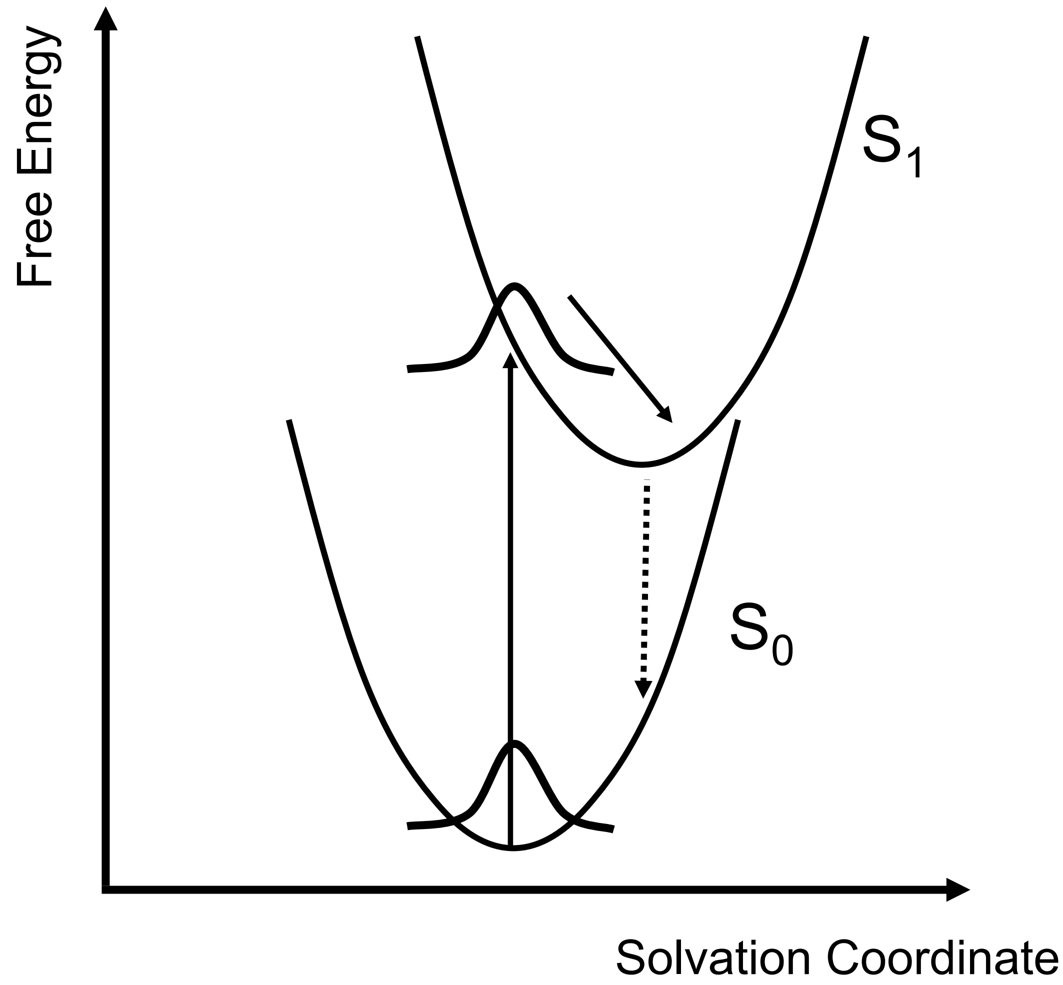
Solvation



Central Limit Theorem

When a random property is the sum of many random properties, e.g.:

$$P = \sum_{i=1}^{N} \mu_z$$

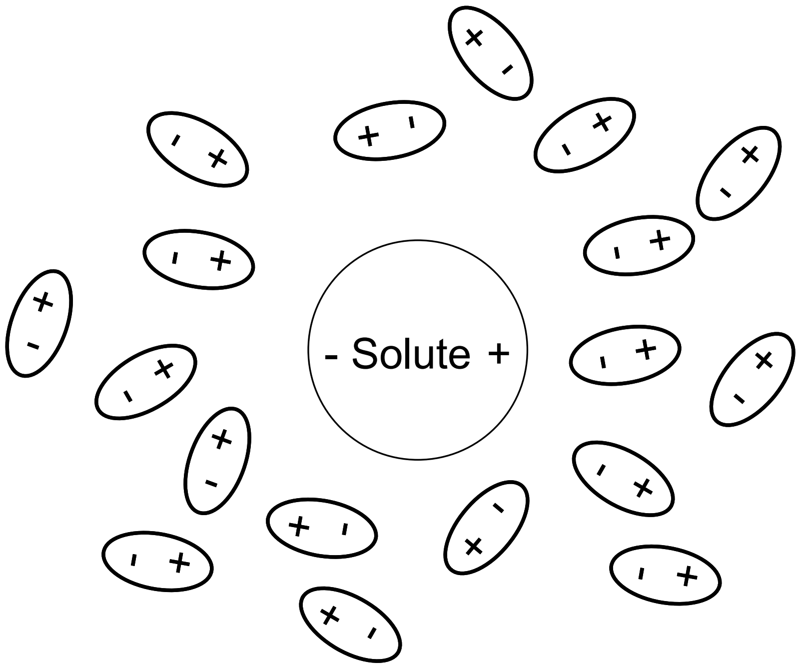
then, the sum (P) is Gaussian distributed (in the limit $N \rightarrow \infty$), regardless what the distribution of the individual terms (μ_z) is. The mean of the sum is:

$$\langle P \rangle = N \langle \mu_z \rangle$$

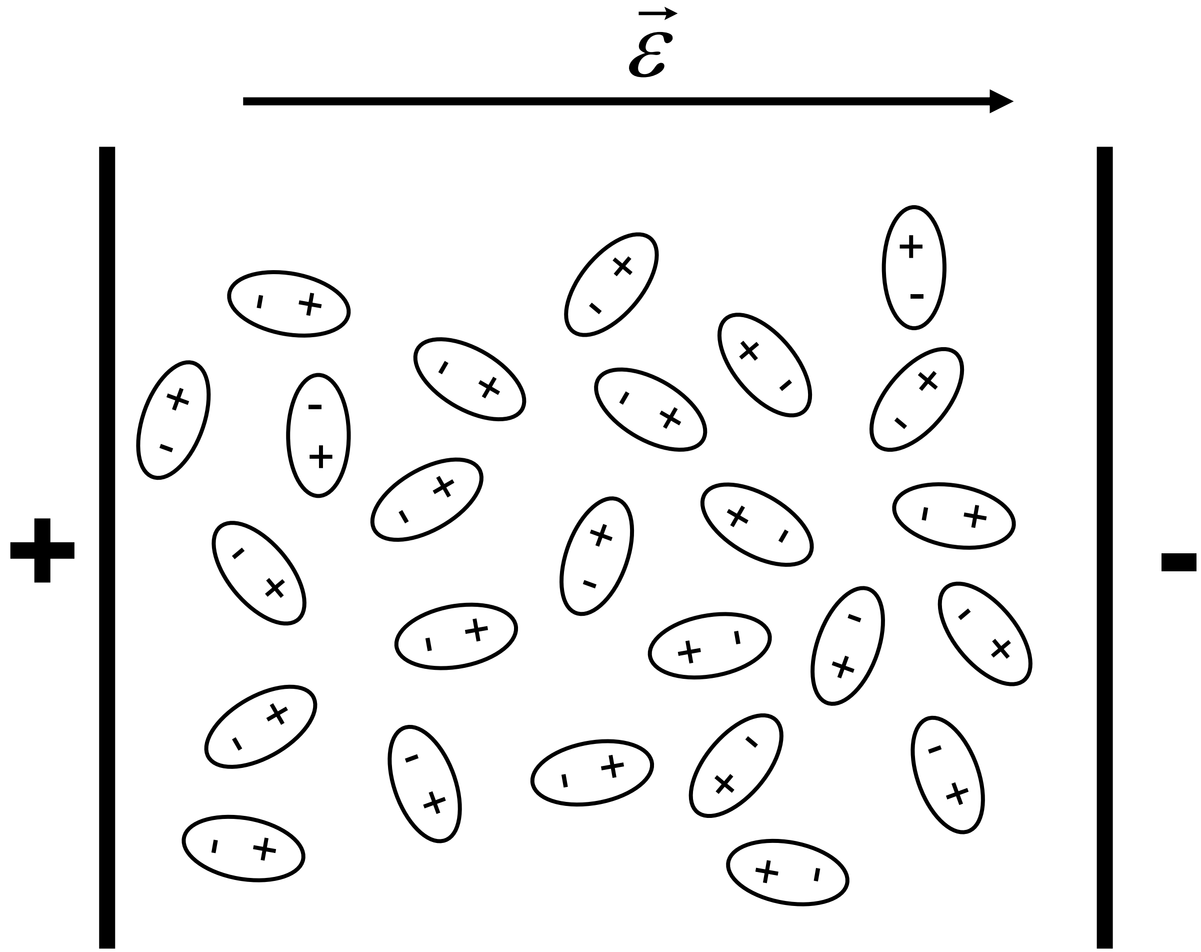
and the variance:

$$\left\langle \left(P - \langle P \rangle \right)^2 \right\rangle = N \left\langle \left(\mu_z - \langle \mu_z \rangle \right)^2 \right\rangle$$

Polarisation around a dipole

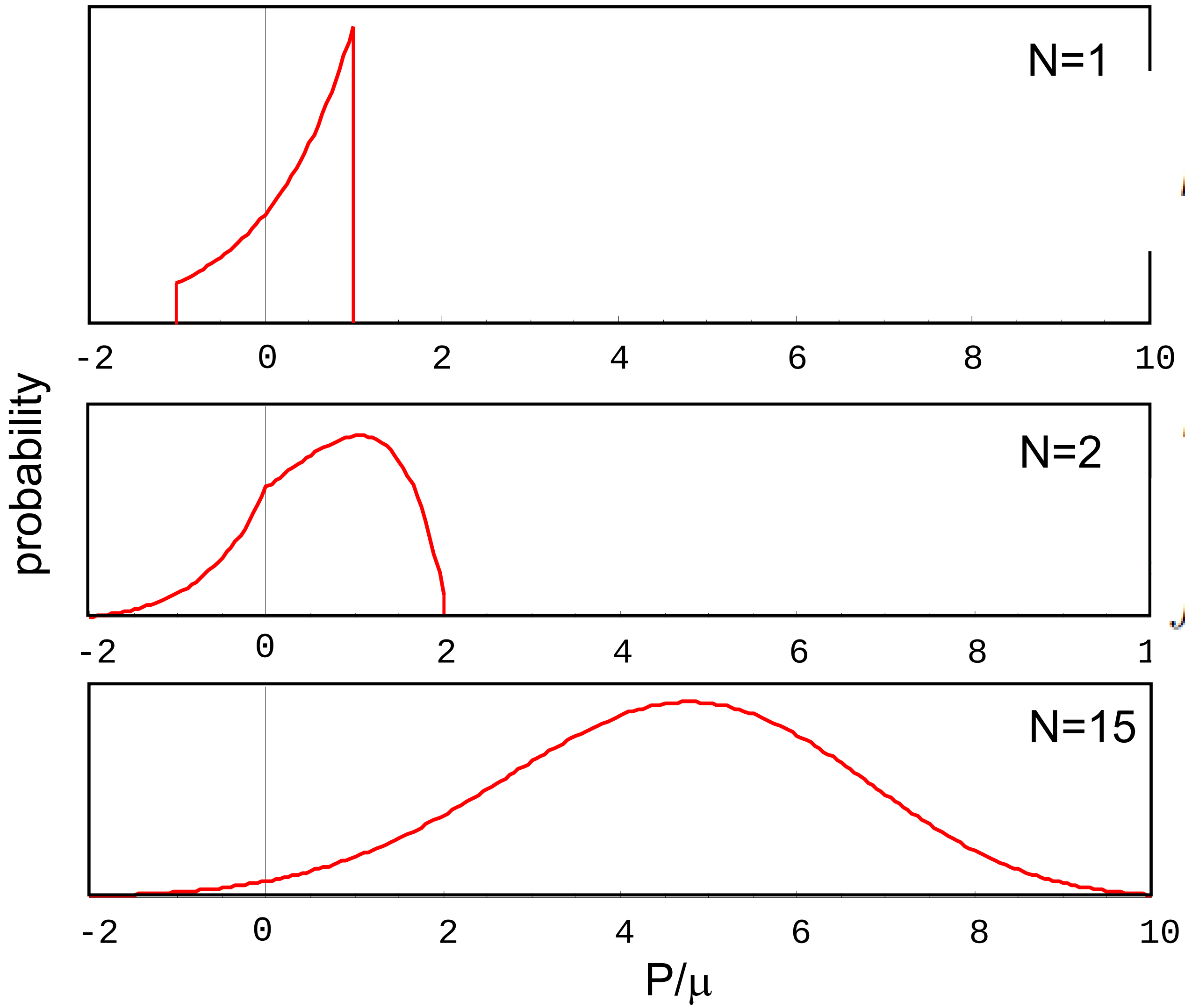


Polarisation in a Plate Capacitor



Energy of a single solute molecule $E = -\vec{\epsilon} \cdot \vec{\mu} = -\epsilon_x \mu_x$

Polarisation in a Plate Capacitor

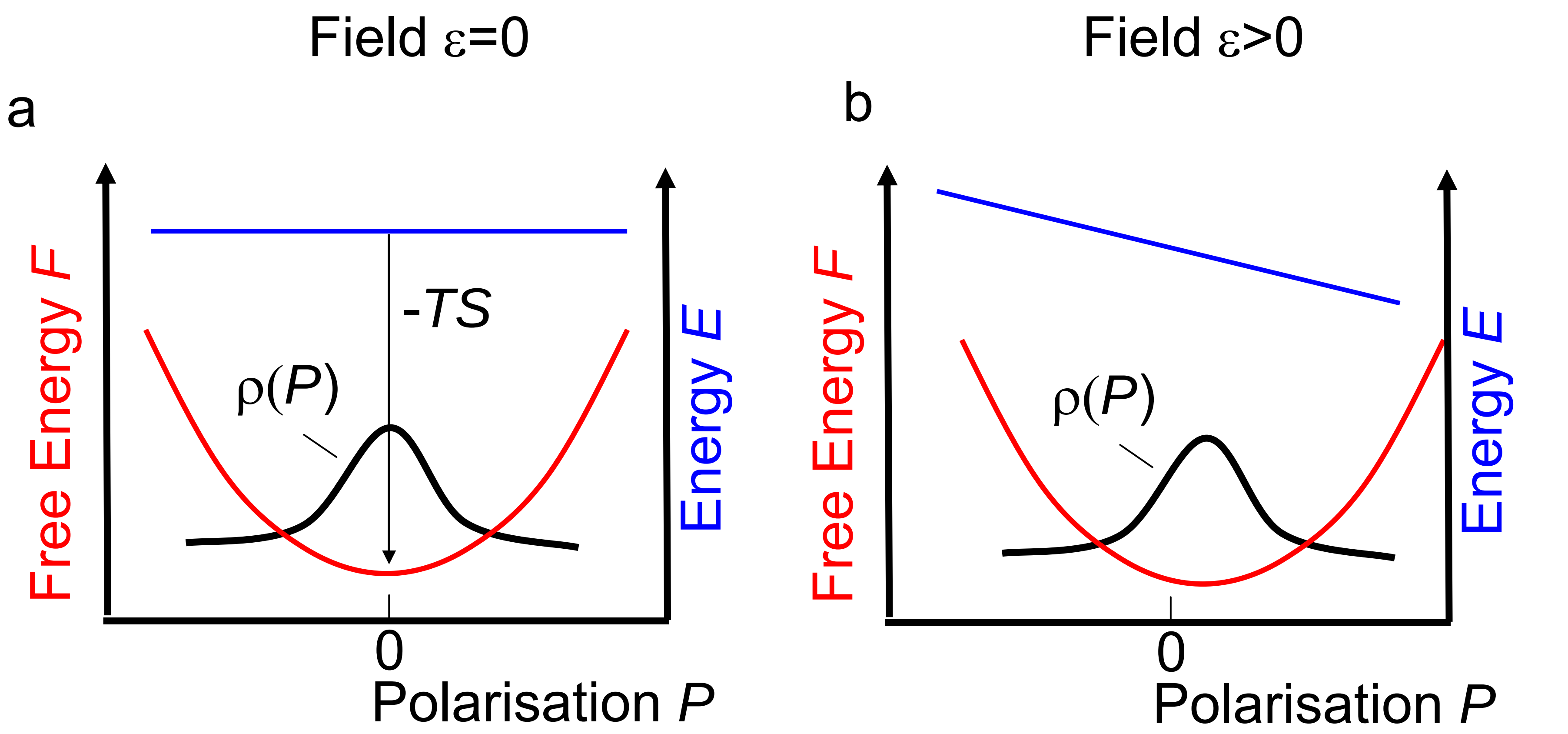


$$\rho(\mu_x) = \frac{1}{n} e^{\frac{\epsilon_x \mu_x}{k_B T}}$$

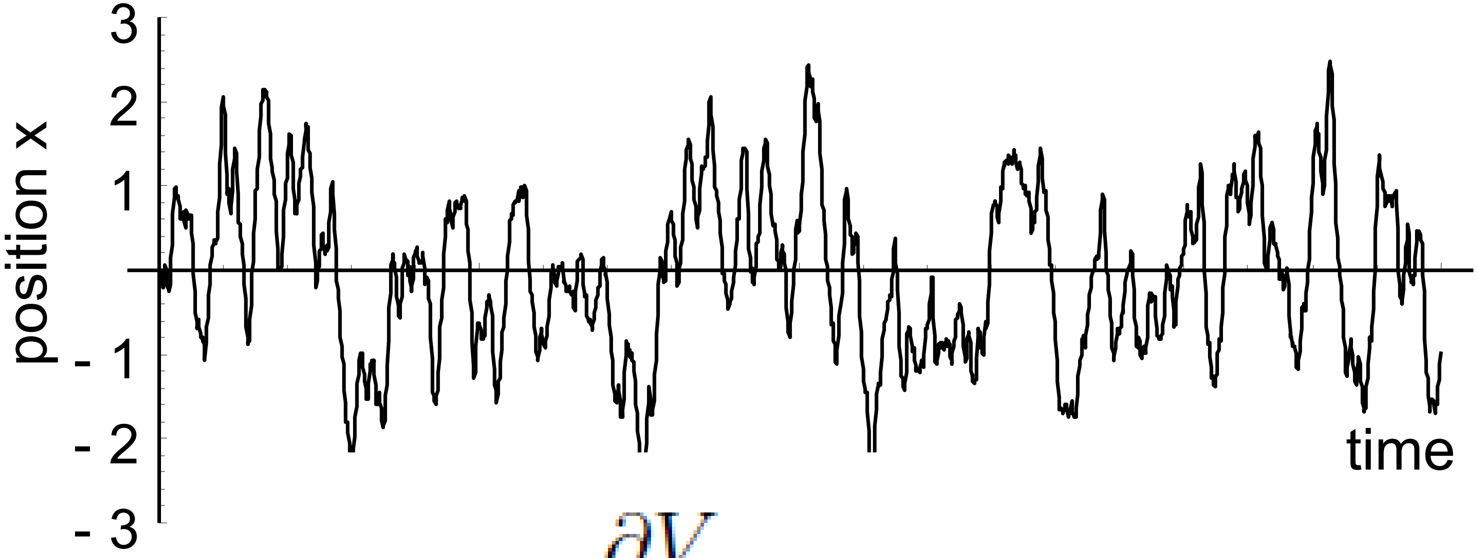
$$\rho'(P) =$$

$$\int_{-N|\vec{\mu}|}^{+N|\vec{\mu}|} \rho(\mu_x)\rho(P-\mu_x)d\mu_x$$

Polarisation in a Plate Capacitor



Langevin Dynamics



$$m\ddot{x} = -\frac{\partial V}{\partial x} - \gamma m\dot{x} + \delta F(t)$$

with $\langle F(0)F(t)\rangle = \delta F_0^2 \cdot \delta(t)$

$$\delta F_0^2 = 2\gamma m k_B T$$

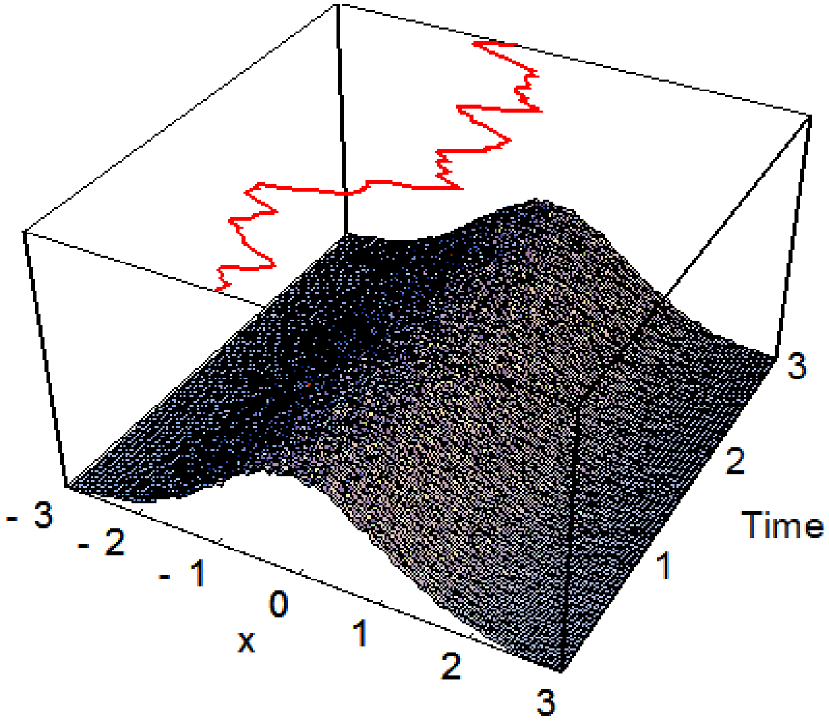
Fluctuation-Dissipation Theorem

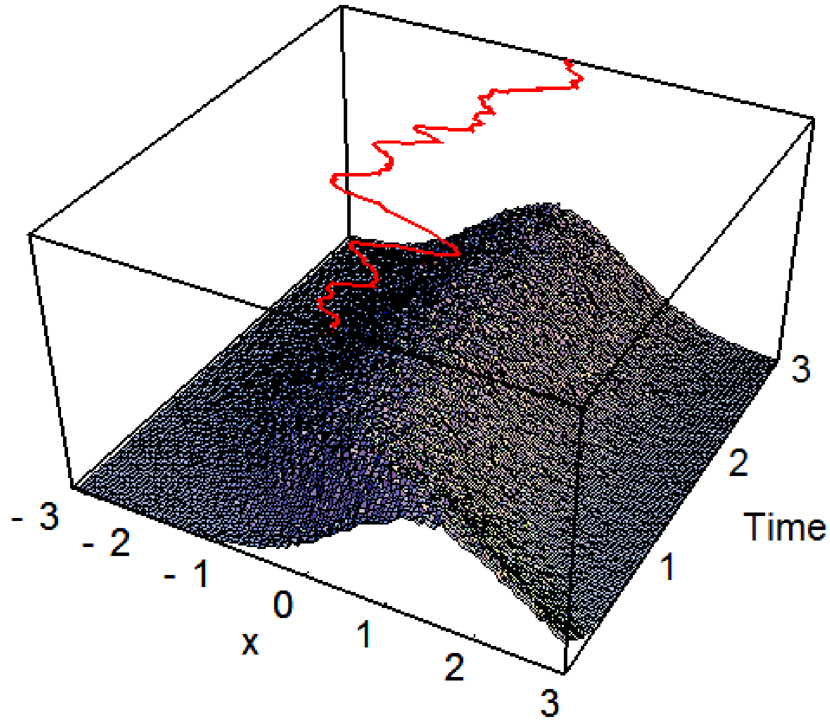
Ensemble of Particles

thermal equilibrium

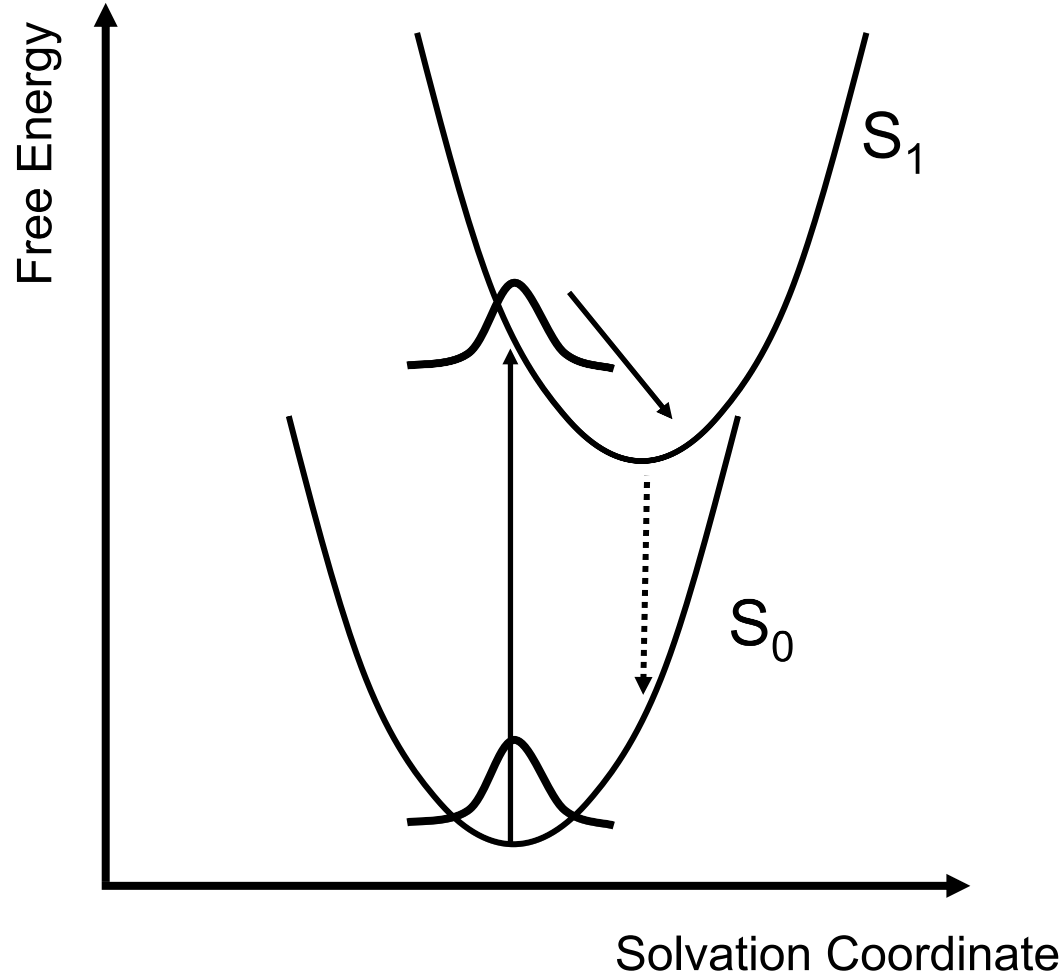
non-equilibrium

$$\rho(x) = e^{-\frac{V(x)}{k_B T}}$$

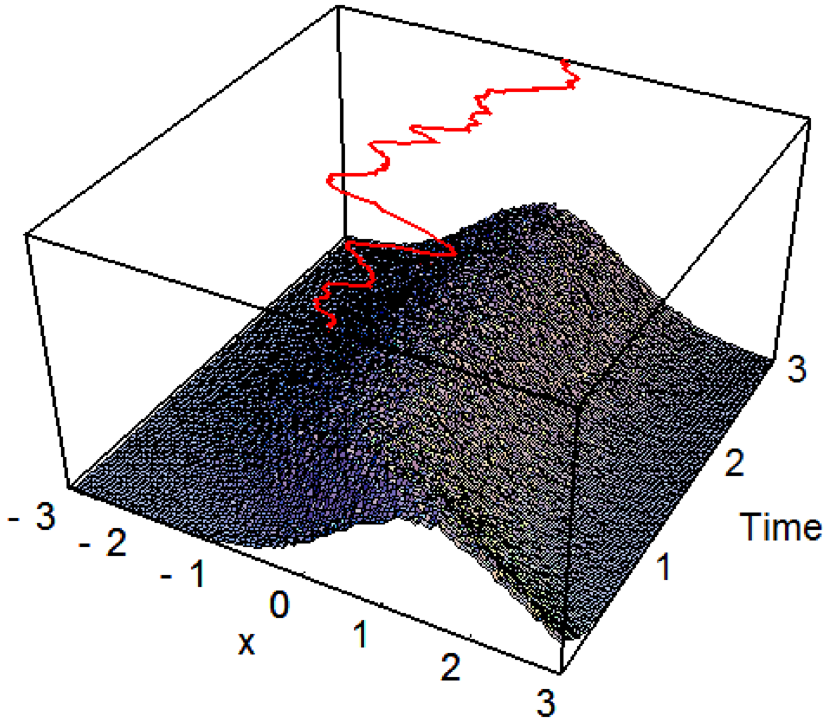


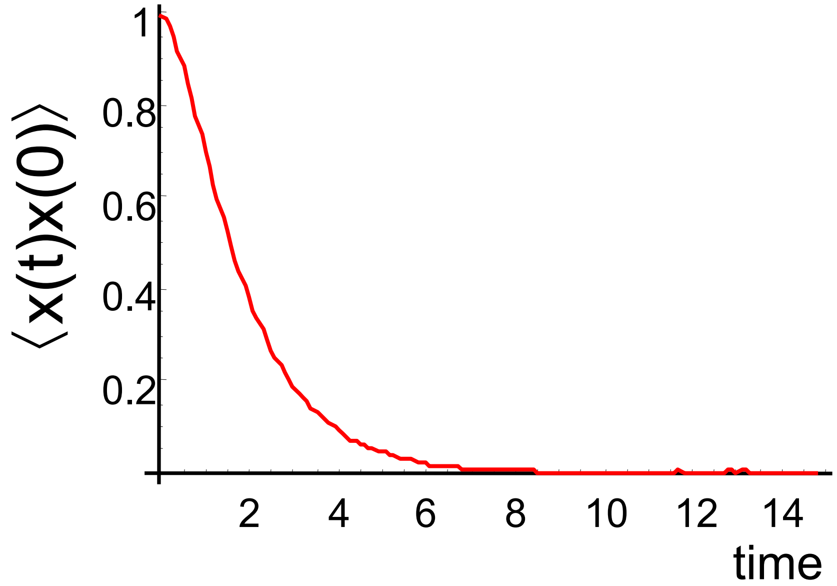


Solvation



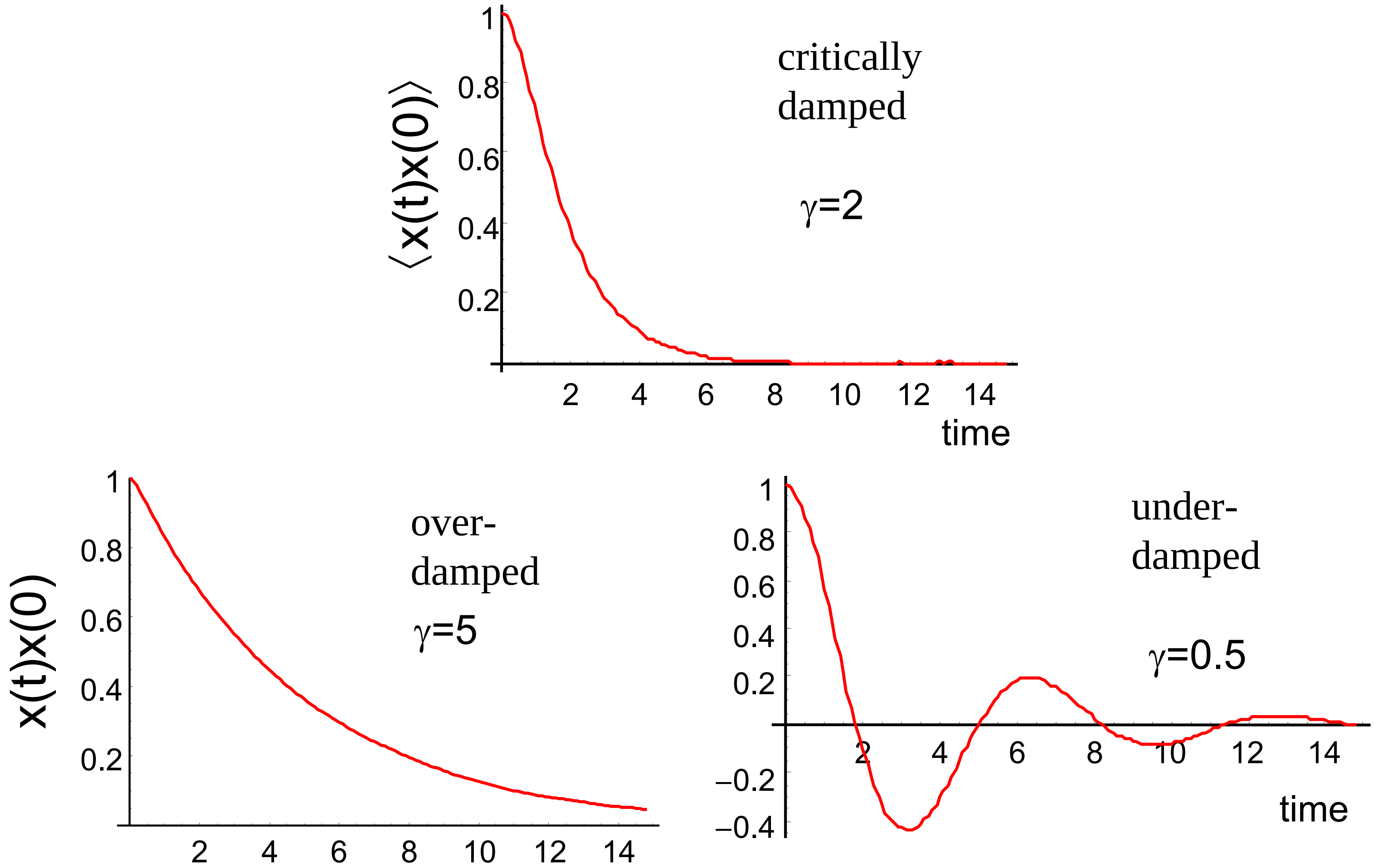
Onsager Regresssion Hypothesis



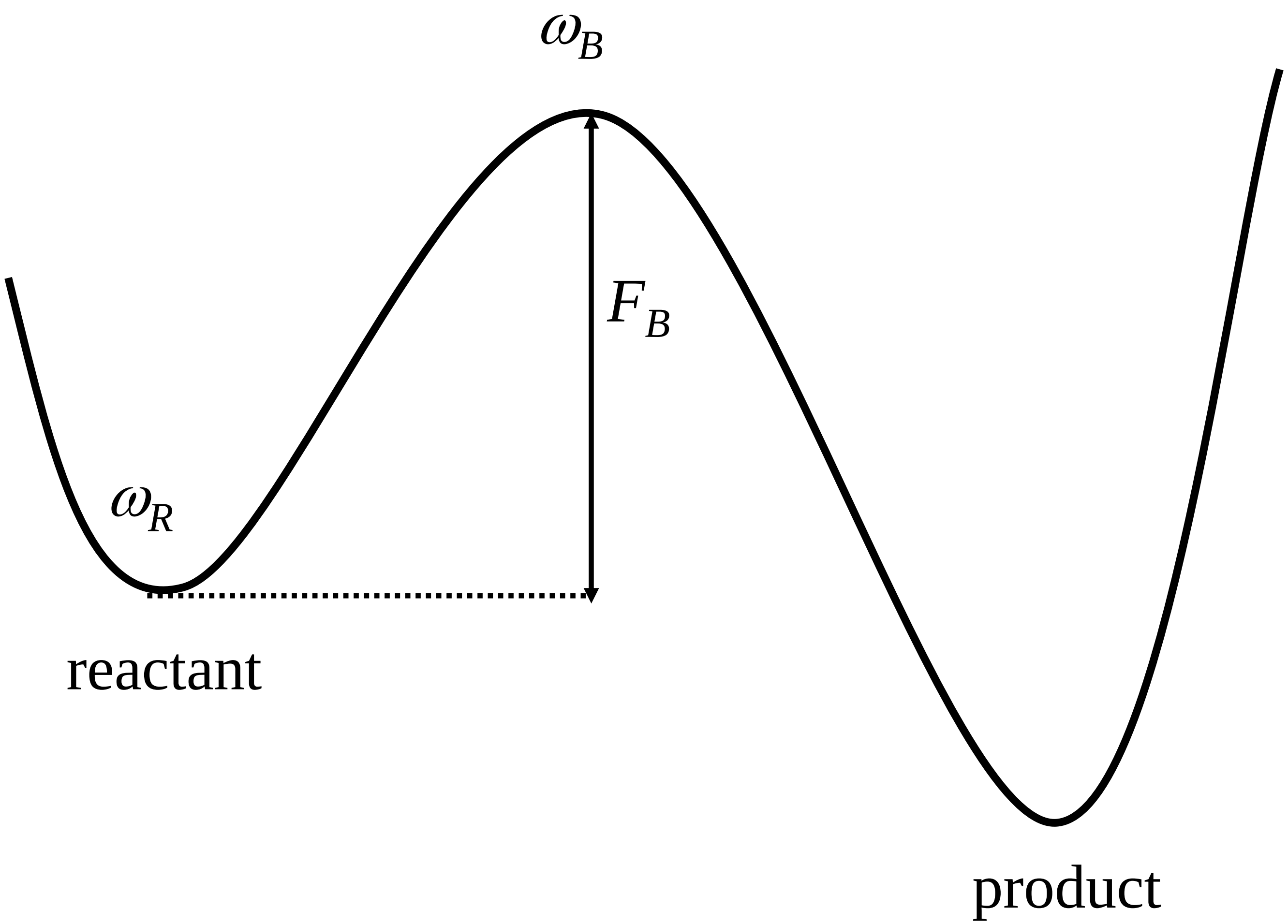


$$\langle x(t)\rangle_{noneq} \propto \langle x(t)x(0)\rangle_{eq}$$

Correlation Function

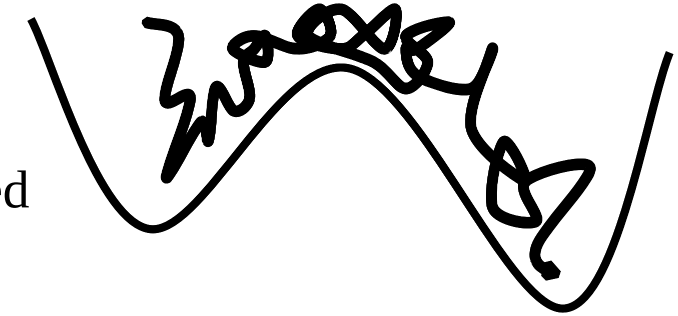


Kramers Theory of Reaction Kinetics



Kramers Theory of Reaction Kinetics

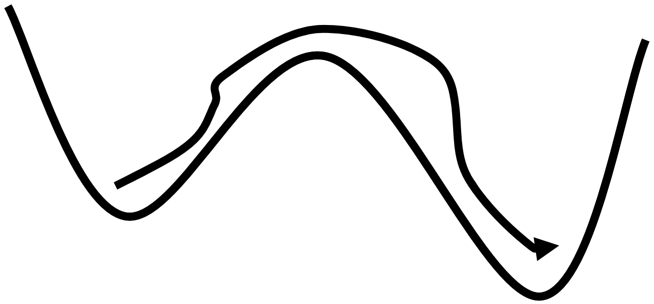
strongly overdamped



$$\gamma >> \omega_R$$

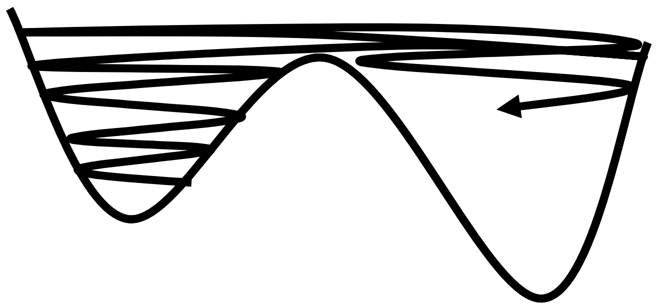
$$k_R = \frac{\omega_B \omega_R}{2\pi\gamma} e^{-\frac{E_b}{k_B T}}$$

critically damped



$$k_R = \frac{1}{\omega_B}\left(-\frac{\gamma}{2} + \sqrt{\frac{\gamma^2}{4} - \omega_B^2}\right)\left\{\frac{\omega_R}{2\pi} e^{-\frac{E_b}{k_B T}}\right\}$$

under-damped

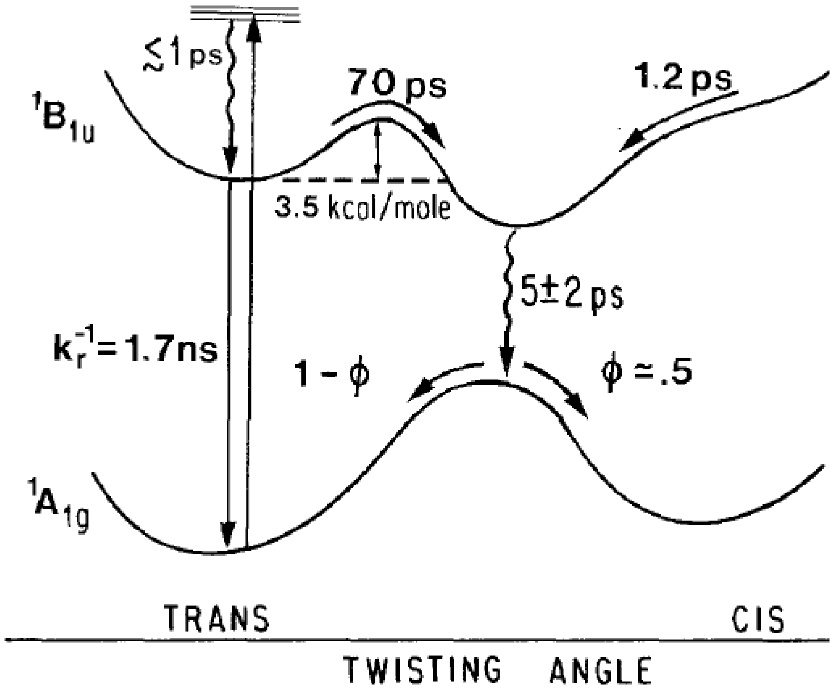


$$k_R = p\gamma \frac{I(E_b)}{k_B T}\left\{\frac{\omega_R}{2\pi} e^{-\frac{E_B}{k_B T}}\right\}$$

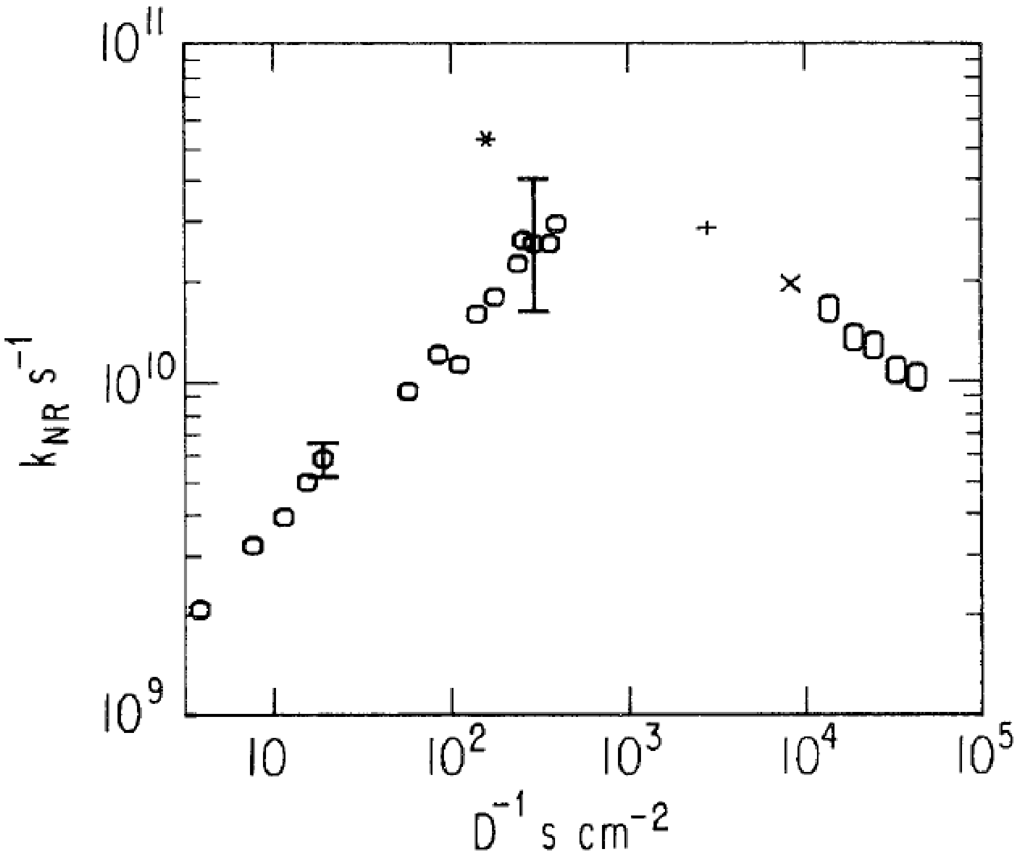
P. Hänggi et al., Rev. Mod. Physics, 62 (1990) 251

Photoisomerisation of Stilbene: Dependence on Solvent Viscosity

a



b



G. R. Fleming, S. H. Courtney, M. W. Balk, J. Stat. Phys. 42 (1986) 83

Femtochemistry: Basic Concepts

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- Motion in Quantum Mechanics: Wavepackets
- Franck-Condon Transition
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- **Electron Transfer Theory**
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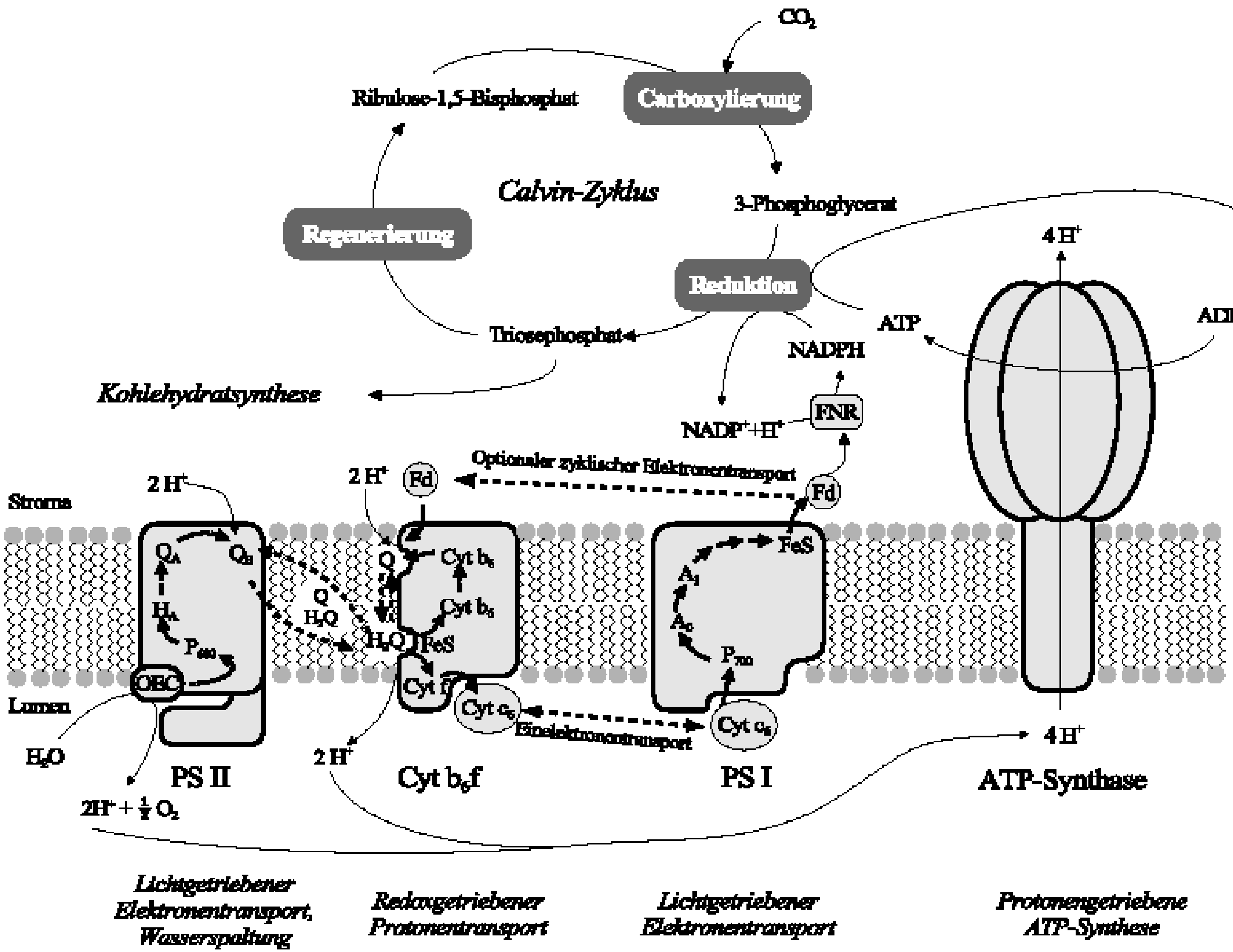
Photochemical Reactions in Nature: Electron Transfer in Photosynthesis



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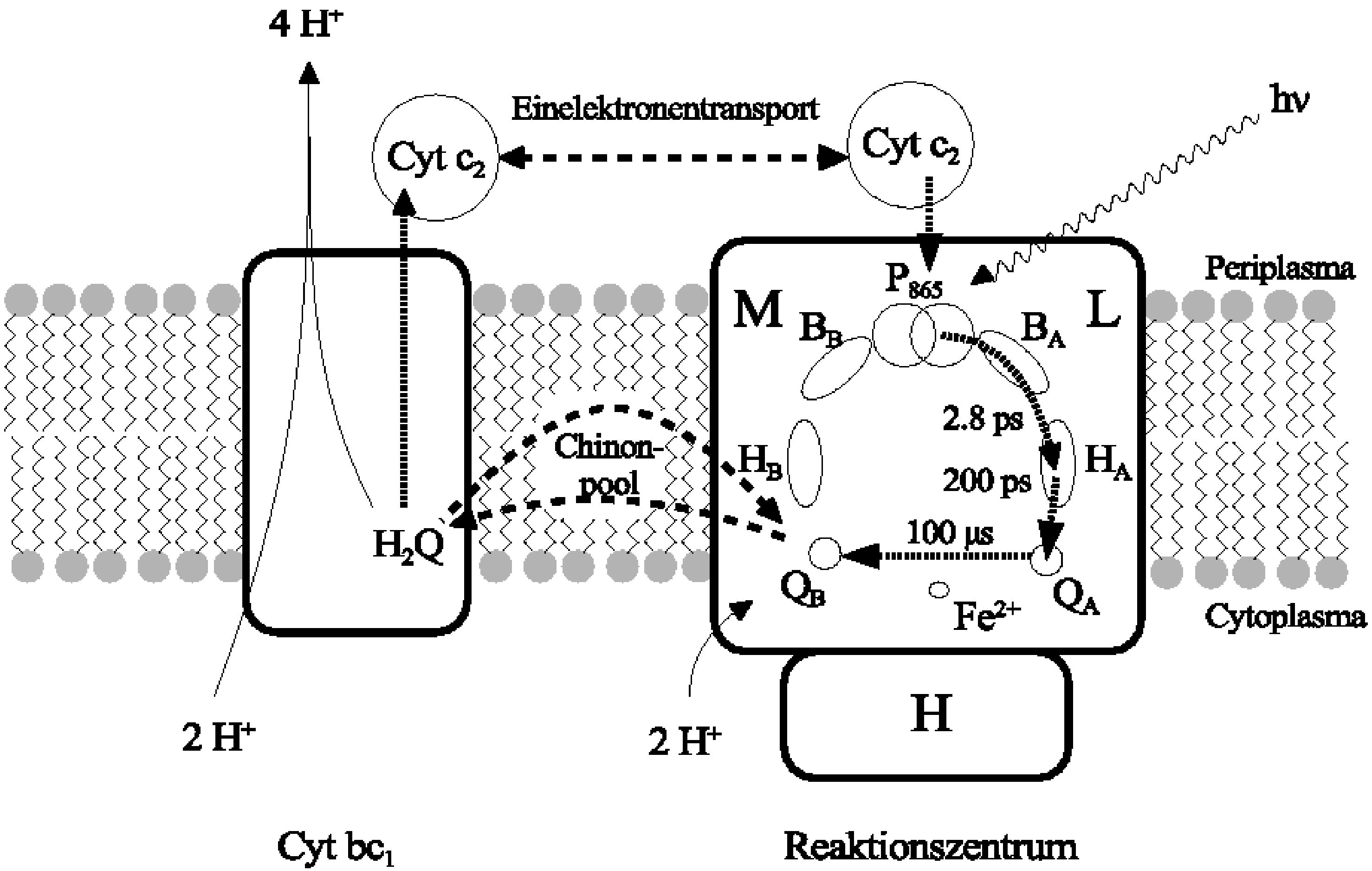
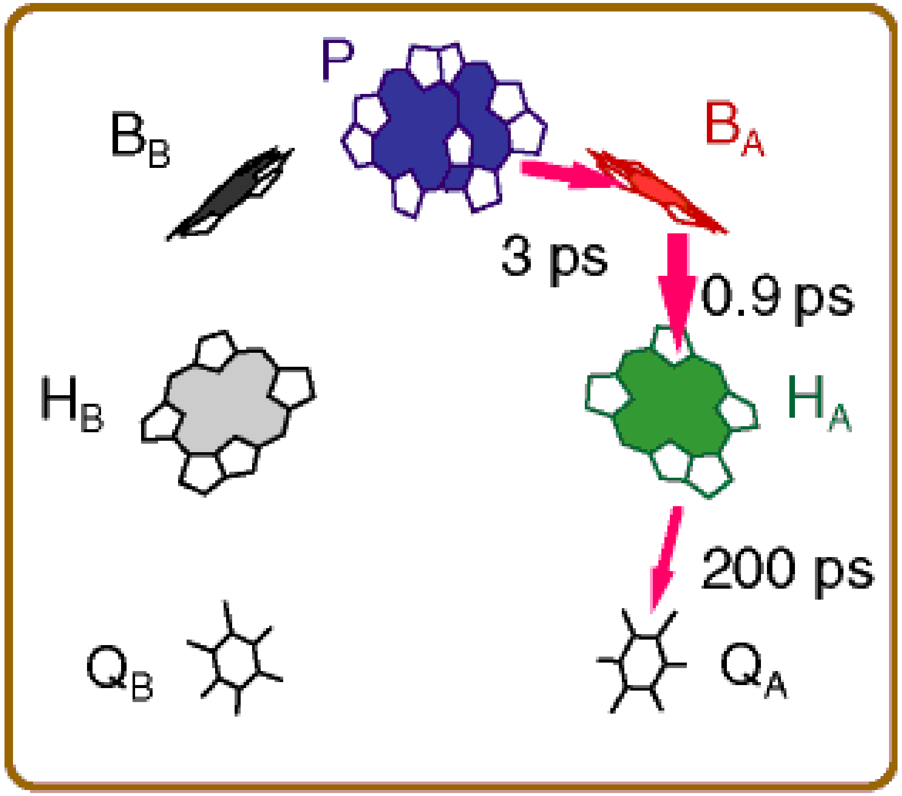


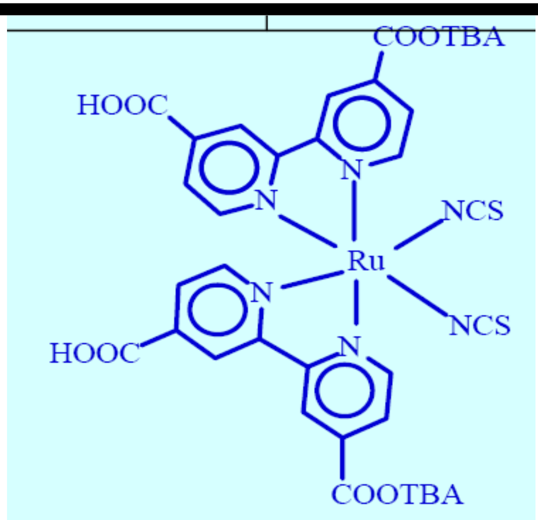
Photochemical Reactions in Nature: Electron Transfer in Photosynthesis

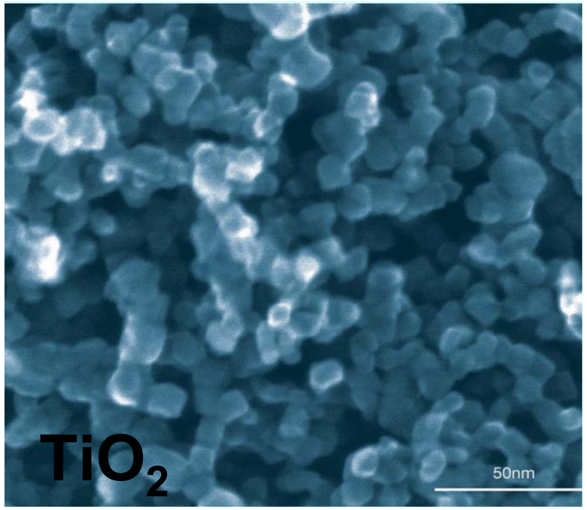
Der primäre Elektronentransfer im Reaktionszentrum

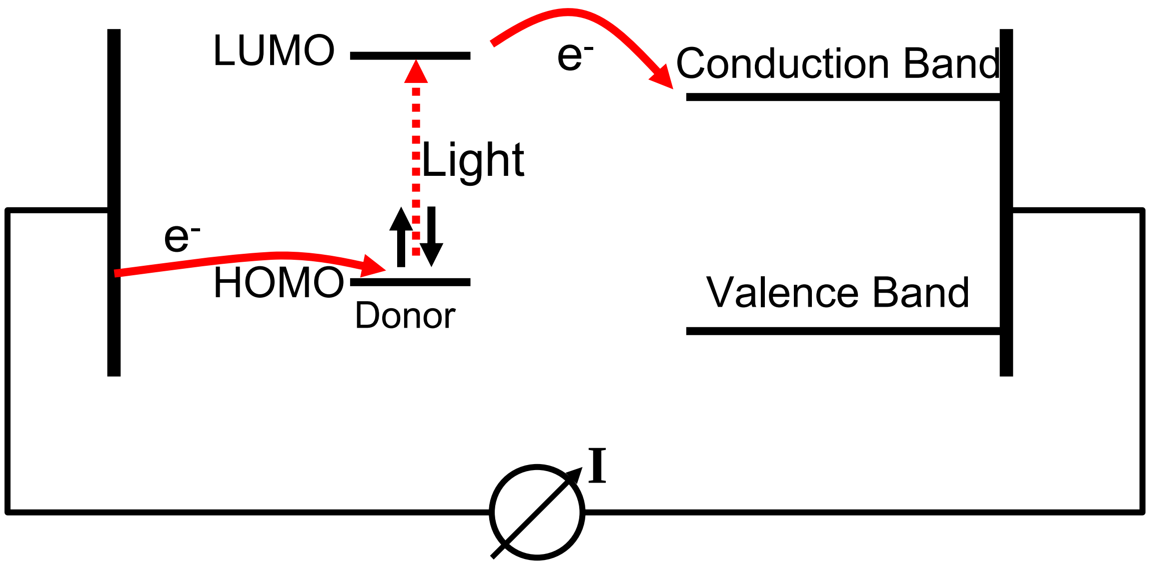


$$P^* \xrightarrow{3\ ps} P^+B_A^- \xrightarrow{0.9\ ps} P^+H_A^- \xrightarrow{200\ ps} P^+Q_A^-$$

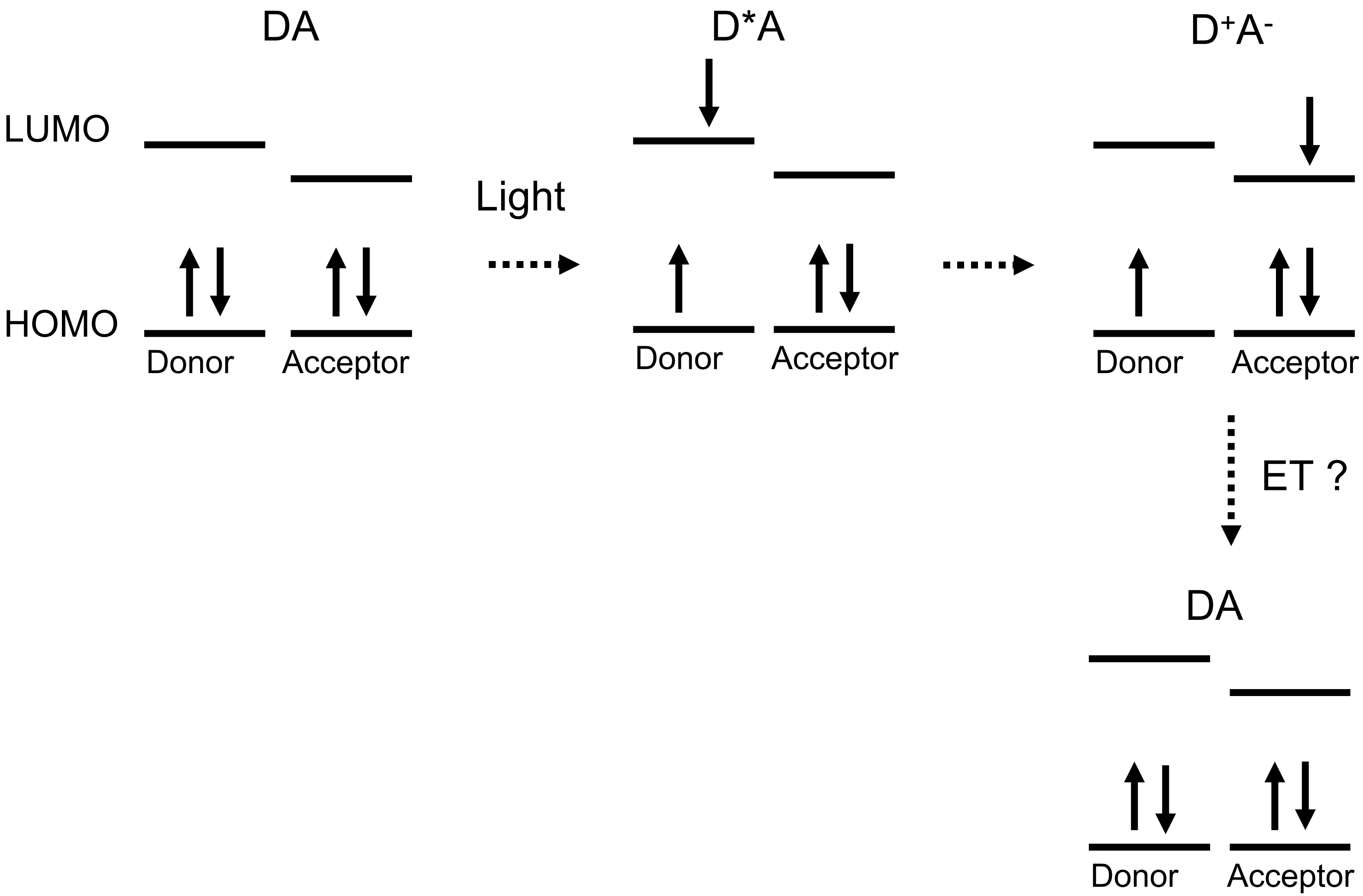
Artificial Photosynthesis: Grätzel Cell

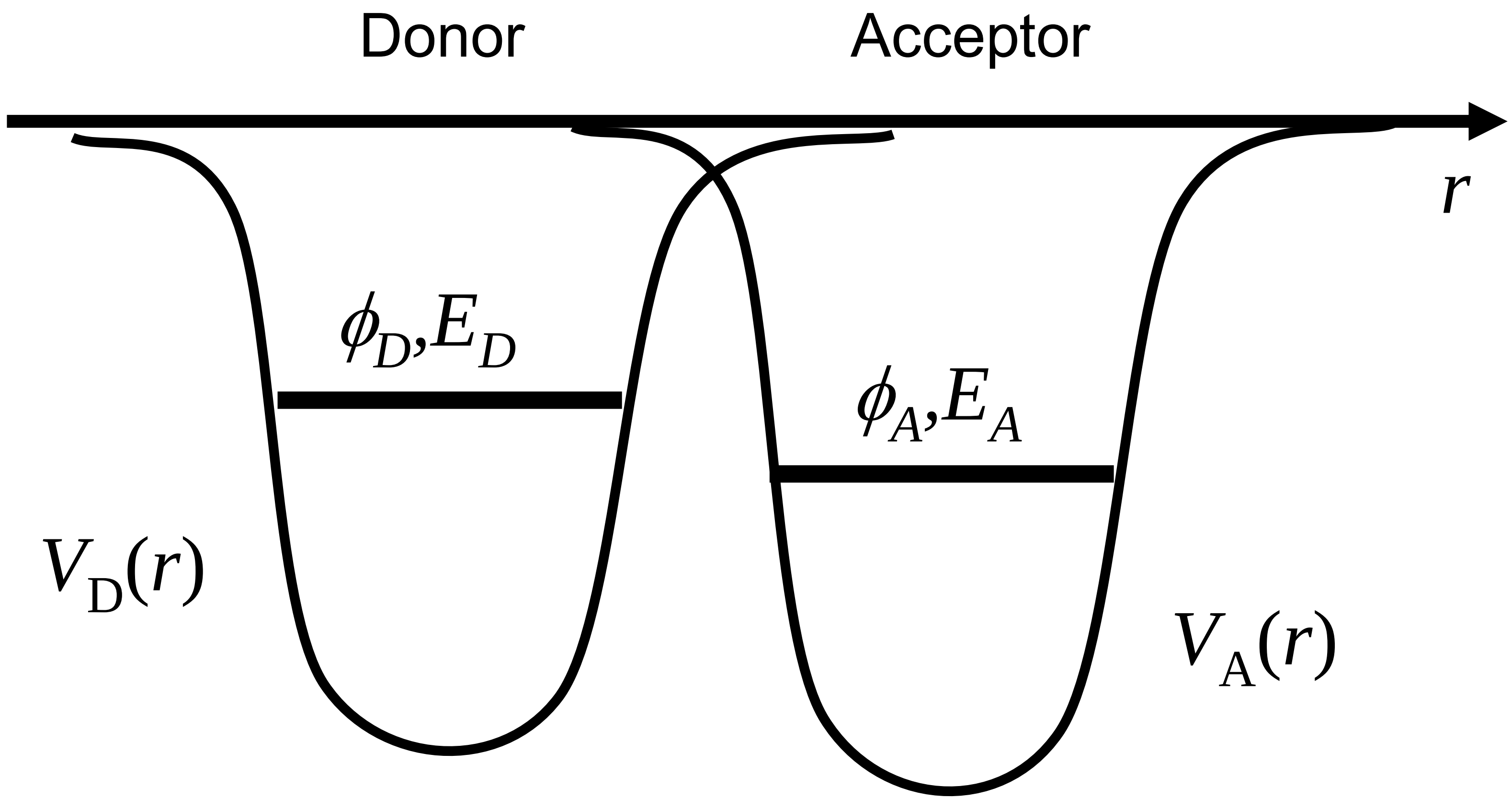






M. Grätzel, Nature 2001, 414, 338−344.


DA
LUMO
HOMO
Donor
Acceptor
Light
D*A
Donor
Acceptor
D+A-
Donor
Acceptor
ET ?
DA
Donor
Acceptor



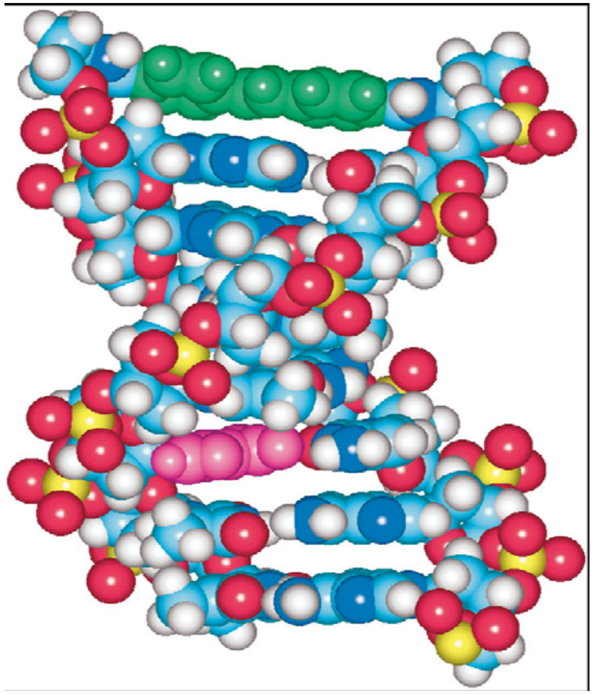
$$H_{el} = \begin{pmatrix} E_{DA} & V_{DA} \\ V_{DA} & E_{D+A-} \end{pmatrix}$$

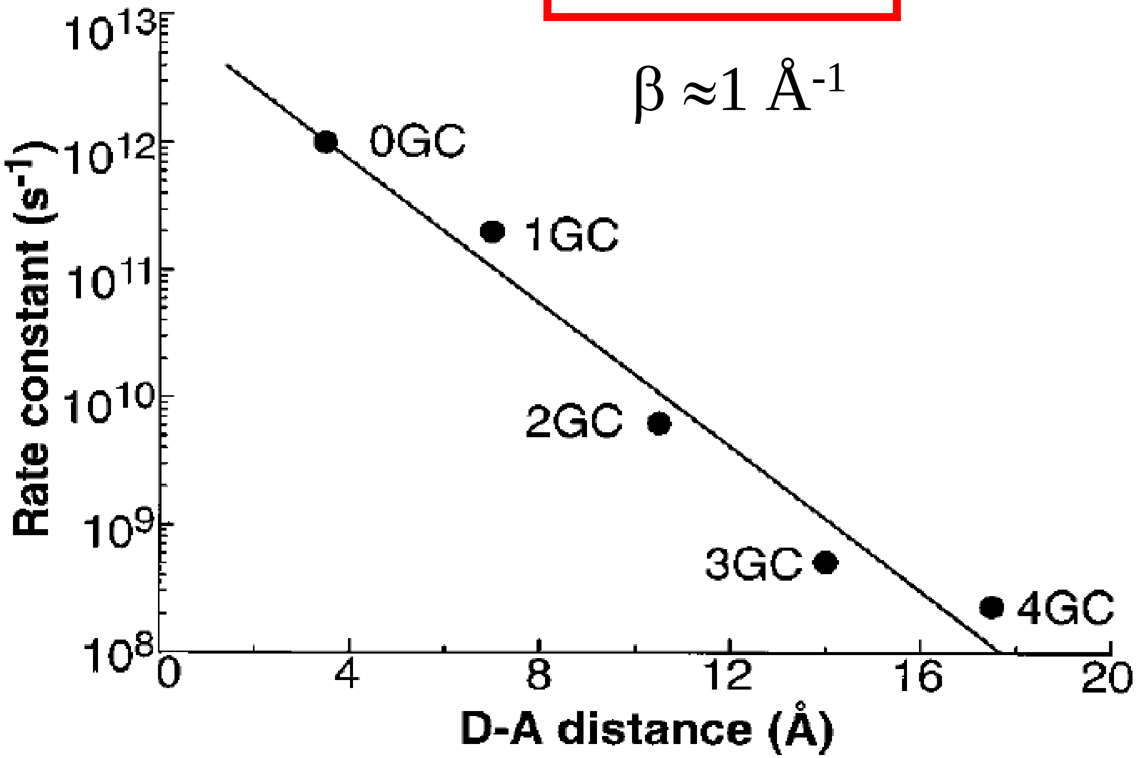
$$V_{DA} \propto e^{-\beta r_{DA}}$$

Distance Dependence of Electron Transfer

$$k \propto e^{-\beta R}$$

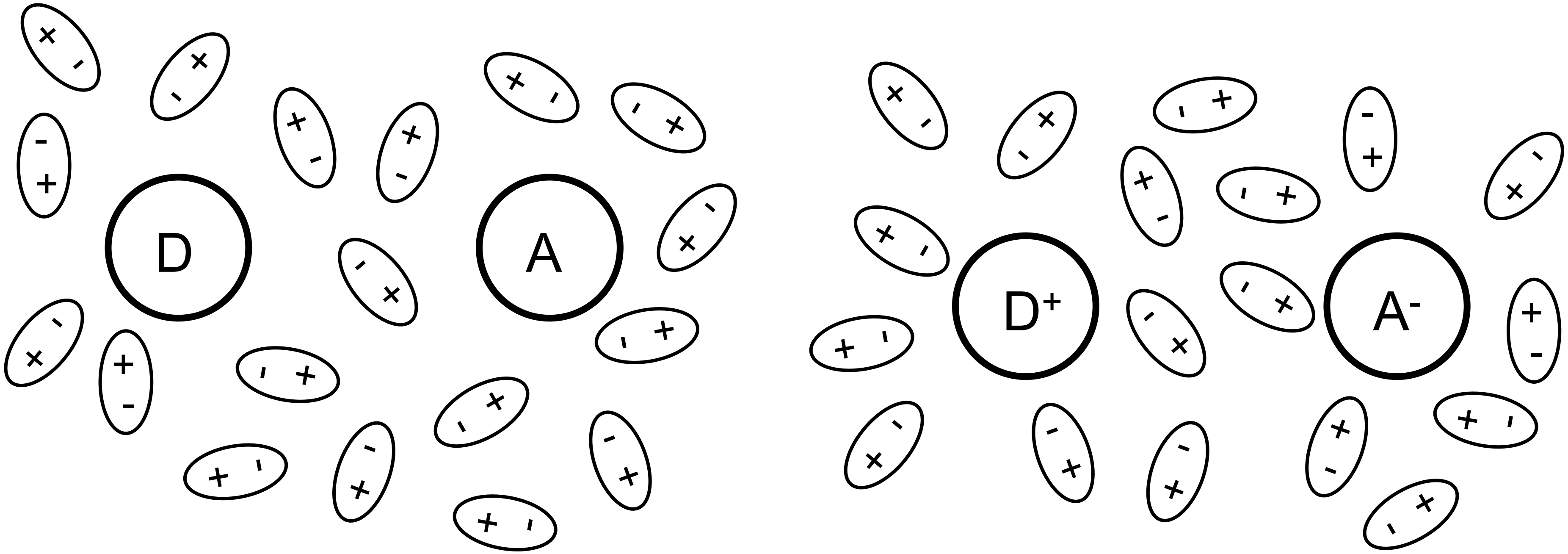
$\beta \approx 1$ Å^{-1}



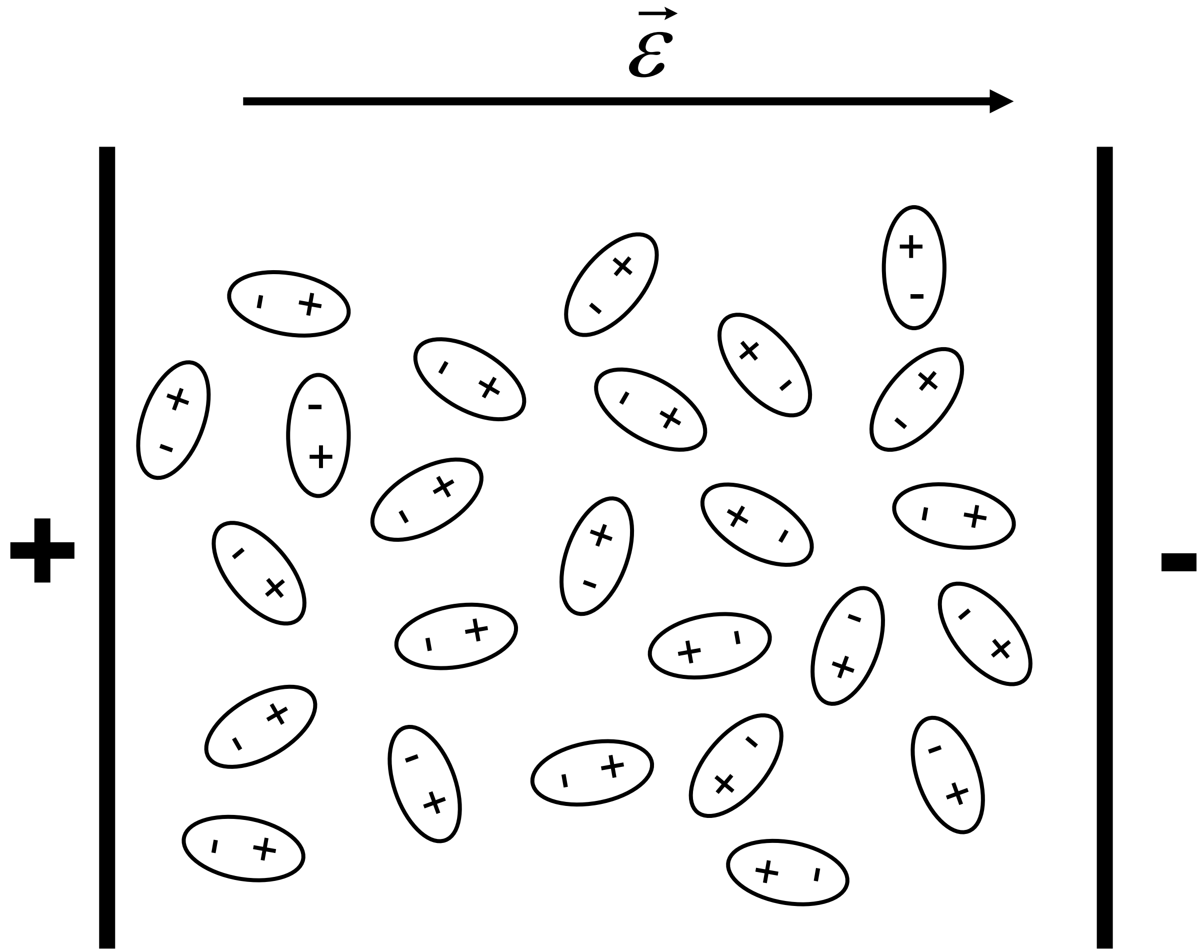


F. D. Lewis,* T. Wu, Y. Zhang, R. L. Letsinger, S. R. Greenfield, M. R. Wasielewski, *Distance-Dependent Electron Transfer in DNA Hairpins* Science 277 (1997) 673

Solvation of a Charge Transfer Complex

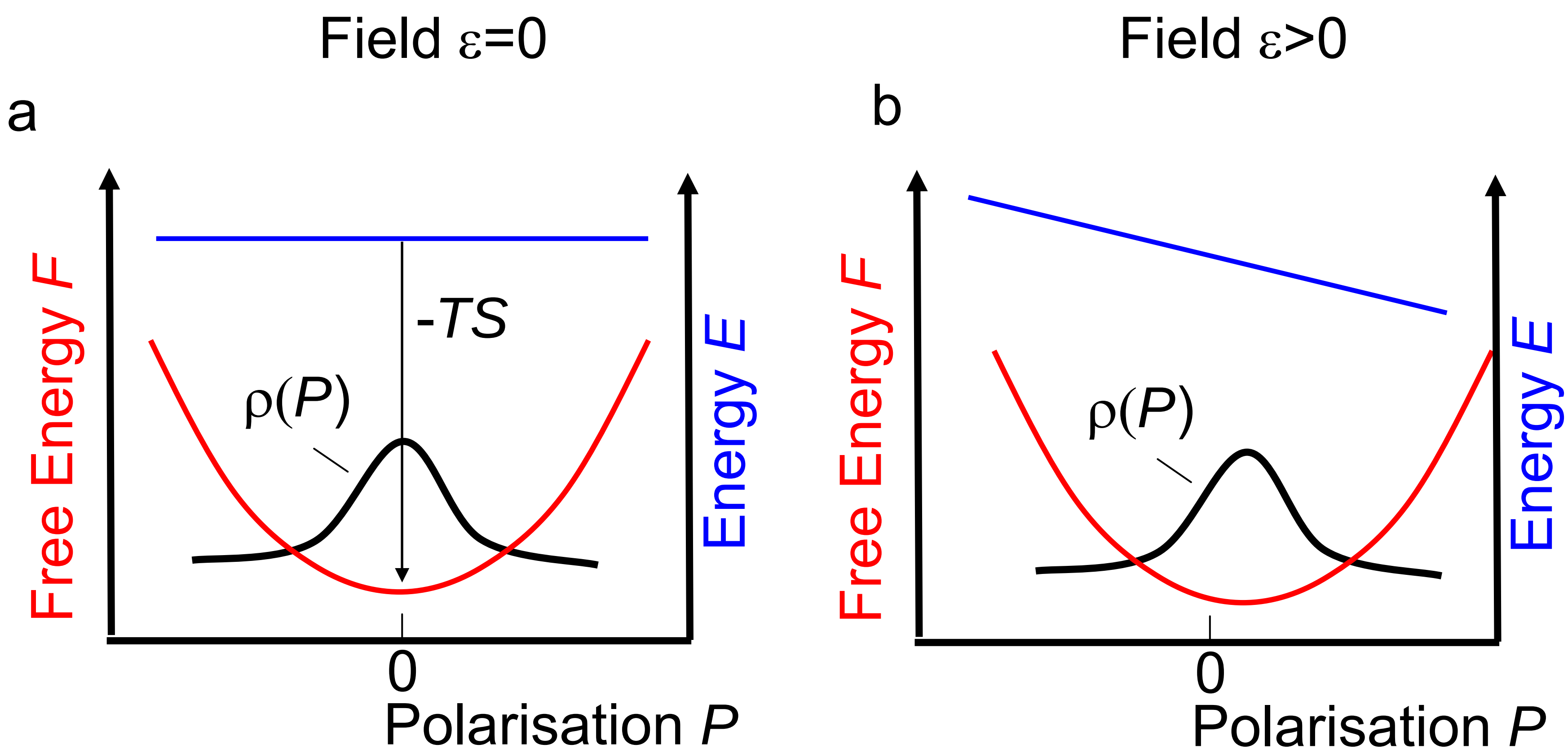


Polarisation in a Plate Capacitor

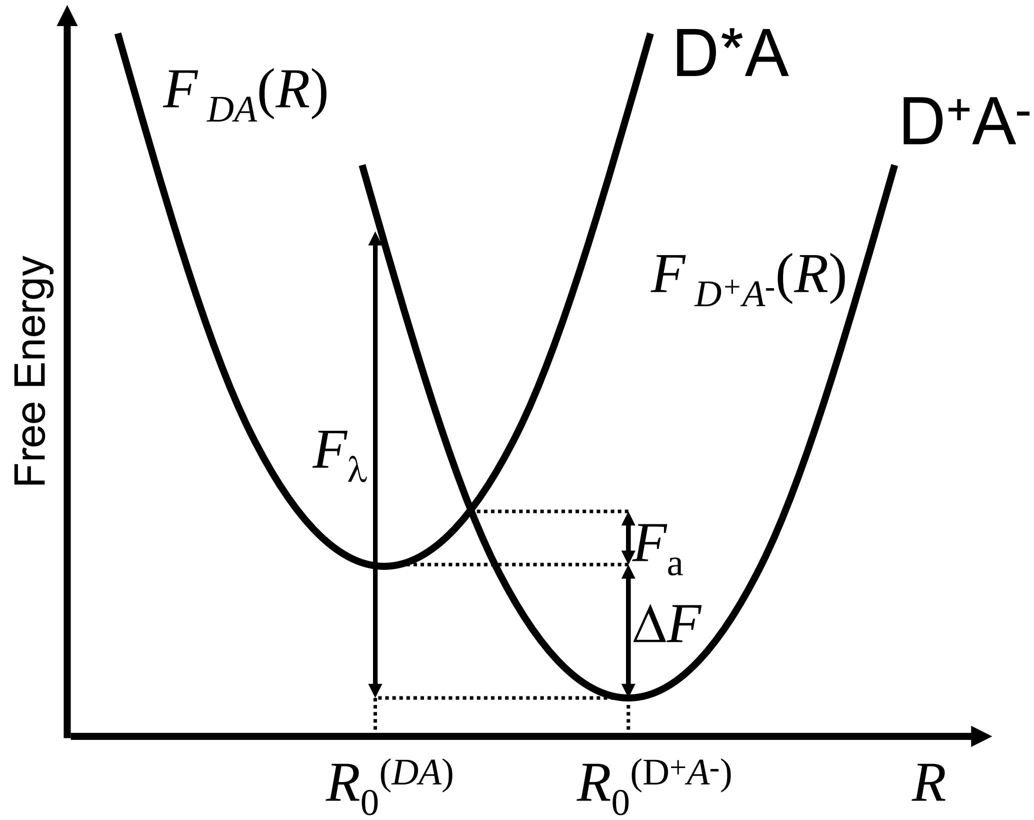


Energy of a single solute molecule $E = -\vec{\epsilon} \cdot \vec{\mu} = -\epsilon_x \mu_x$

Polarisation in a Plate Capacitor

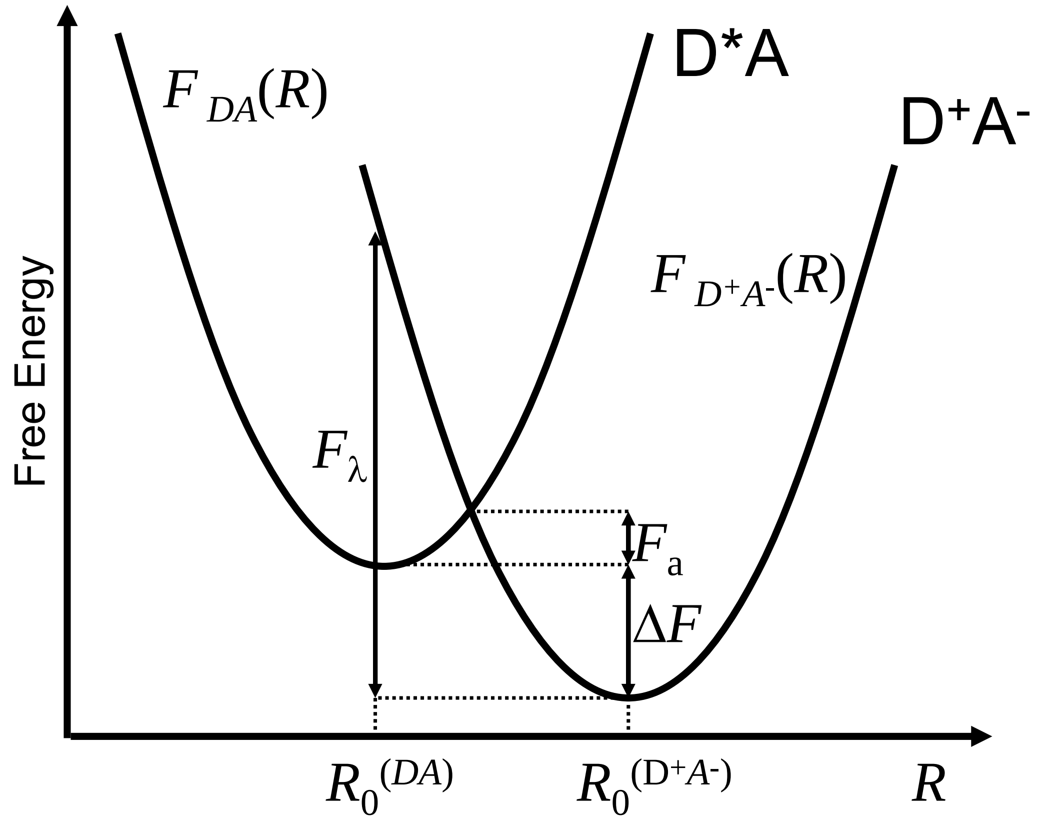


Marcus Theory of Electron Transfer



$$k_{ET} = V_{DA}{}^{2}\sqrt{\frac{\pi}{\hbar^{2}k_{B}TF_{\lambda}}}\exp\left(-\frac{F_{a}}{k_{B}T}\right)$$

Marcus Theory of Electron Transfer

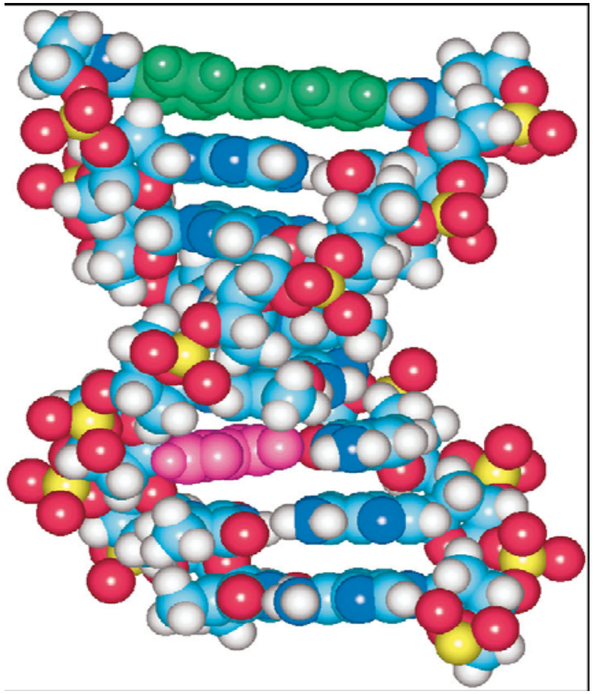


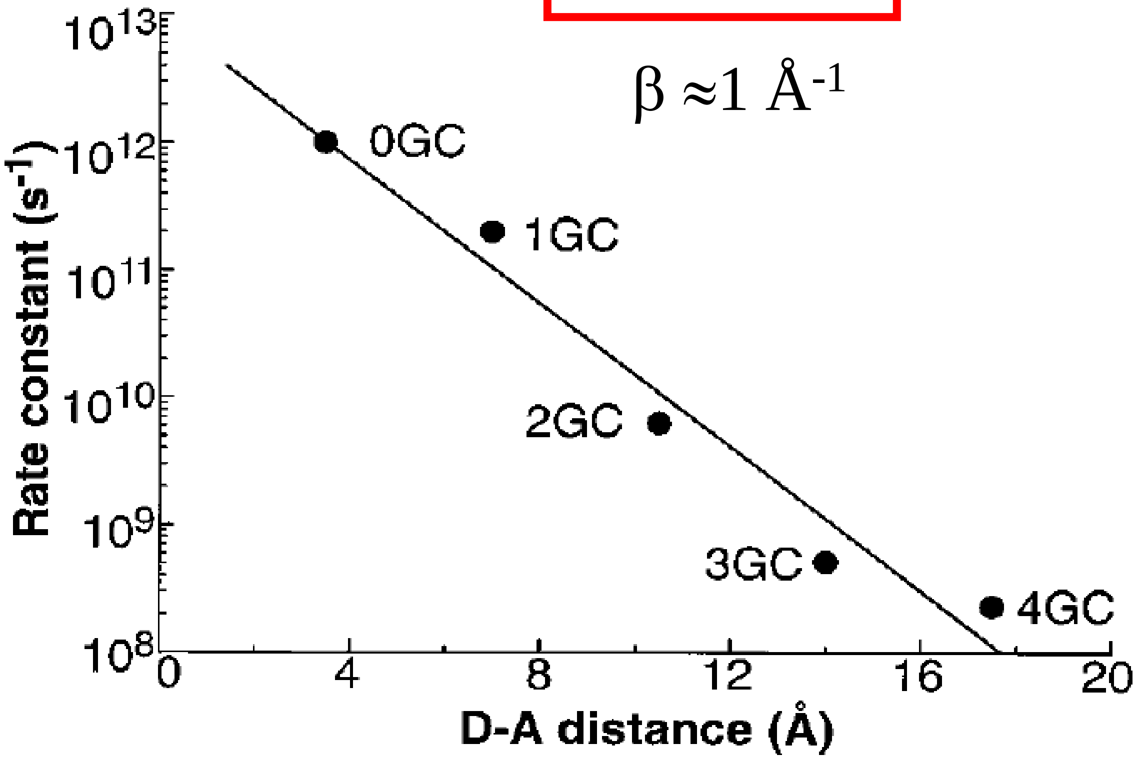
$$k_{ET} = V_{DA}^{\;2} \sqrt{\frac{\pi}{\hbar^2 k_B T F_\lambda}} \exp\left(-\frac{\left(\Delta F - F_\lambda\right)^2}{4 F_\lambda k_B T} \right)$$

Distance Dependence of Electron Transfer

$$k \propto e^{-\beta R}$$

$\beta \approx 1$ Å^{-1}





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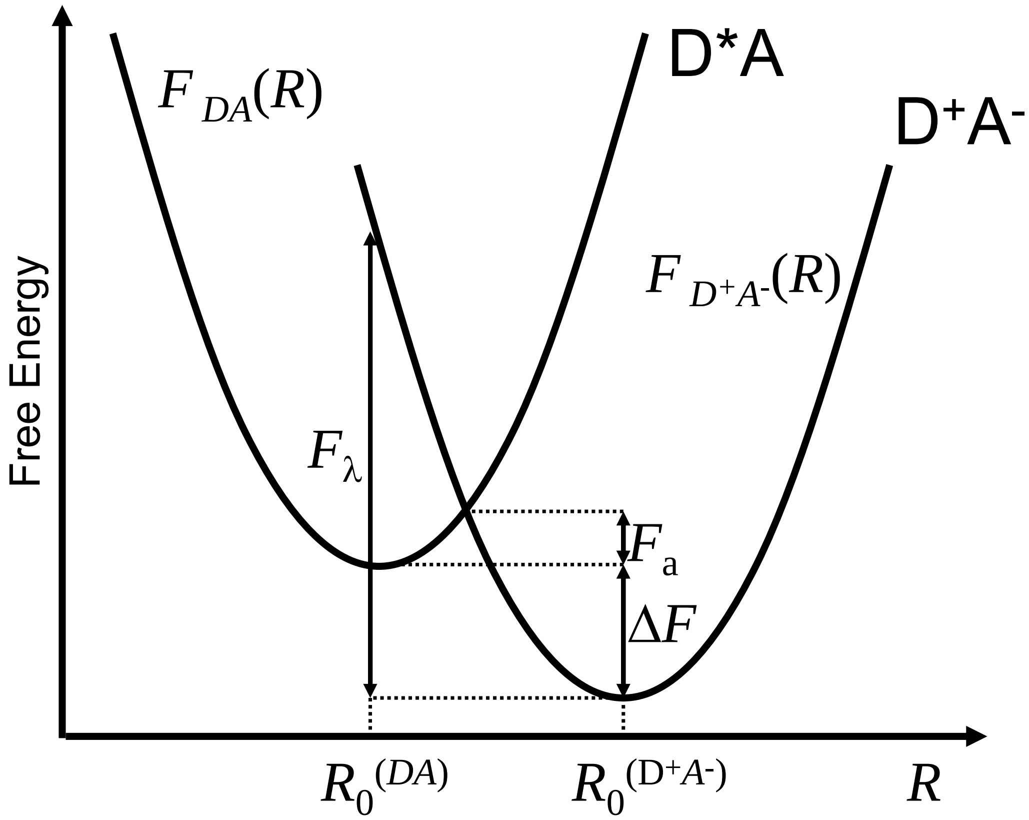
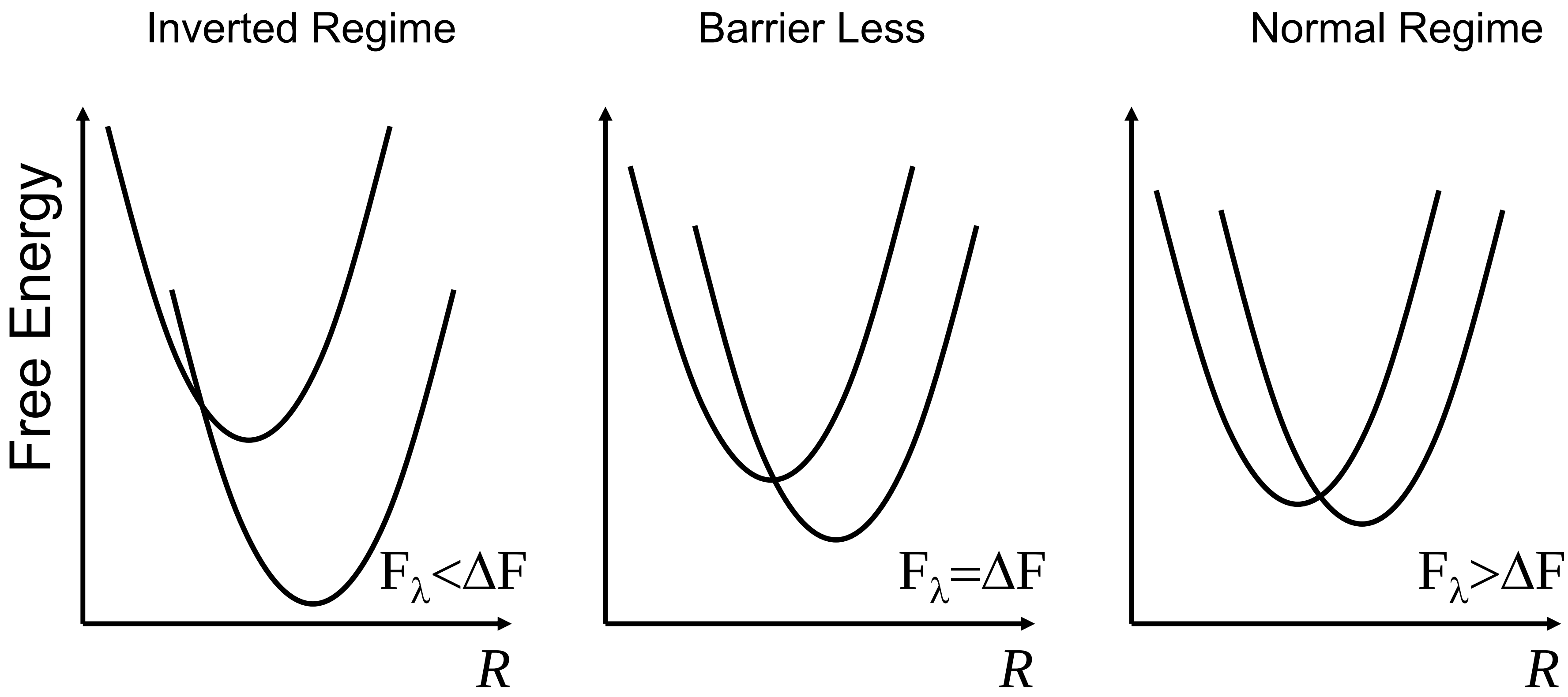


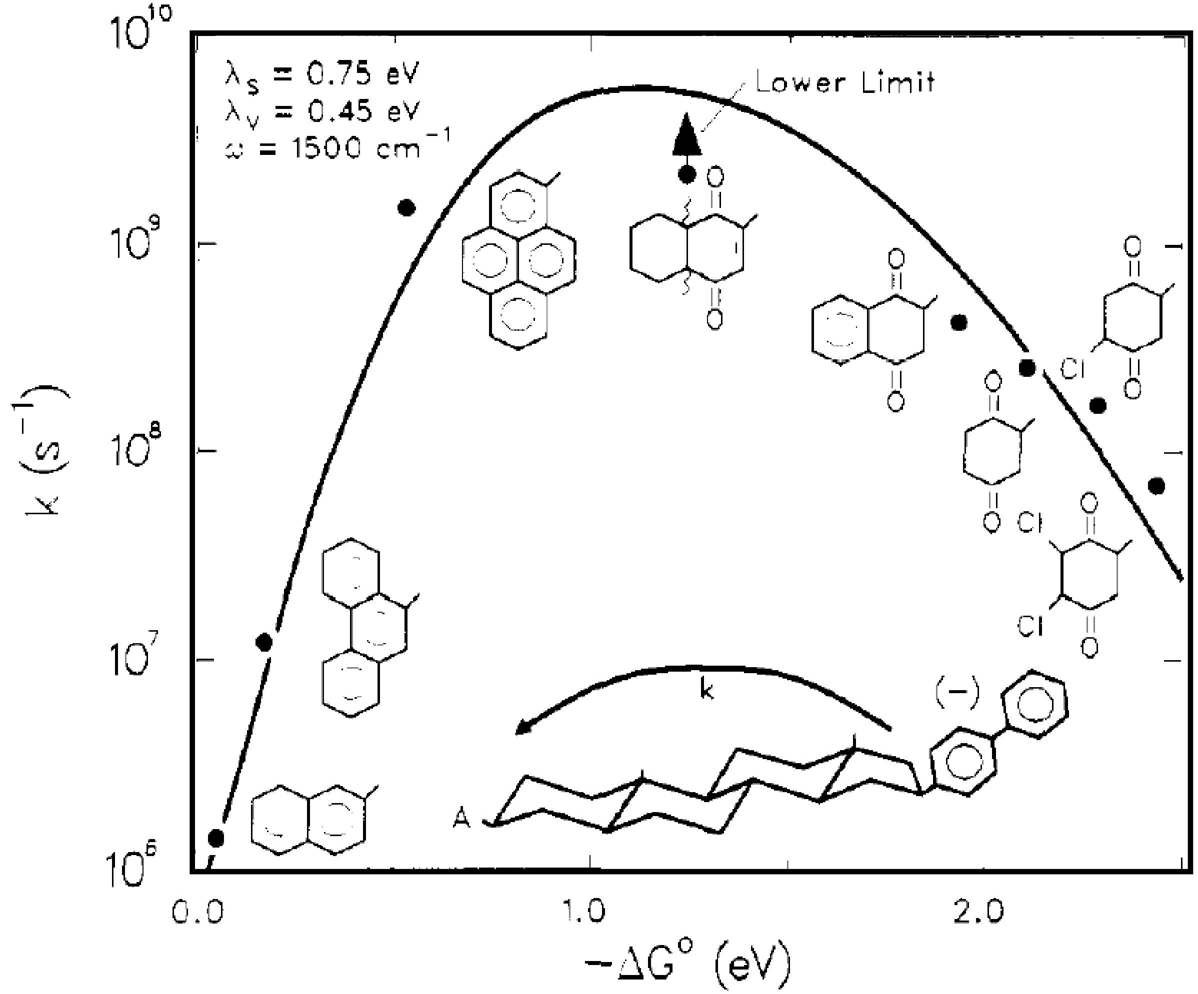
$$k_{ET} = V_{DA}{}^2 \sqrt{\frac{\pi}{\hbar^2 k_B T F_\lambda}} \exp\left(-\frac{(\Delta F - F_\lambda)^2}{4 F_\lambda k_B T} \right)$$

Marcus Theory of Electron Transfer



$$k_{ET} = V_{DA}^{\ 2} \sqrt{\frac{\pi}{\hbar^2 k_B T F_\lambda}} \exp\left(-\frac{(\Delta F - F_\lambda)^2}{4 F_\lambda k_B T} \right)$$

Marcus Parabola



J. R. Miller, L. T. Calcaterra, G. L. Closs *Intramolecular long-distance electron transfer in radical anions. The effects of free energy and solvent on the reaction rates J. Am. Chem. Soc.;* **1984**; *106*(10); 3047-3049.

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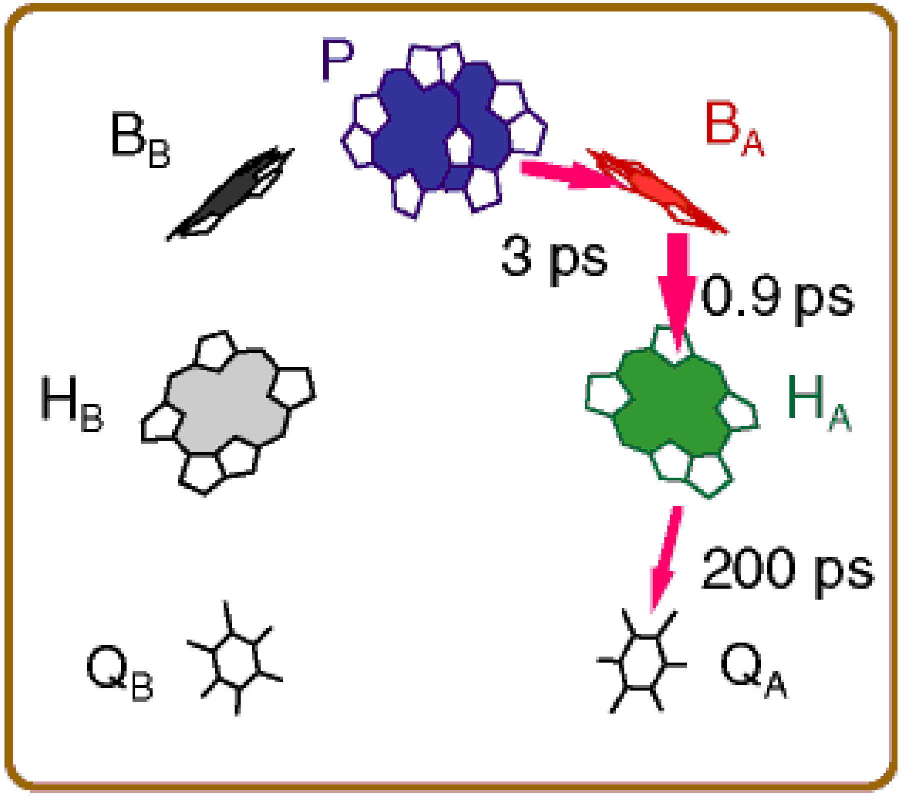

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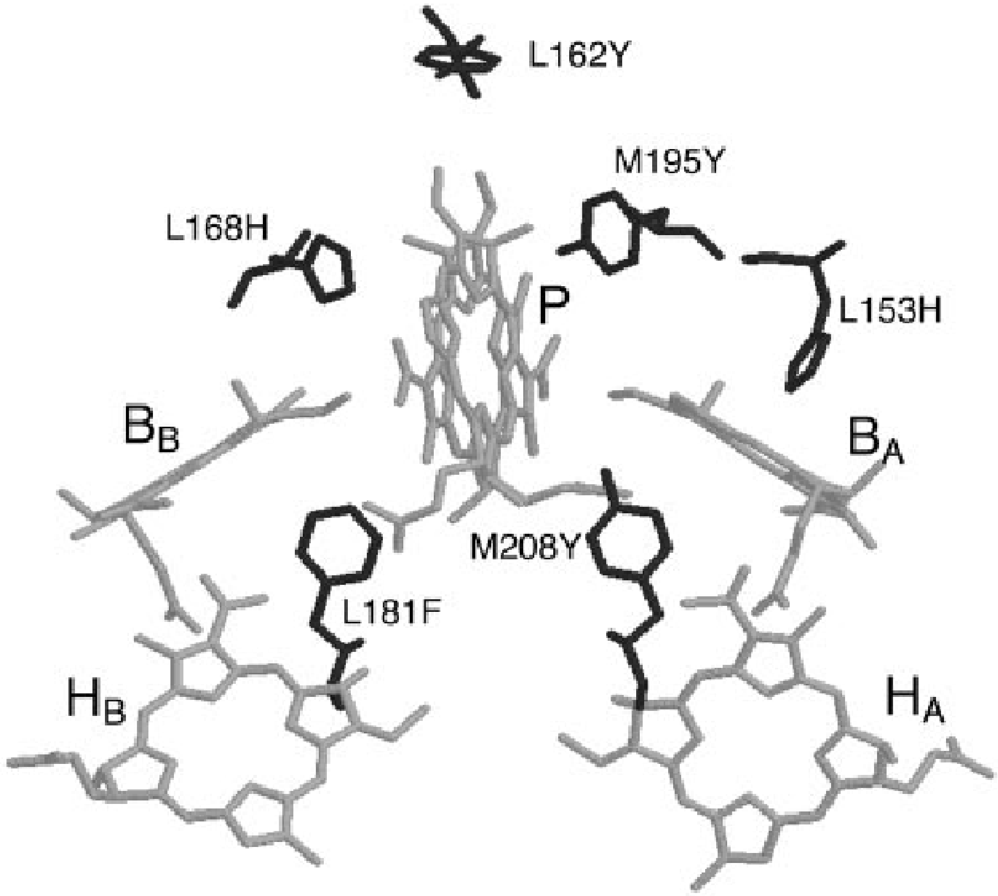
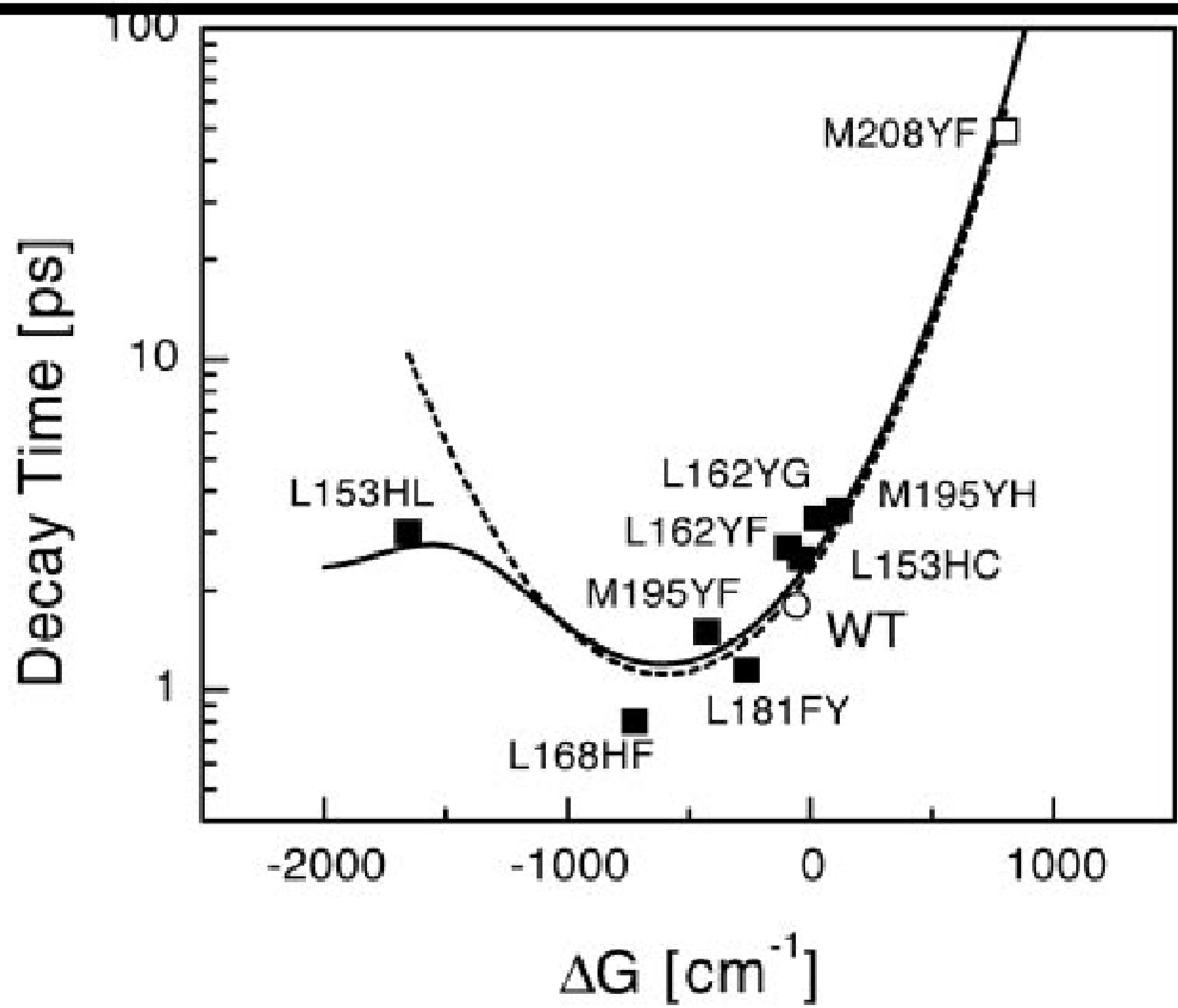
Marcus Parabola



P. Huppman,* T. Arlt,* H. Penzkofer,* S. Schmidt,* M. Bibikova, B. Dohse, D. Oesterhelt, J. Wachtveit,* and W. Zinth* *Kinetics, Energetics, and Electronic Coupling of the Primary Electron Transfer Reactions in Mutated Reaction Centers of Blastochloris viridis* Biophys J, 2002, 3186 82

Marcus Parabola



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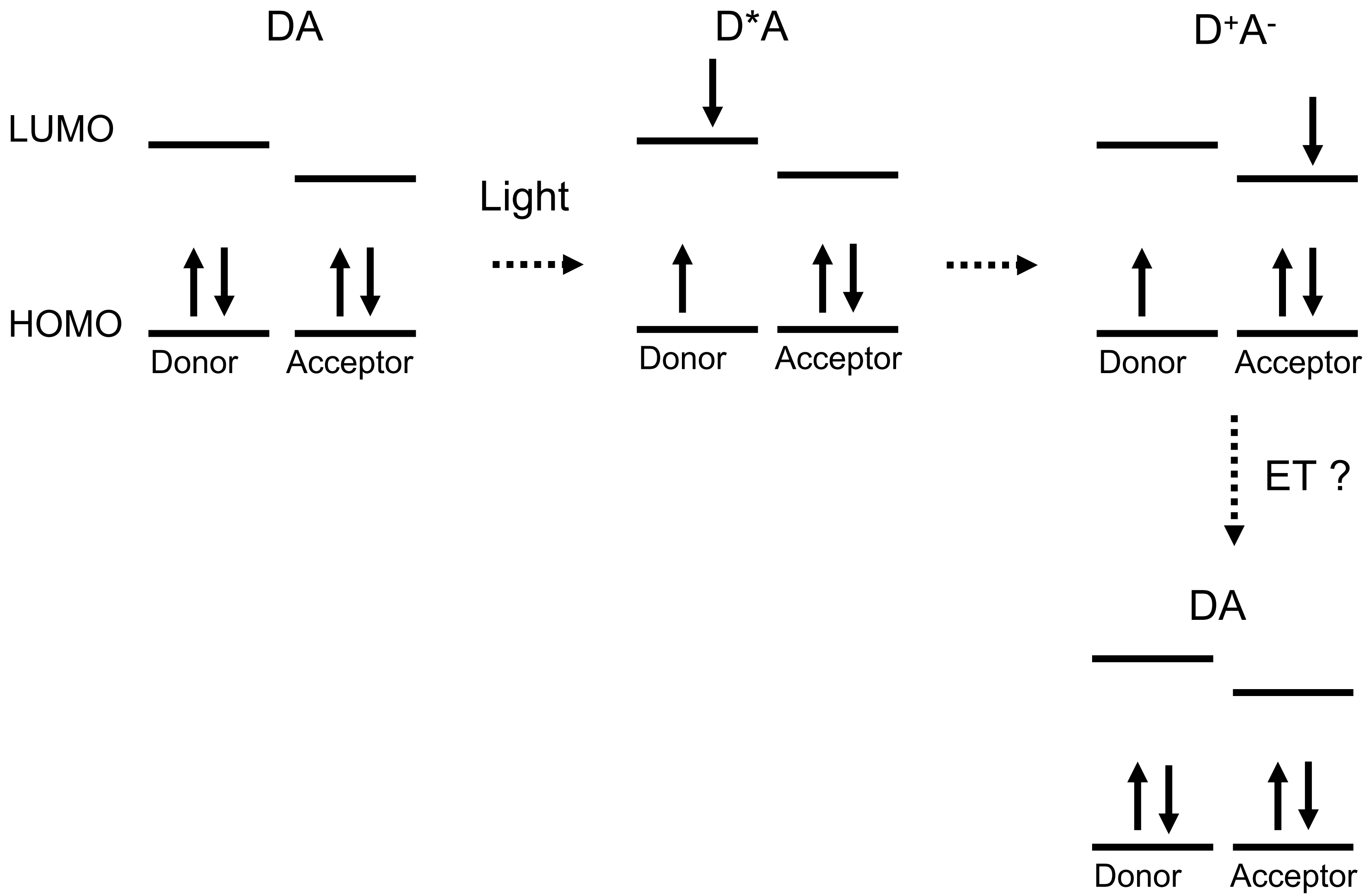
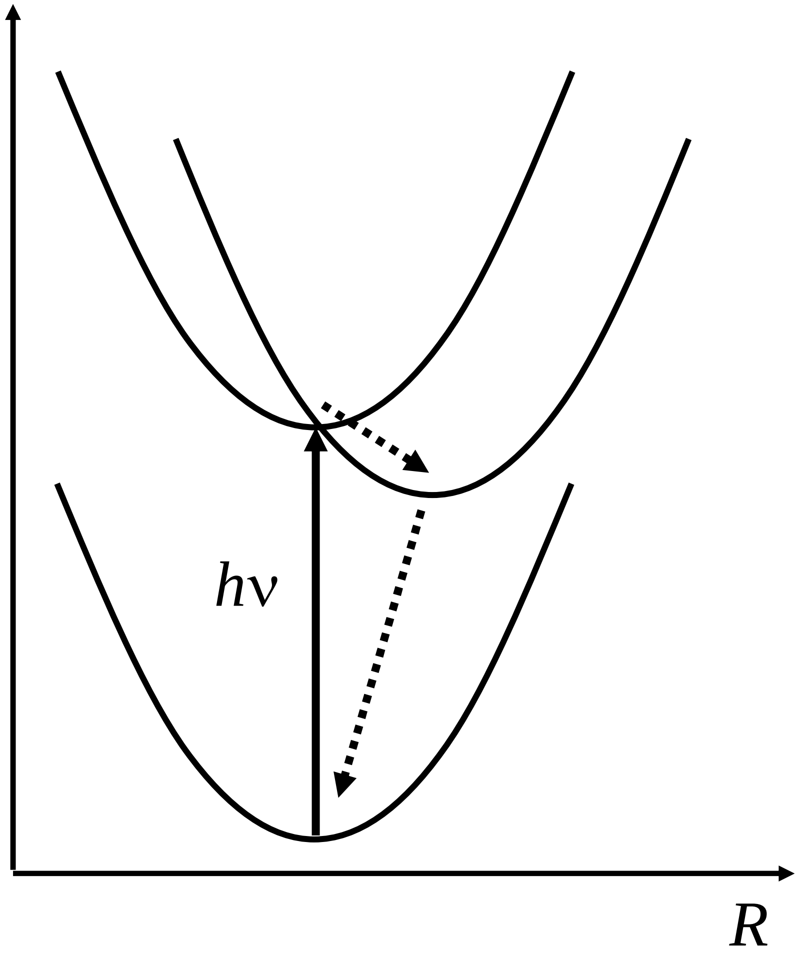

DA
LUMO
HOMO
Donor
Acceptor
Light
D*A
Donor
Acceptor
D+A-
Donor
Acceptor
ET ?
DA
Donor
Acceptor

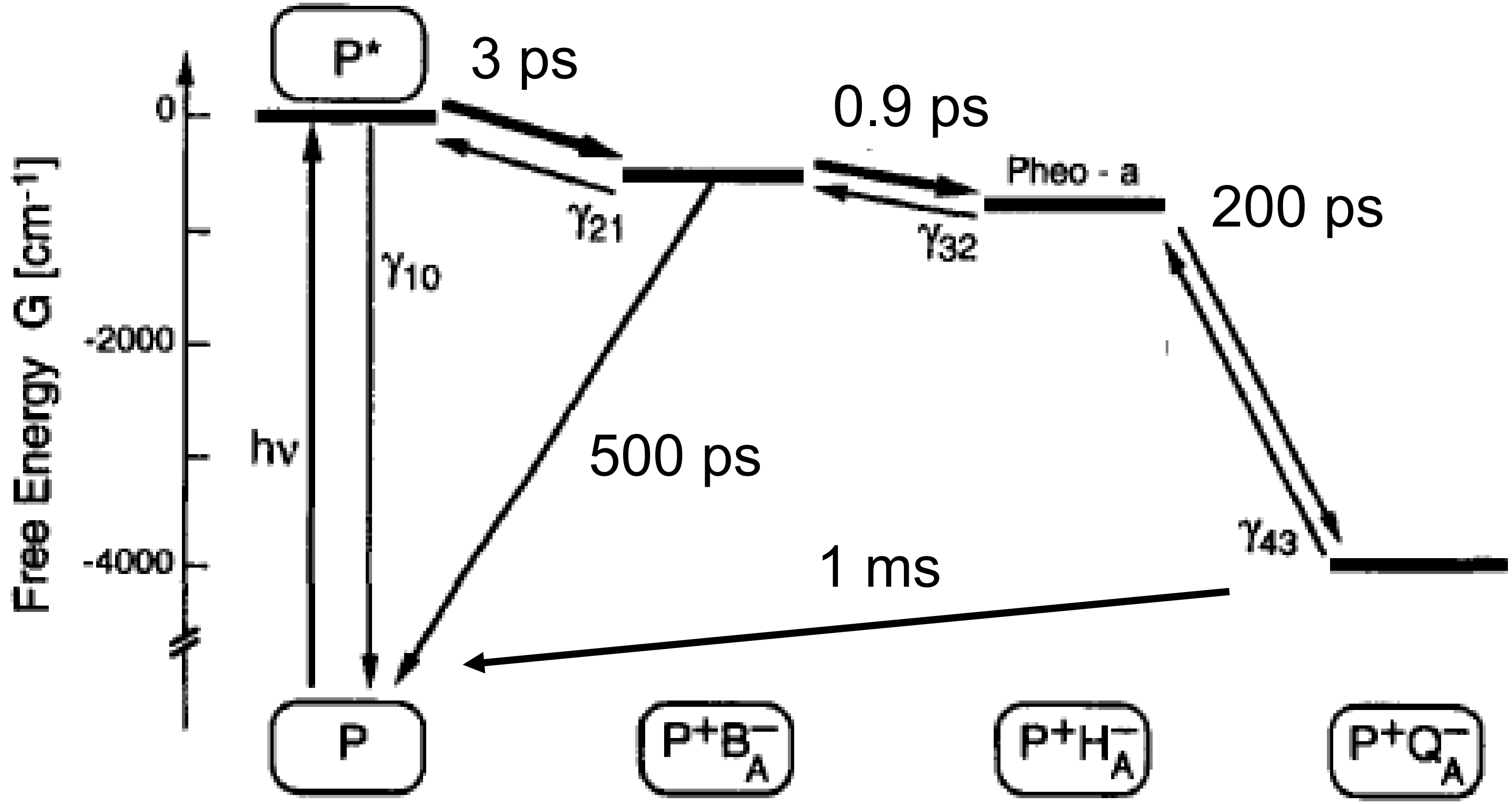
Supressing Back Electron Transfer



Forward ET: $\Delta F = F_\lambda$ and small
$\Rightarrow$ barrier less

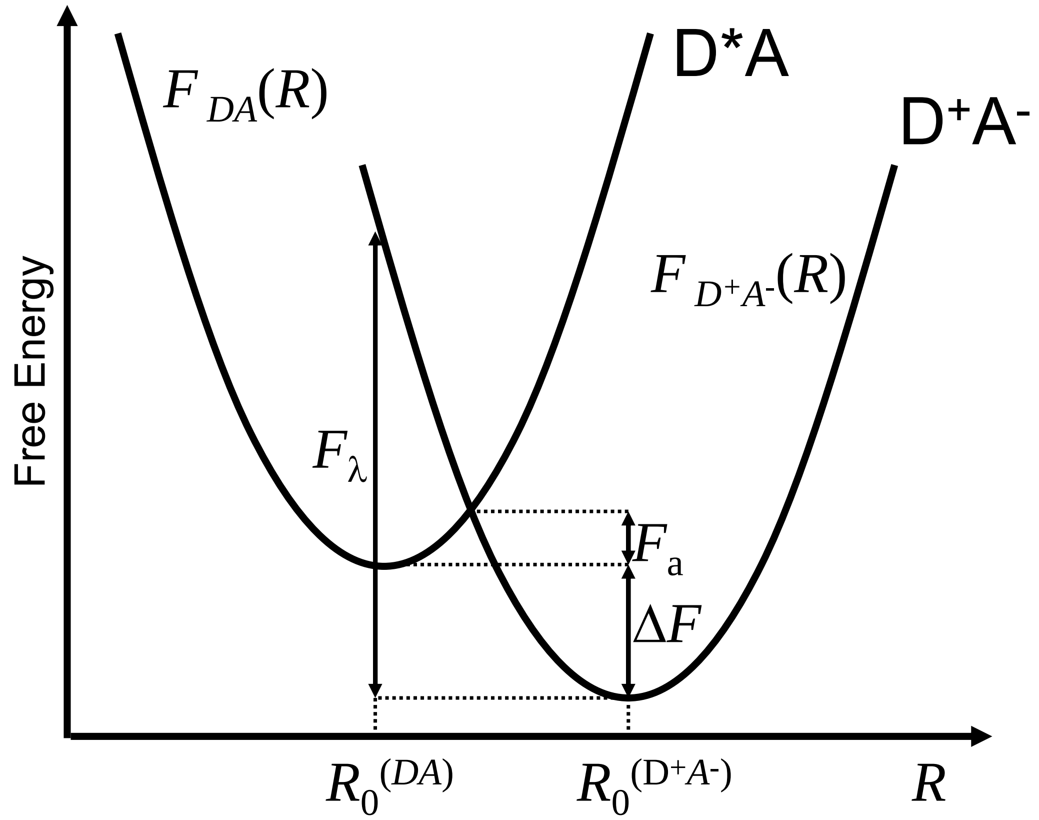
Backward ET: $\Delta F \gg F_\lambda$ and large
$\Rightarrow$ strongly in the inverted regime

Photochemical Reactions in Nature: Electron Transfer in Photosynthesis



Zinth et al. Spectrochimica Acta Part A 51 (1995) 1565-1578 and
Feher at al. J. Phys. Chem. 1994,98, 3417-3423

Marcus Theory of Electron Transfer



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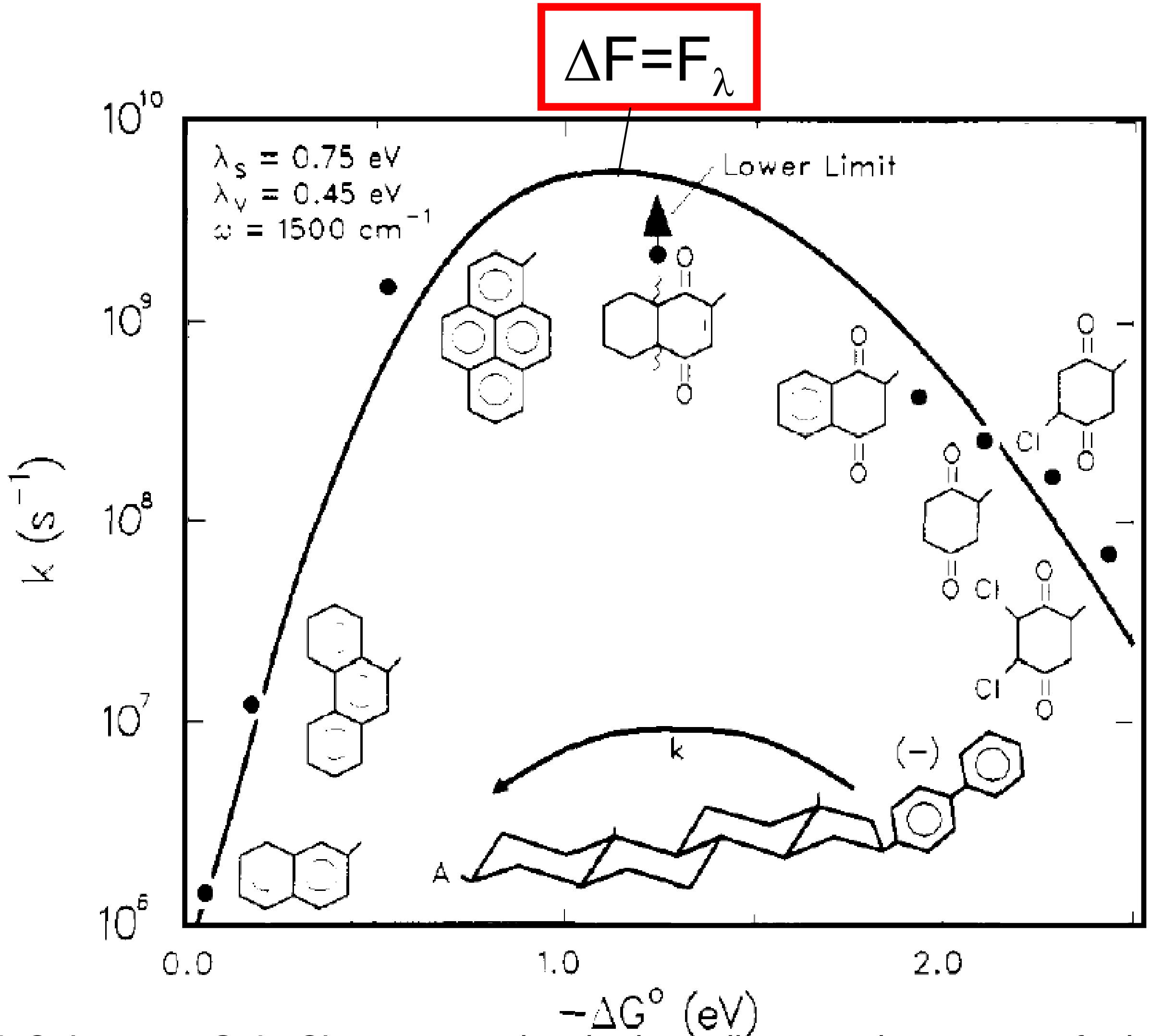

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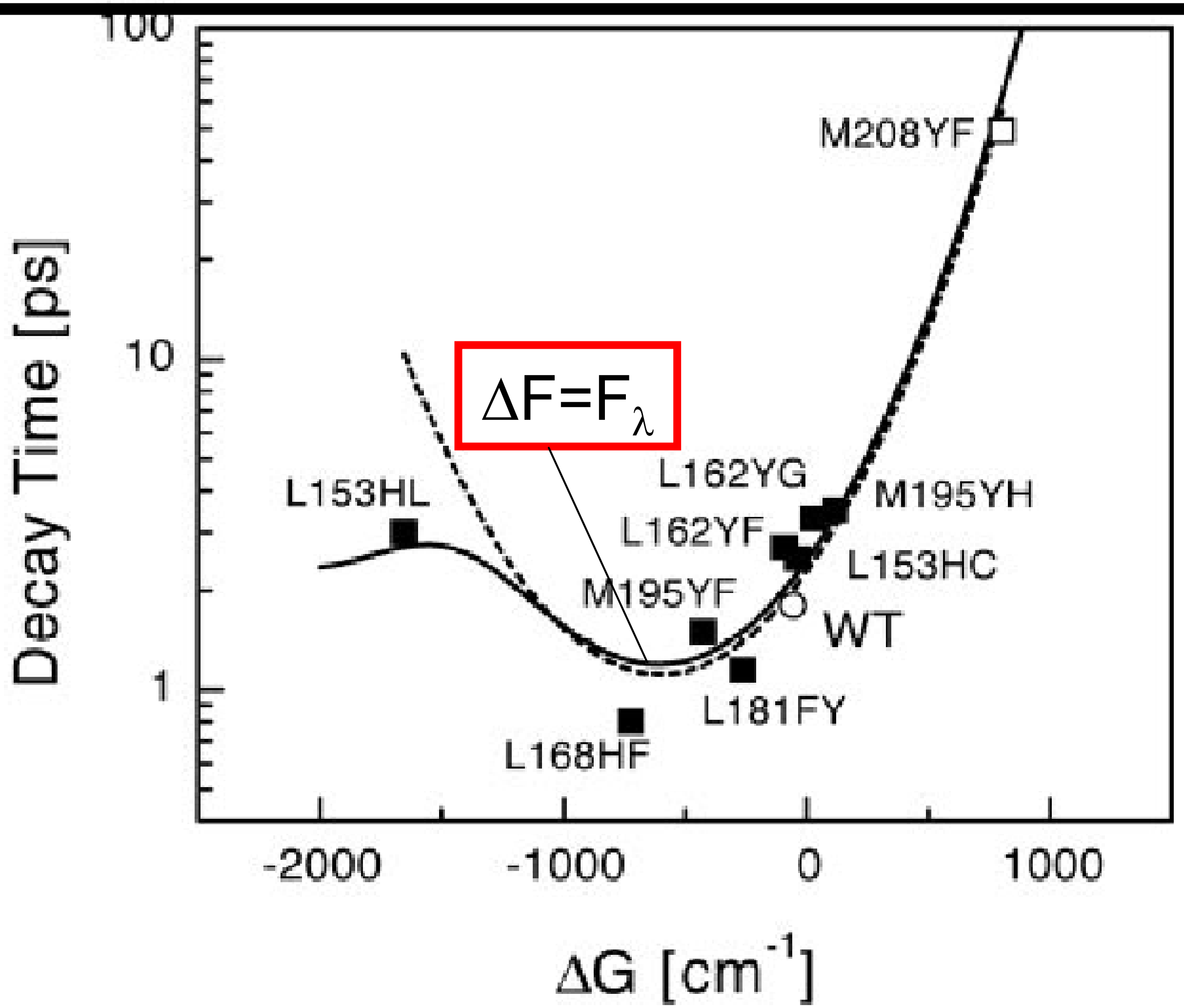

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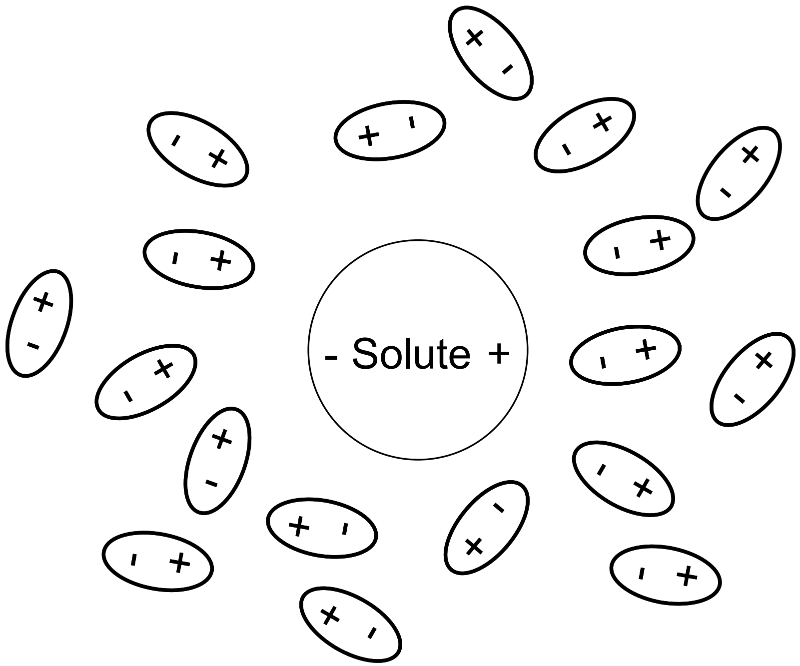
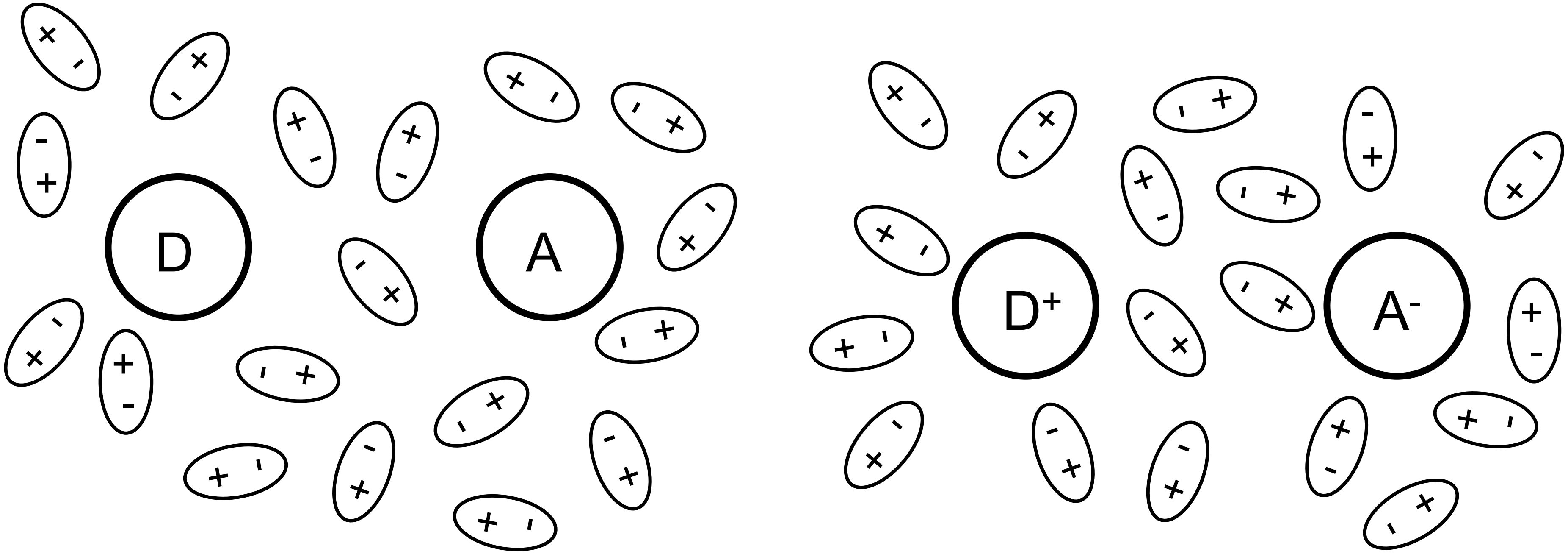
Solvation Energy



$$\Delta E = \frac{(\varepsilon - 1)}{(2\varepsilon + 1) r^3} \mu^2$$

Onsager's Reaction Field Model

Solvation of a Charge Transfer Complex



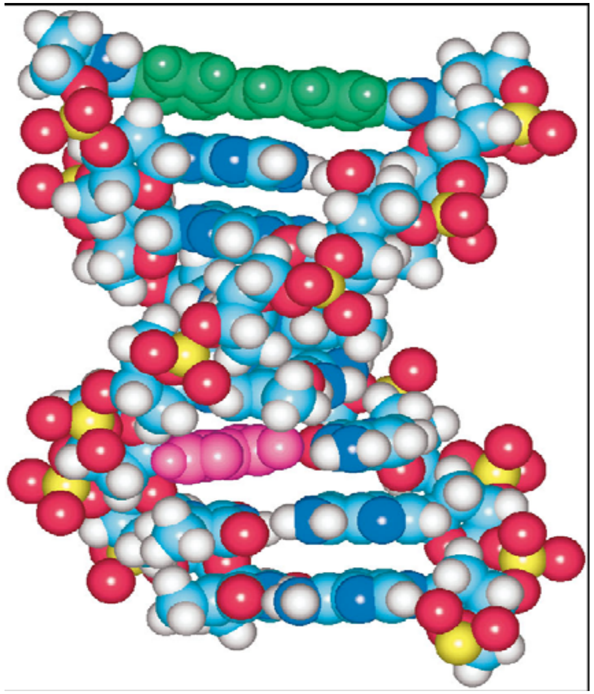
$$E_\lambda = \frac{1}{8\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_r}\right)\left(\frac{e^2}{2R_D} + \frac{e^2}{2R_A} - \frac{e^2}{r_{DA}}\right)$$

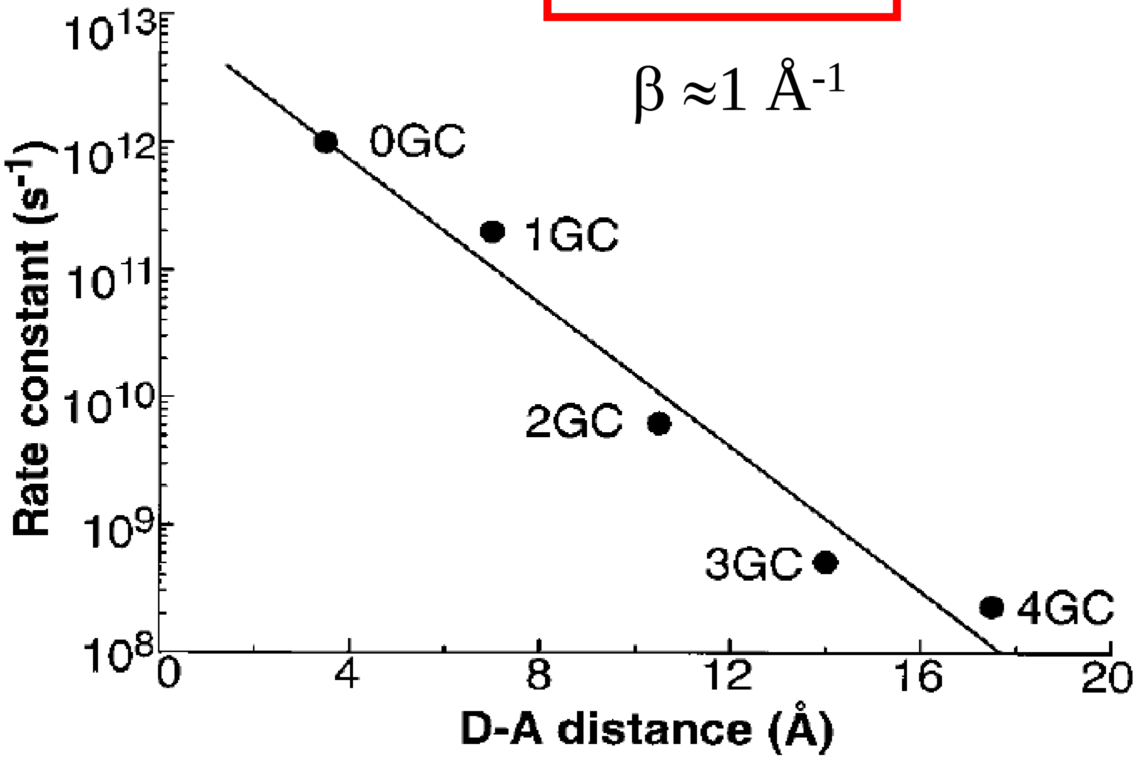
in analogy to Onsager‘s Reaction Field Model

Distance Dependence of Electron Transfer

$$k \propto e^{-\beta R}$$

$\beta \approx 1$ Å^{-1}





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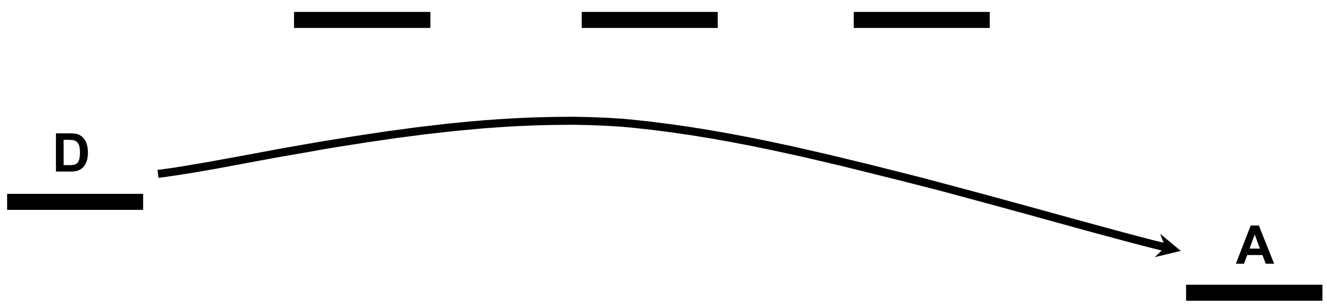
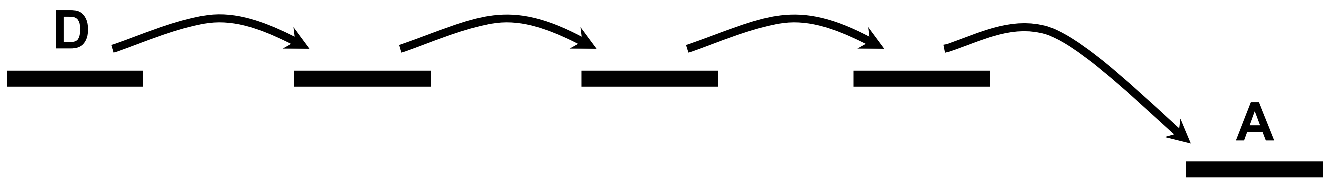
Bridged Electron Transfer

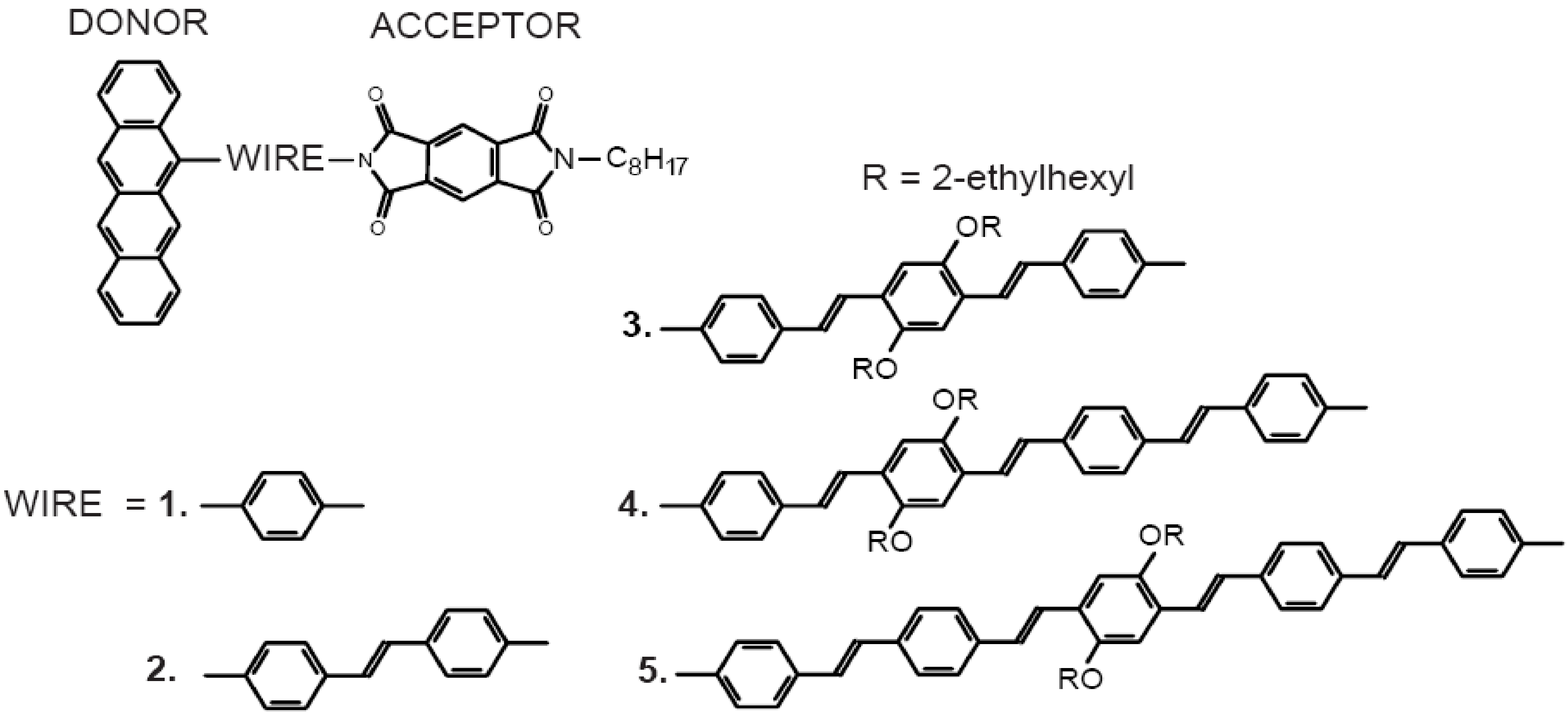
Superexchange



Hopping

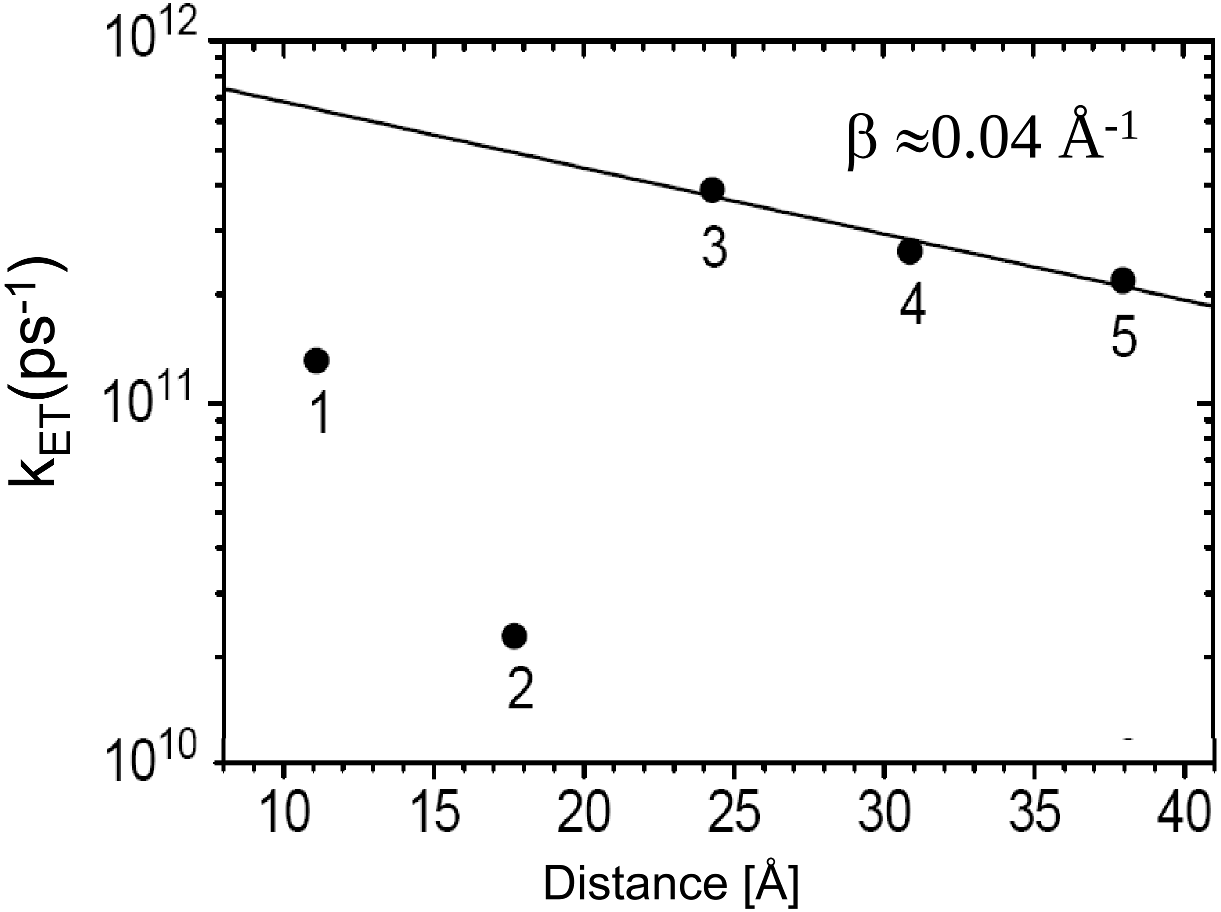


Bridged Electron Transfer



W. B. Davis, W. A. Svec, M. A. Ratner, M. R., Nature 396, 60 - 63 (1998)

Bridged Electron Transfer



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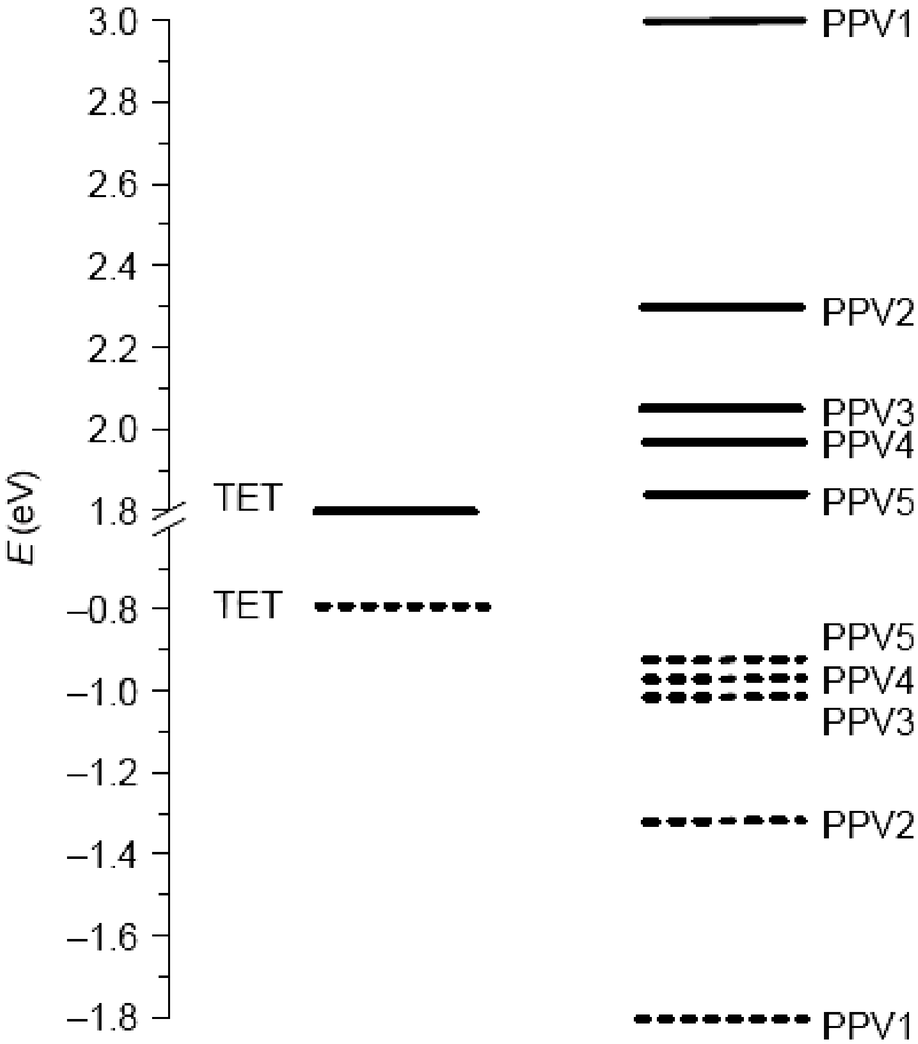
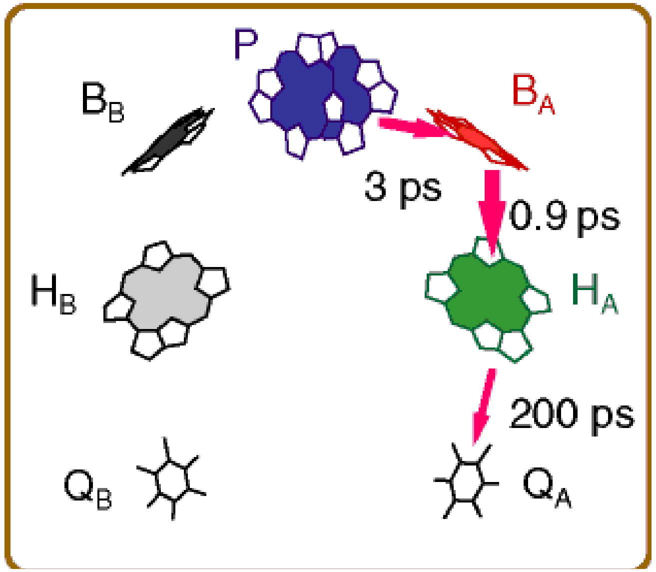
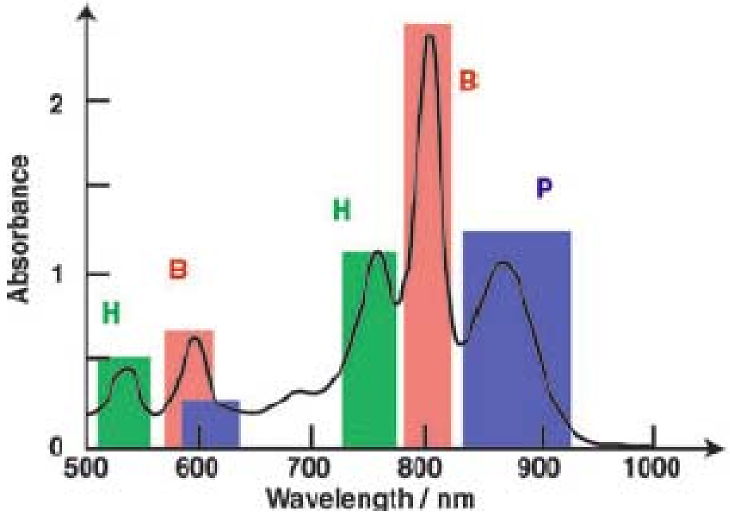
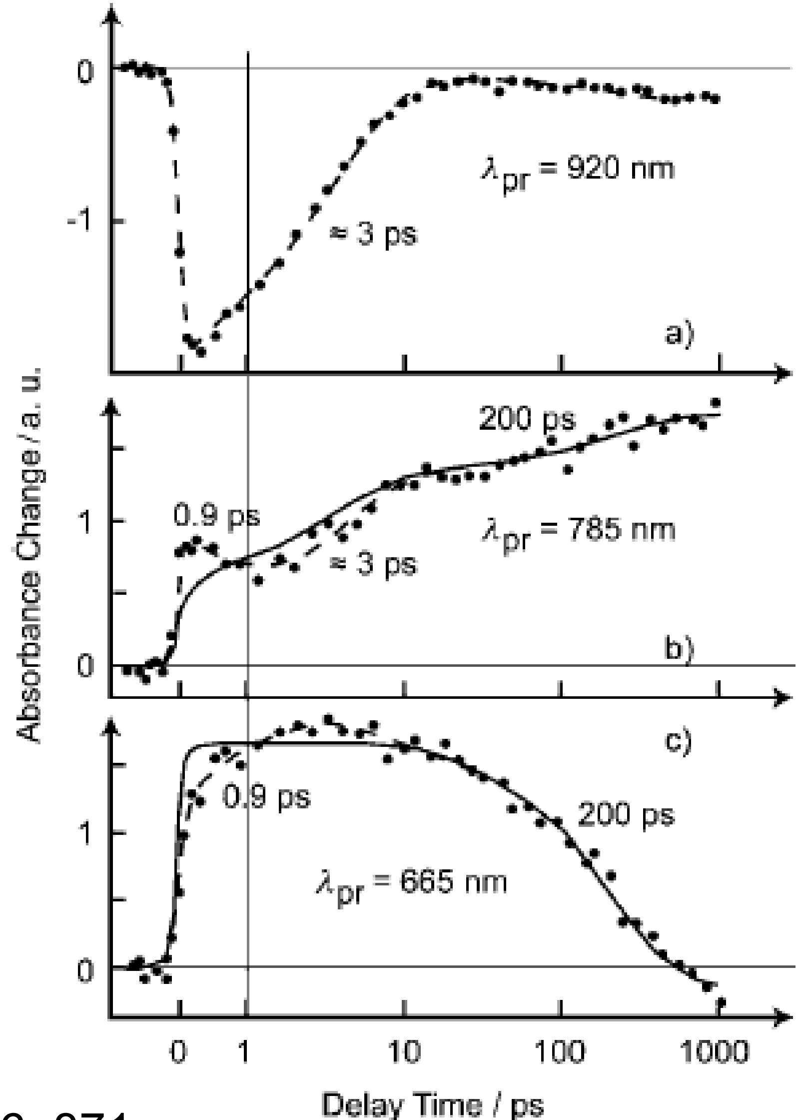


W. B. Davis, W. A. Svec, M. A. Ratner, M. R., Nature 396, 60 - 63 (1998)

Superexchange in Reaction Center?







Wachtveitl and Zinth, ChemPhysChem 2005, 6, 871

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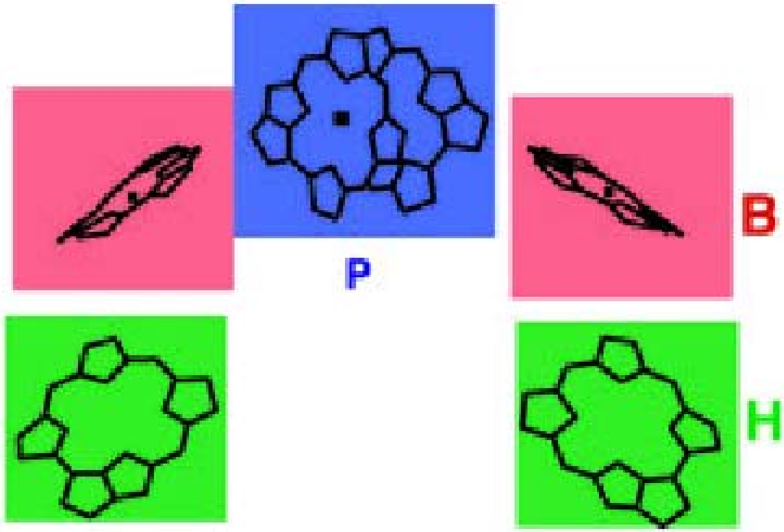
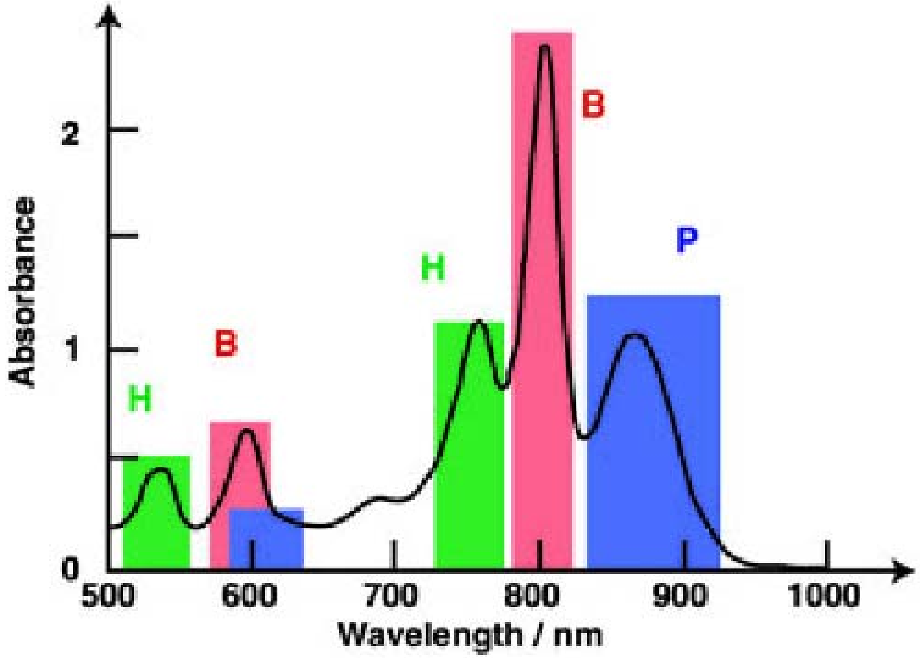
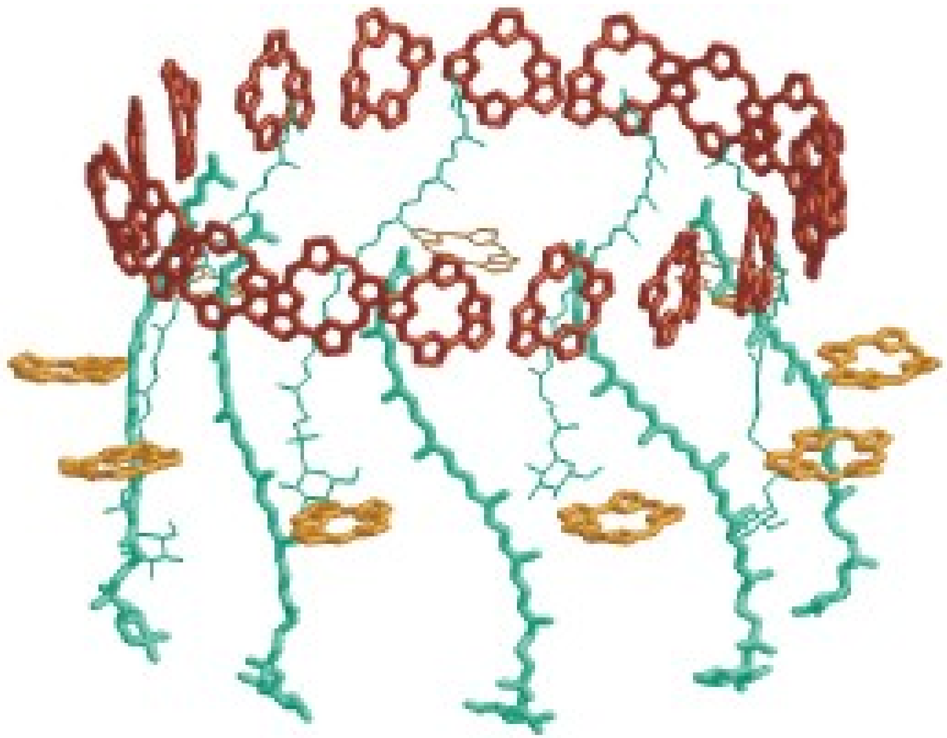
Special Pair in Reaction Center

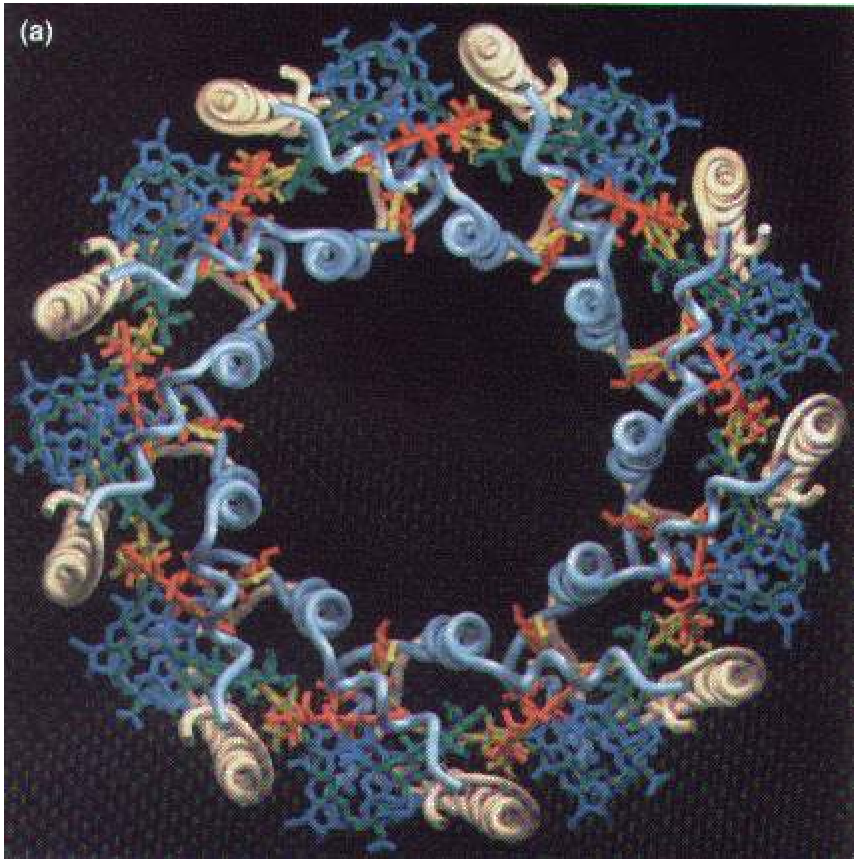




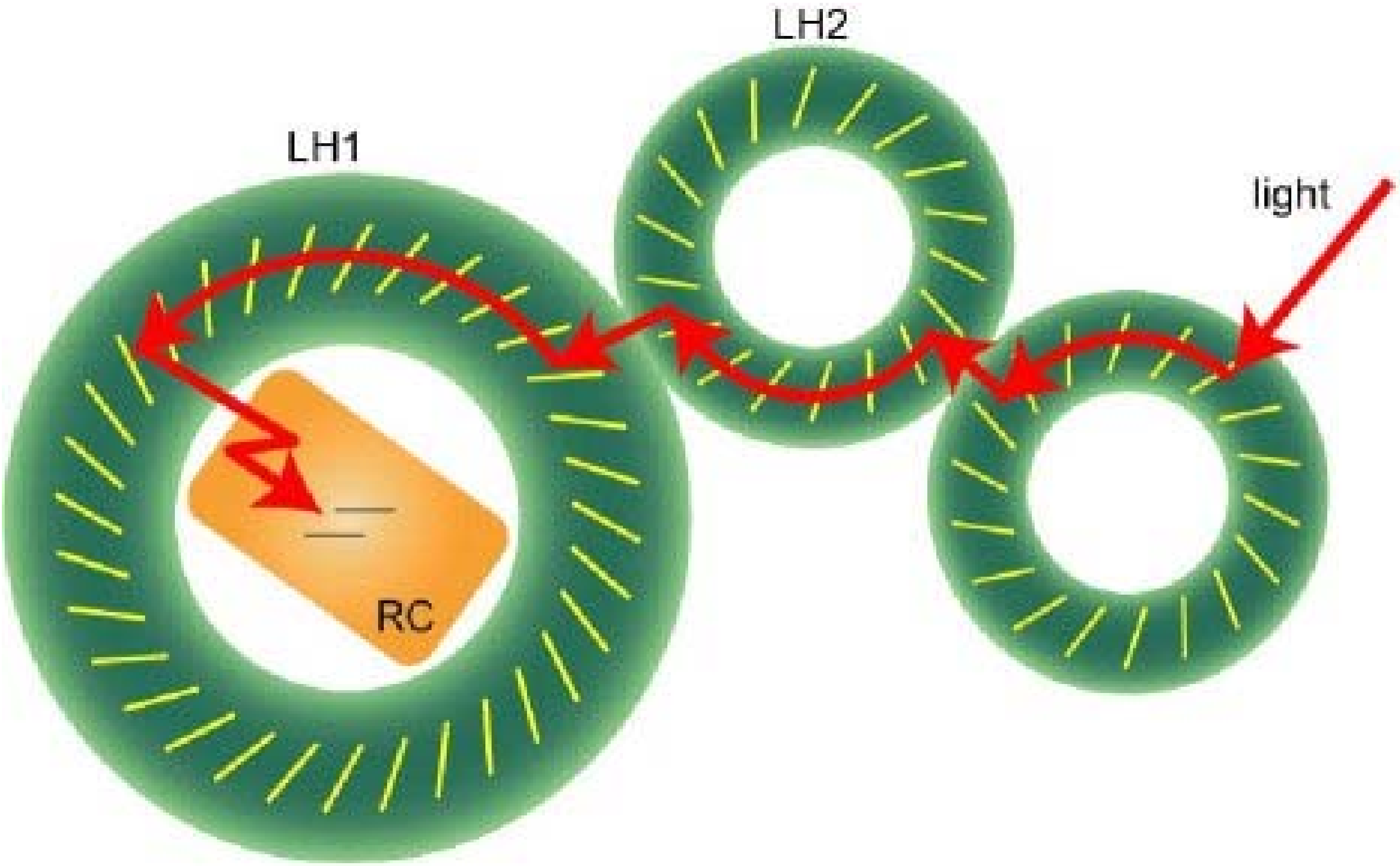
W. Zinth, J. Wachtveitl ChemPhysChem 2005, 6, 871 – 880

LH II Antenna Complex

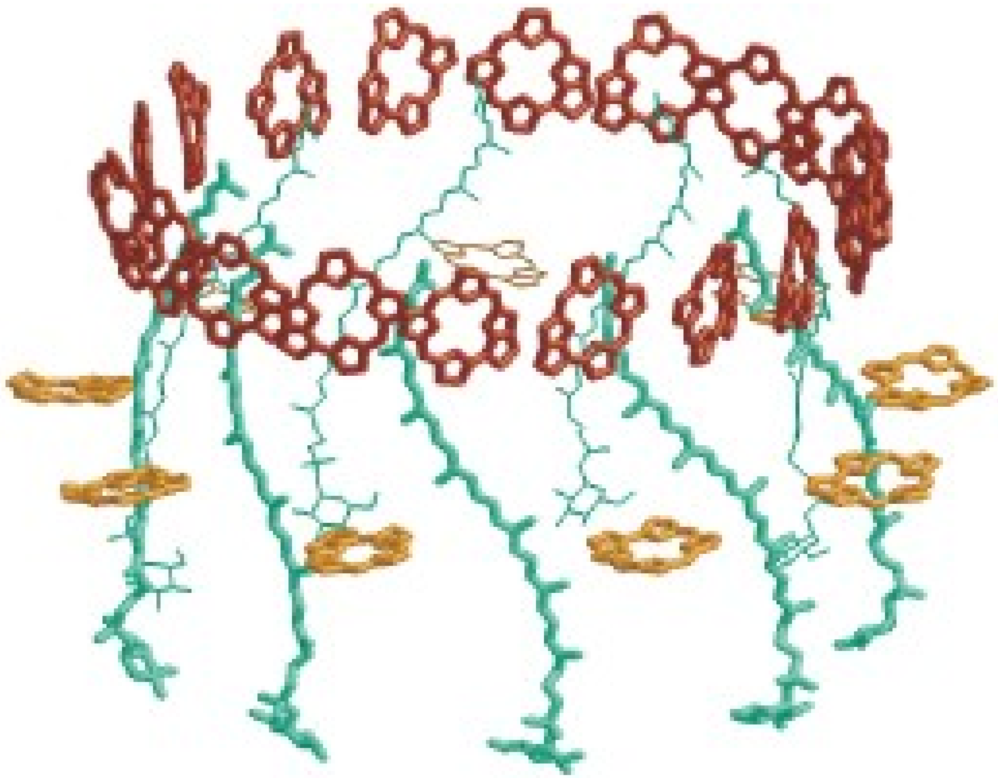


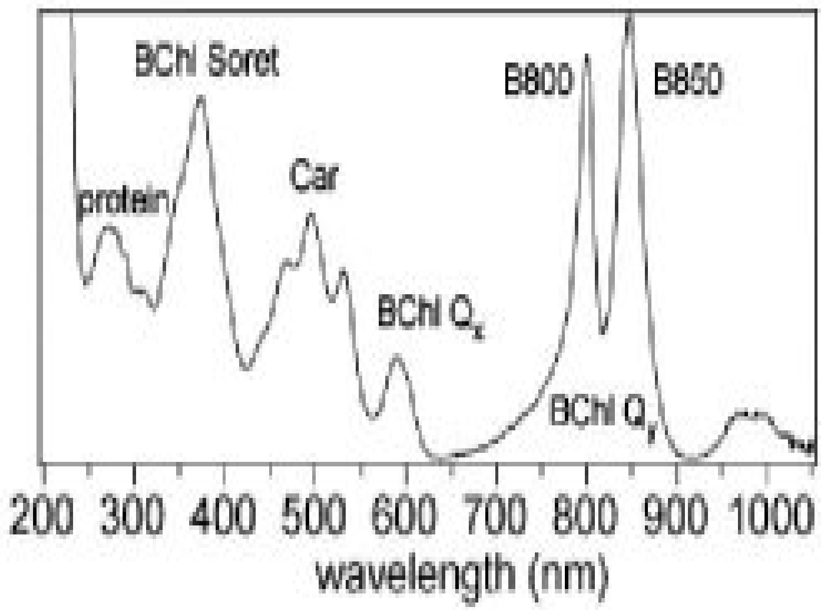


LH II Antenna Complex

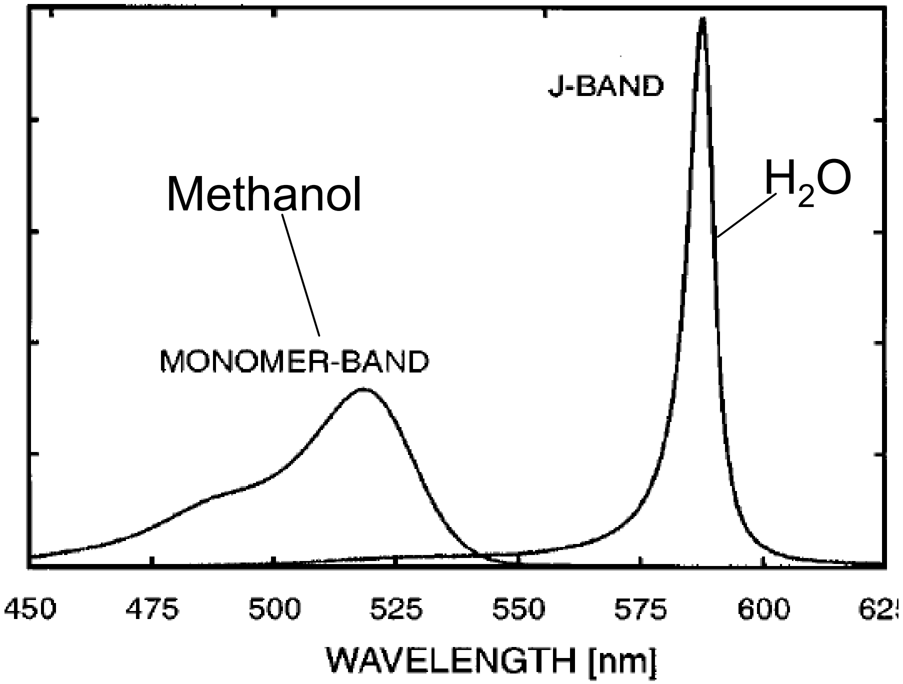


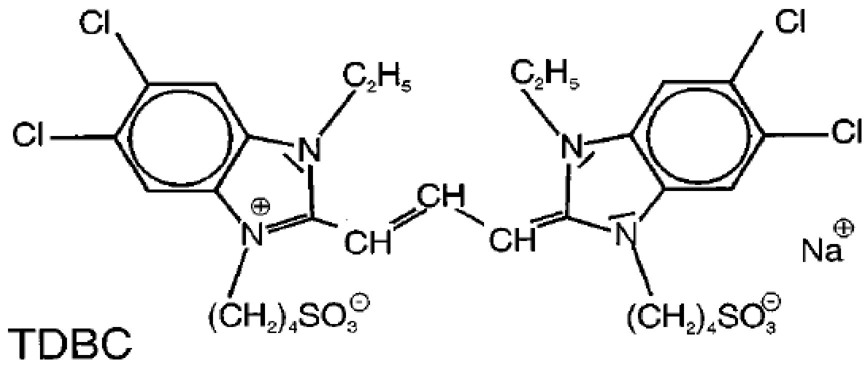
LH II Antenna Complex





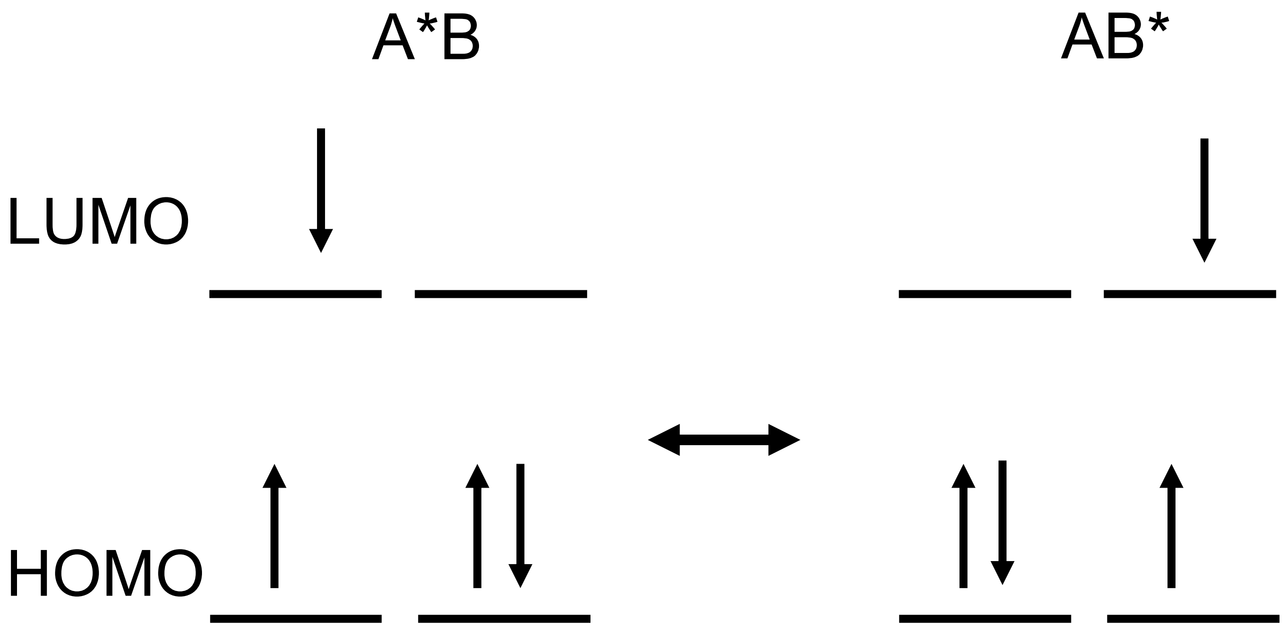
J-Aggregates





J. Moll, S. Daehne, J. R. Durrant and D. A. Wiersma, *Optical dynamics of excitons in J aggregates of a carbocyanine dye,* JCP 102, (1995) 6362

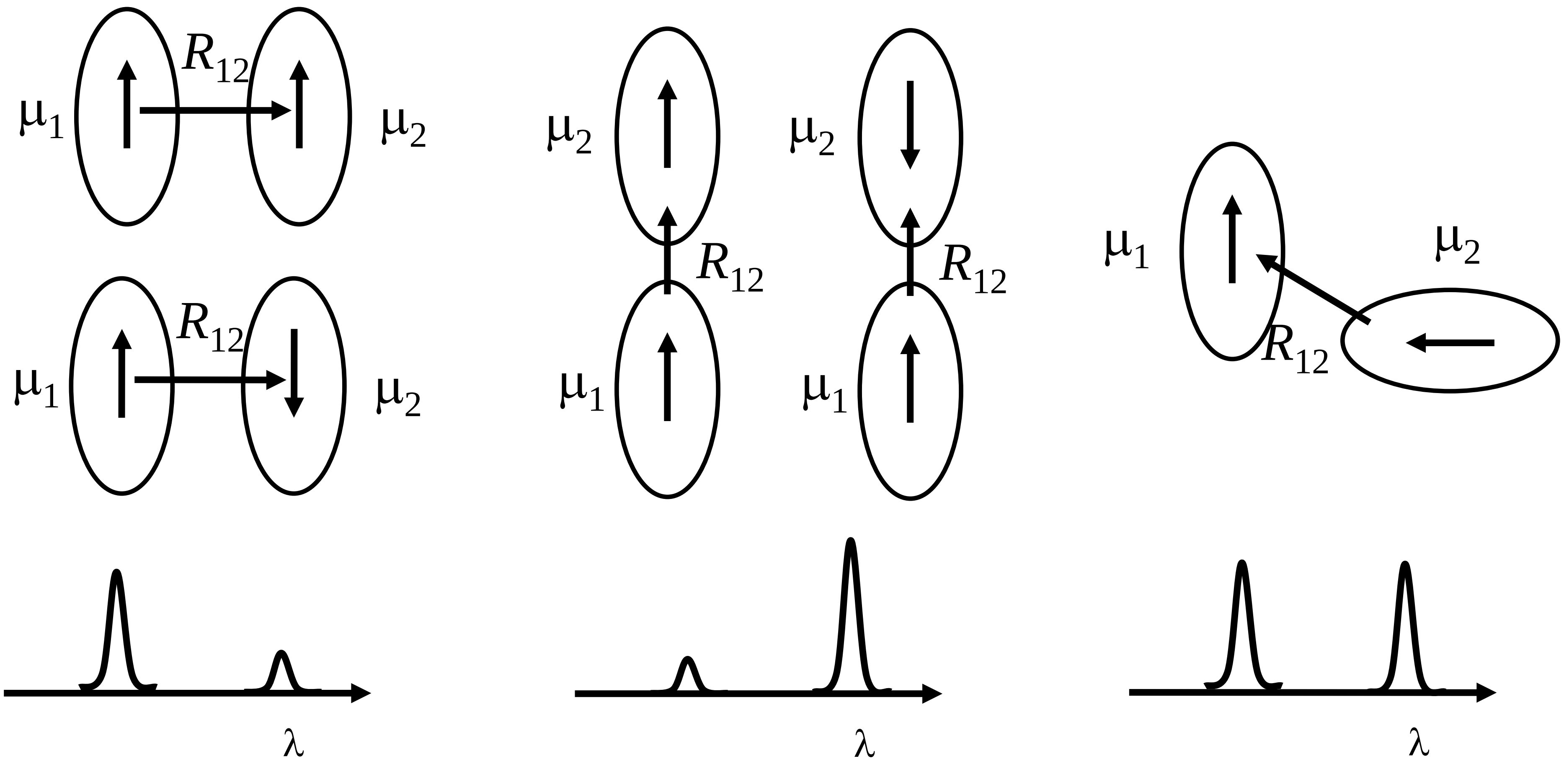
Excitation (Exciton) Transfer



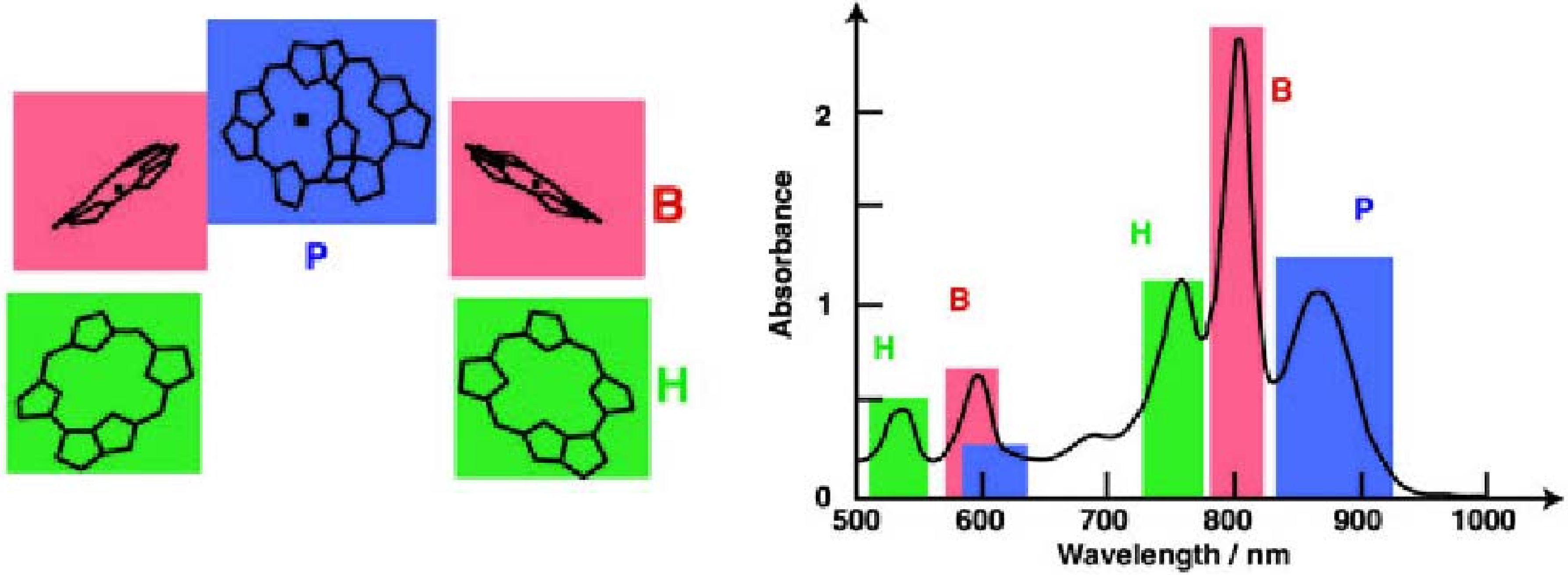
$$H_{ex} = \begin{pmatrix} E_1 & V_{12} \\ V_{12} & E_2 \end{pmatrix} \qquad V_{12} \approx \frac{\vec{\mu}_1 \vec{\mu}_2}{R_{12}^3} - 3\frac{(\vec{\mu}_1 \vec{R}_{12})(\vec{\mu}_2 \vec{R}_{12})}{R_{12}^5}$$

Excitonic Coupling

$$V_{12} \approx \frac{\vec{\mu}_1 \vec{\mu}_2}{R_{12}^3} - 3\frac{(\vec{\mu}_1 \vec{R}_{12})(\vec{\mu}_2 \vec{R}_{12})}{R_{12}^5}$$

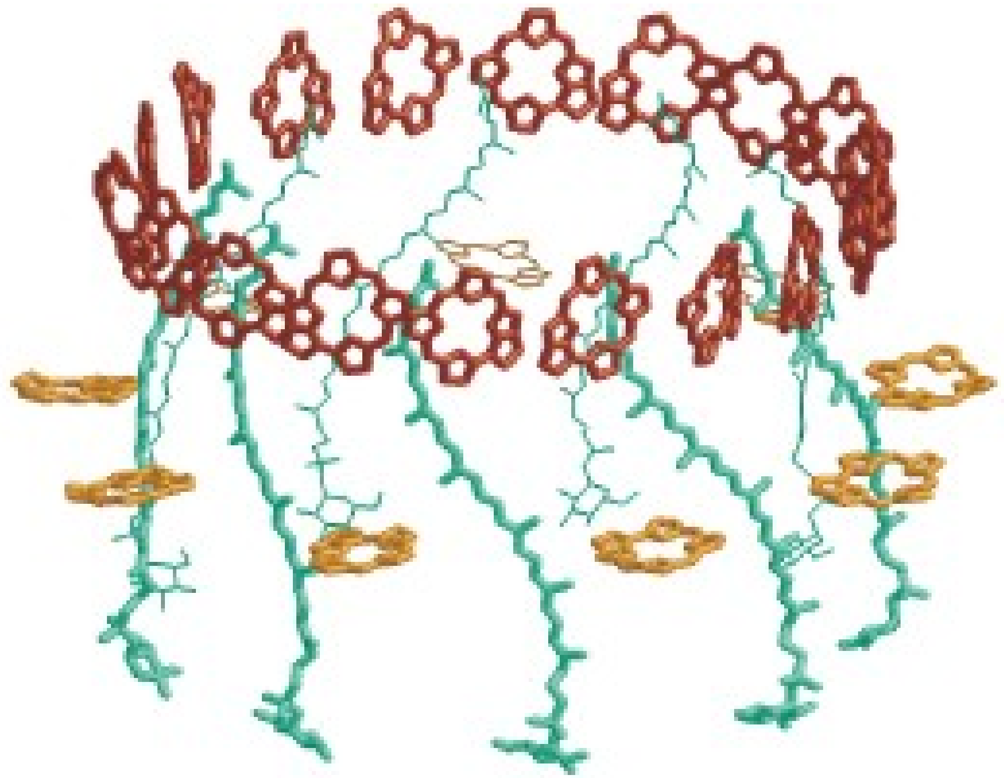


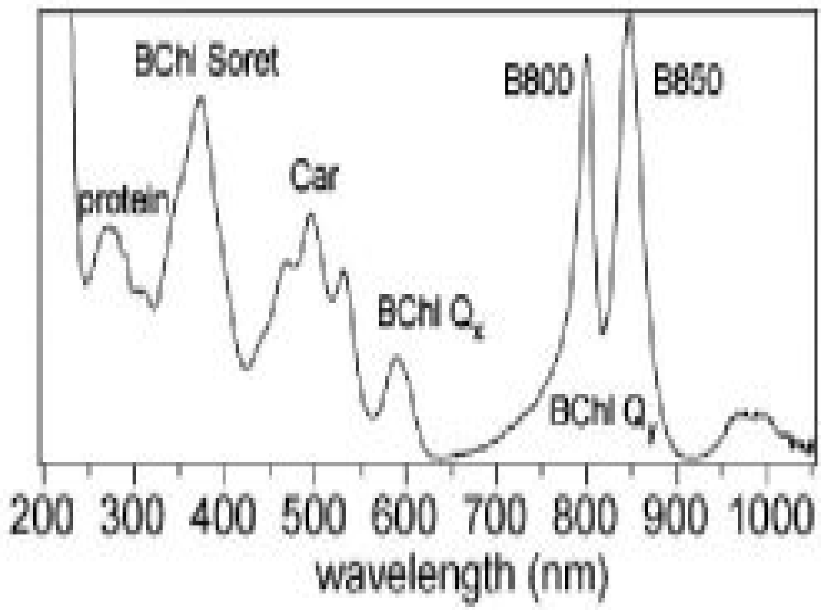
Photosynthesis



W. Zinth, J. Wachtveitl ChemPhysChem 2005, 6, 871 – 880

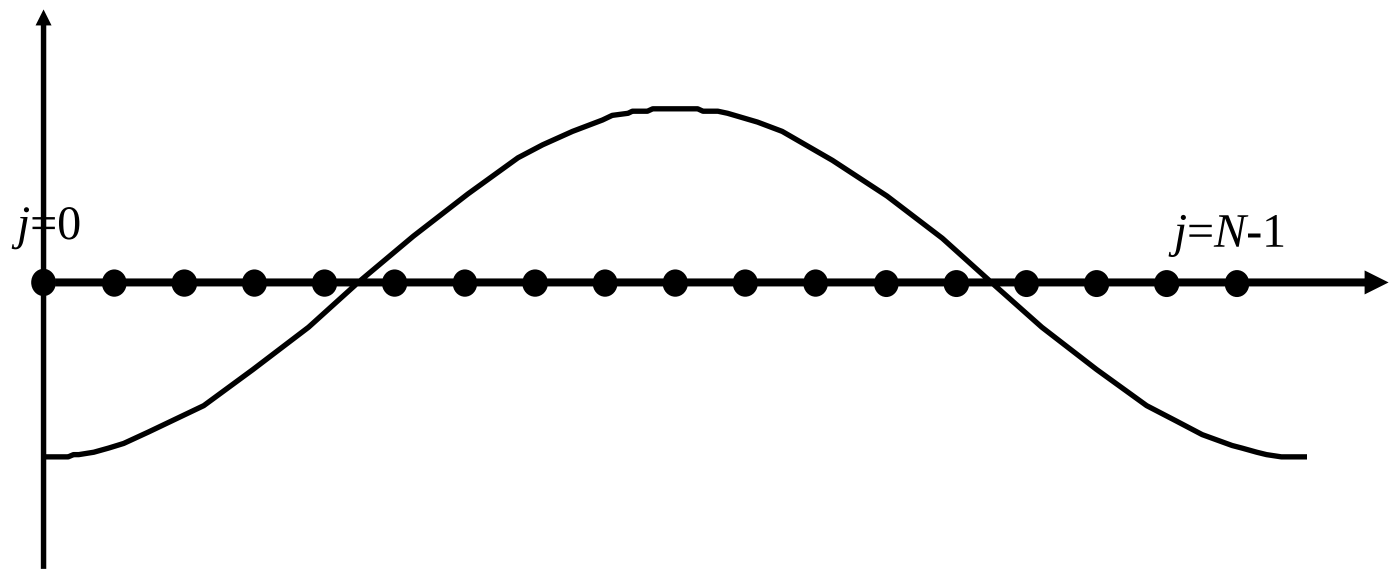
LH II Antenna Complex



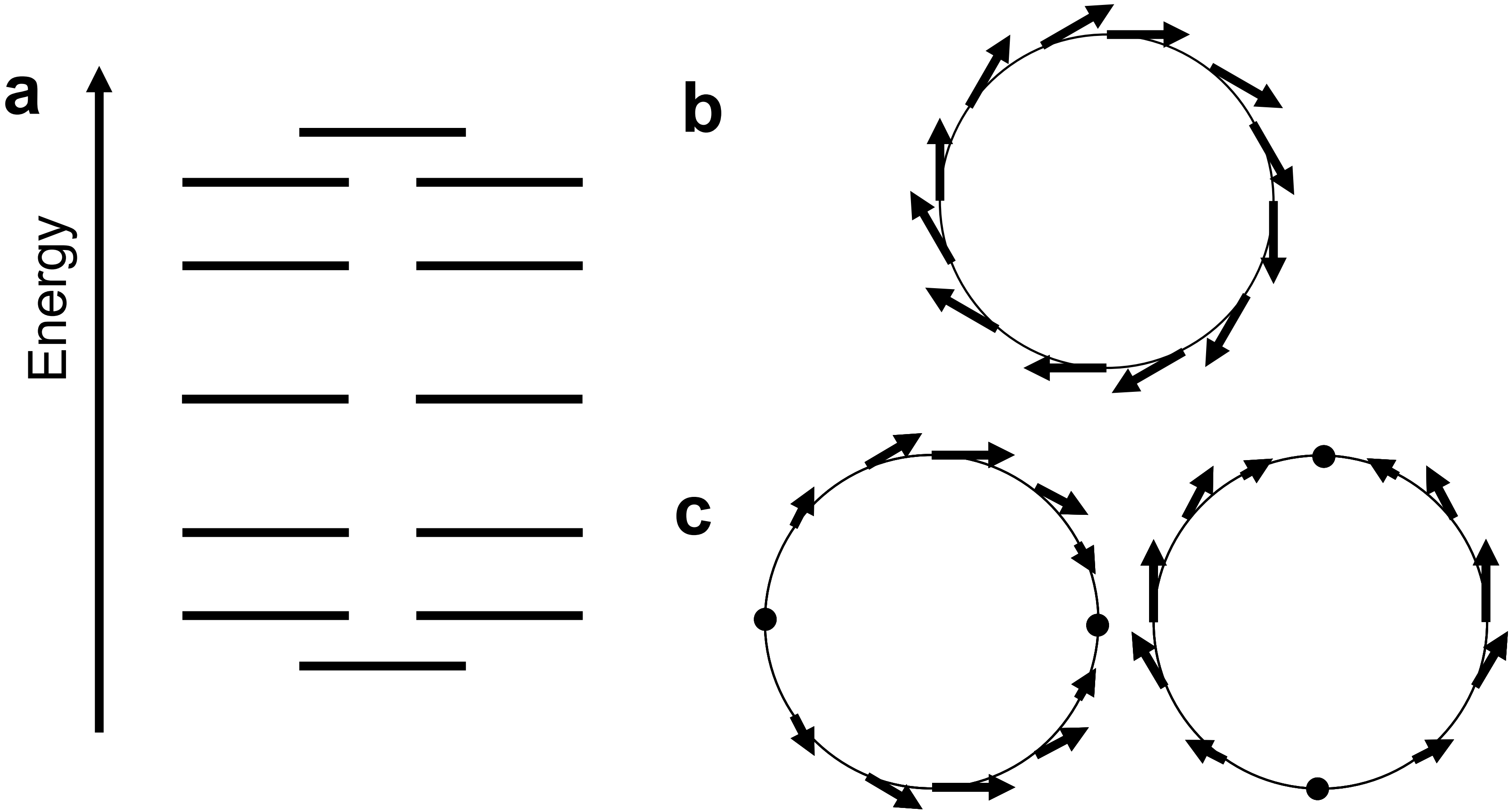


Excitons in a Ring

$$\varepsilon_\alpha = \varepsilon_0 + 2J\cos\alpha = \varepsilon_0 + 2J\cos\frac{2\pi j}{N}$$

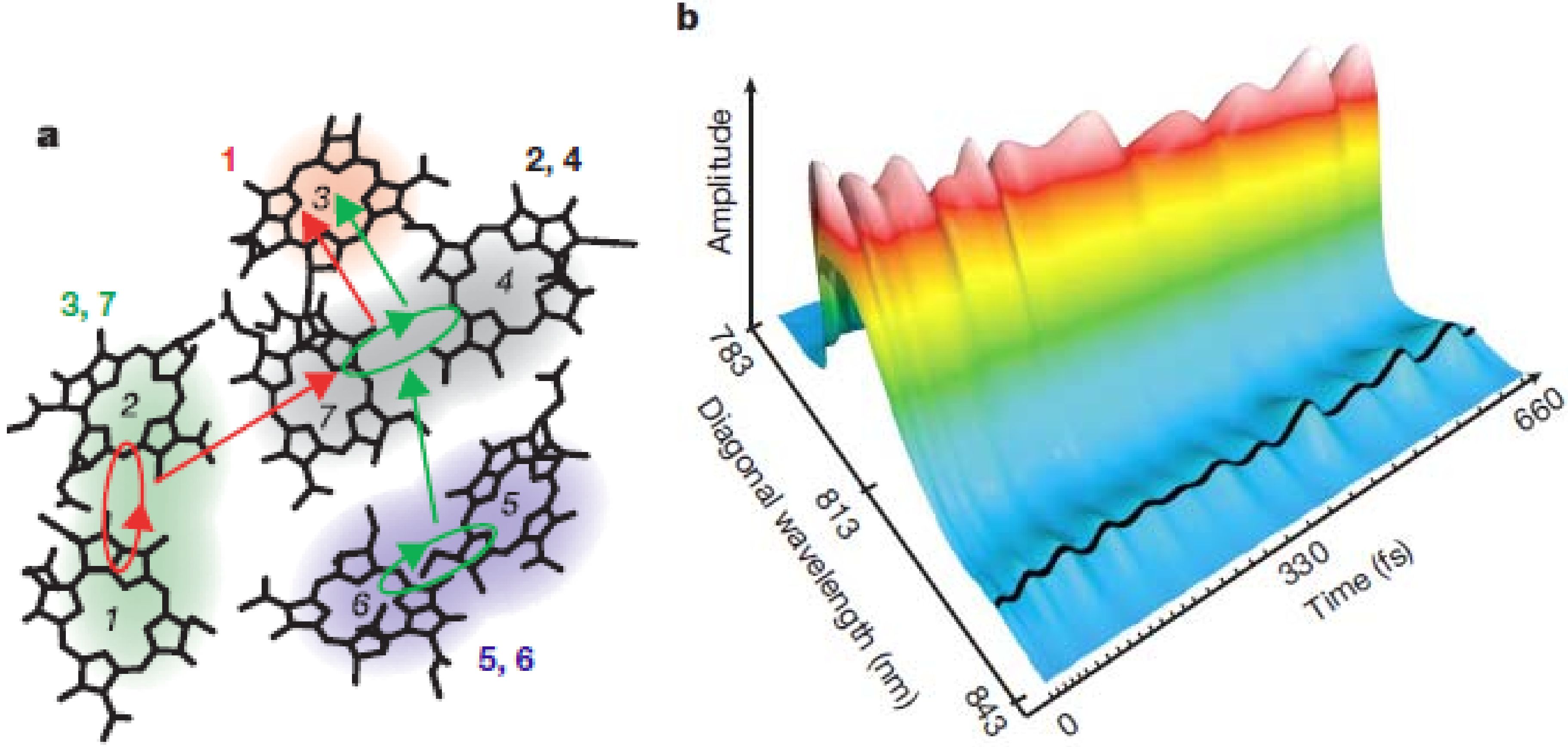


Excitons in a Ring



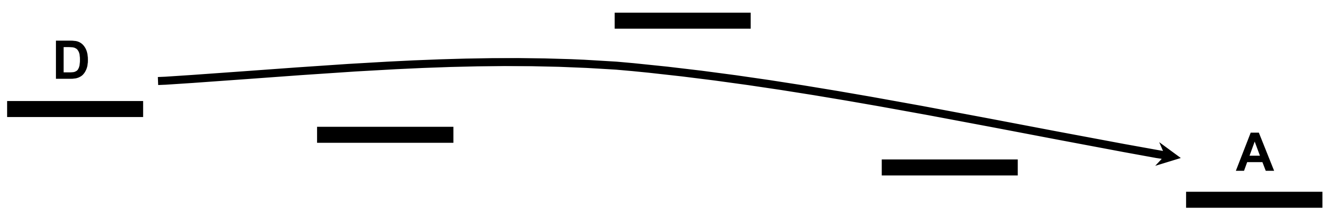
Coherent Transfer of Excitation Energy?

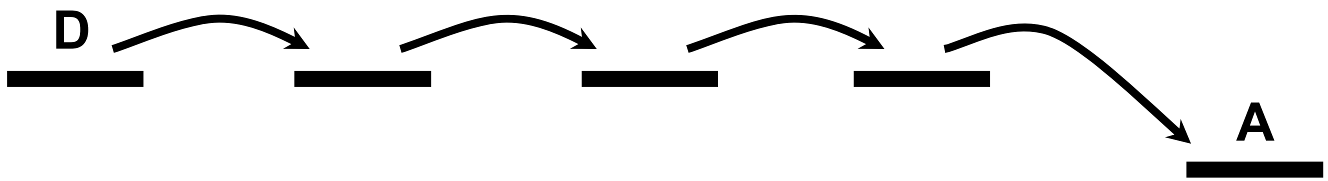
FMO Complex



Fleming et al., Nature 434 (2005) 625 and Nature 446 (2007) 782

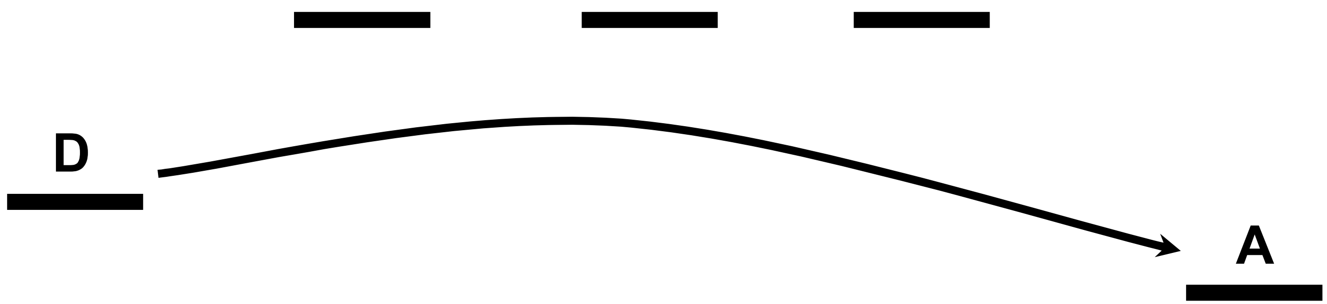
Coherent versus Incoherent Transfer



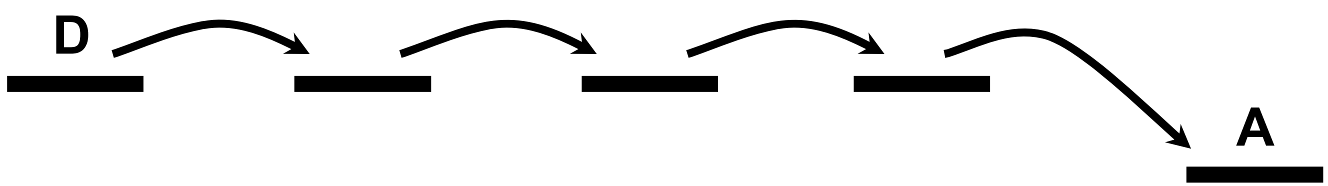


Bridged Electron Transfer

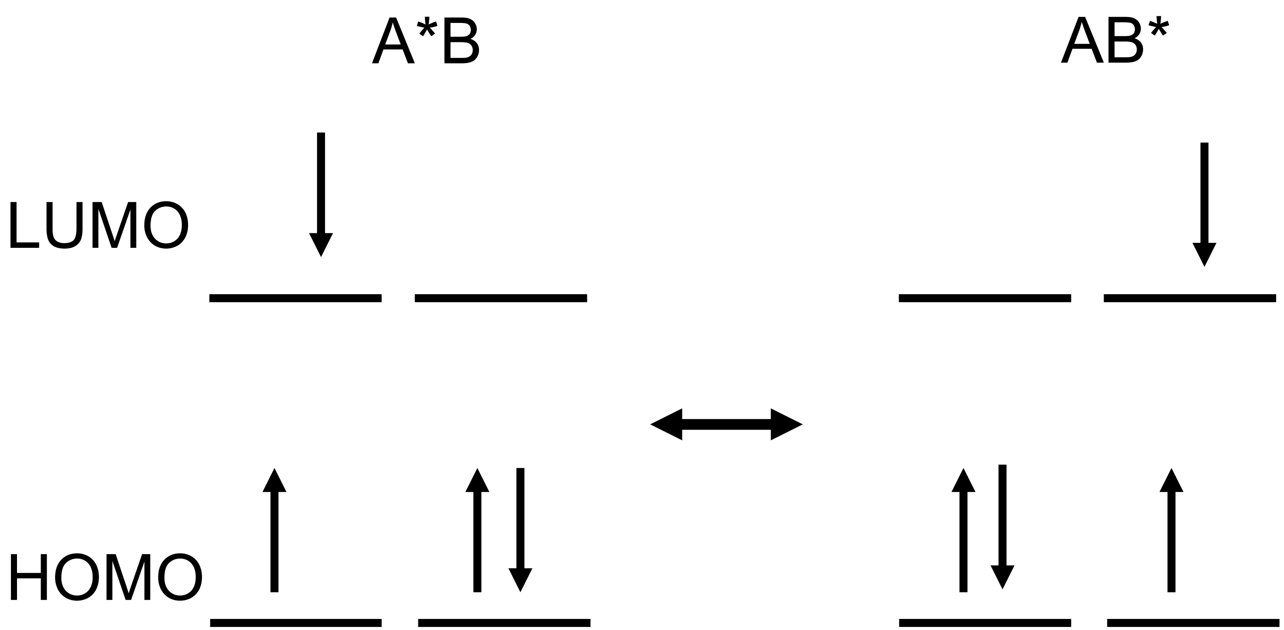
Superexchange



Hopping

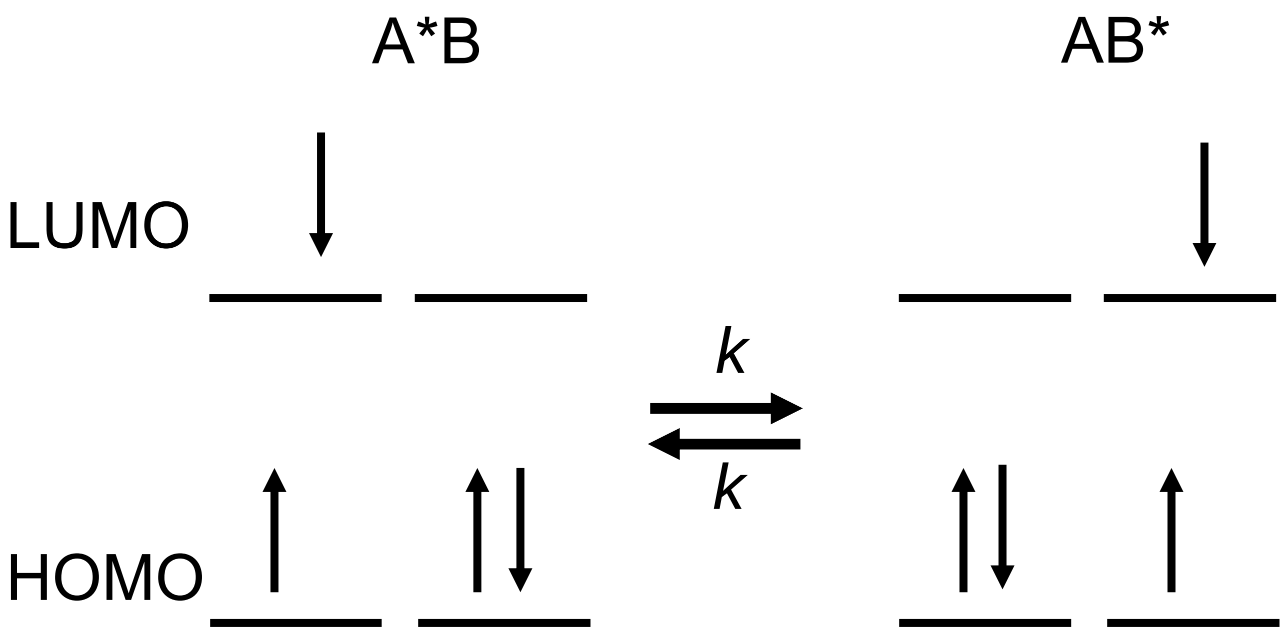


Exciton Transfer: Coherent



$$V_{12} \approx \frac{\vec{\mu}_1 \vec{\mu}_2}{R_{12}^3} - 3\frac{(\vec{\mu}_1 \vec{R}_{12})(\vec{\mu}_2 \vec{R}_{12})}{R_{12}^5}$$

Förster Transfer: Incoherent



$$V_{12} \approx \frac{\vec{\mu}_1 \vec{\mu}_2}{R_{12}^3} - 3\frac{(\vec{\mu}_1 \vec{R}_{12})(\vec{\mu}_2 \vec{R}_{12})}{R_{12}^5}$$

Förster Transfer

Fermi Golden Rule

$$k_{DA} = \frac{2\pi}{\hbar} \int V_{DA}^2 f_D(\omega) f_A(\omega) \delta(E_{D1} - E_{D0} - \hbar\omega)\delta(E_{A1} - E_{A0} - \hbar\omega) d\omega$$

$$V_{DA} = \frac{|\mu_D||\mu_A|}{R_{DA}^3}\kappa \quad \Leftarrow \quad V_{DA} = \frac{\vec{\mu}_1 \vec{\mu}_2}{R_{12}^3} - 3\frac{(\vec{\mu}_1 \vec{R}_{12})(\vec{\mu}_2 \vec{R}_{12})}{R_{12}^5}$$

Absorption and Emission Spectra

$$I_D(\omega) = \frac{4\pi\omega^3}{3c^3}|\mu_D|^2 \int f_D(\omega)\delta(E_{D1} - E_{D0} - \hbar\omega) d\omega$$

$$\alpha_A(\omega) = \frac{4\pi\omega}{3c}|\mu_A|^2 \int f_A(\omega)\delta(\hbar\omega - E_{A1} - E_{A0}) d\omega$$

$$k_{DA} = \frac{9c^4\kappa^2}{8\pi R_{DA}^6} \int \frac{d\omega}{\omega^4} I_D(\omega)\alpha_A(\omega)$$

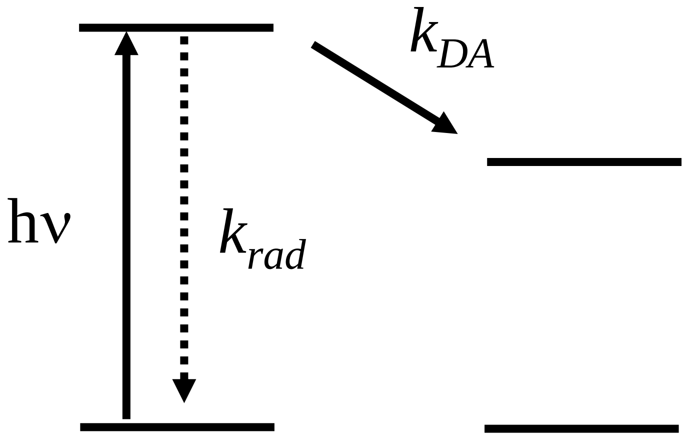
Förster Transfer

$$k_{DA} = \frac{9c^4\kappa^2}{8\pi R_{DA}^6}\int \frac{d\omega}{\omega^4} I_D(\omega)\alpha_A(\omega)$$

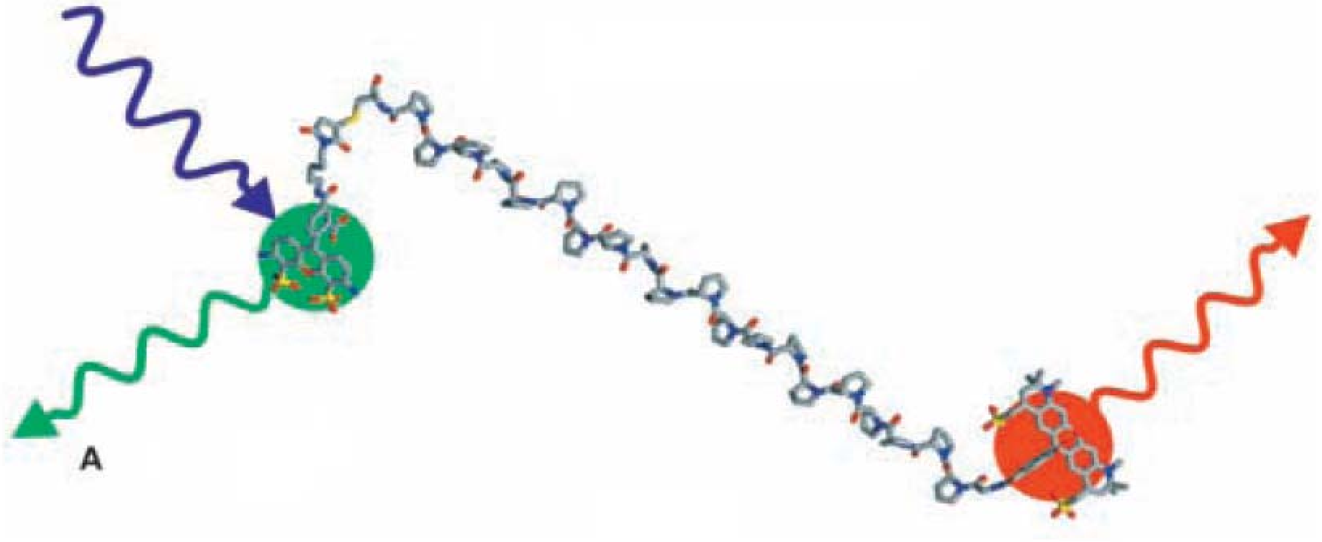
$$k_{DA} = k_{rad}\left(\frac{R_F}{R_{DA}}\right)^6$$

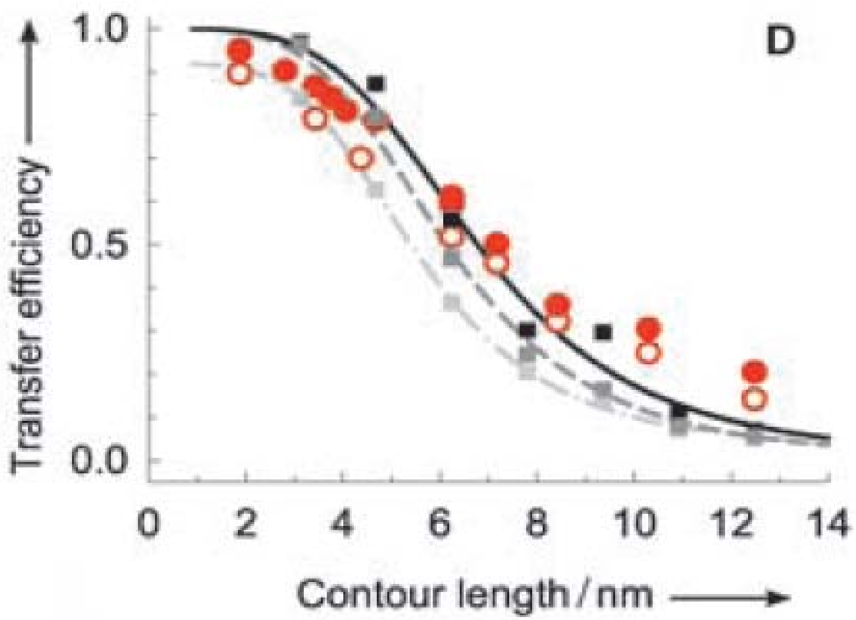
Förster Efficiency

$$\eta_{DA} = \frac{R_F^6}{R_{DA}^6 + R_F^6}$$



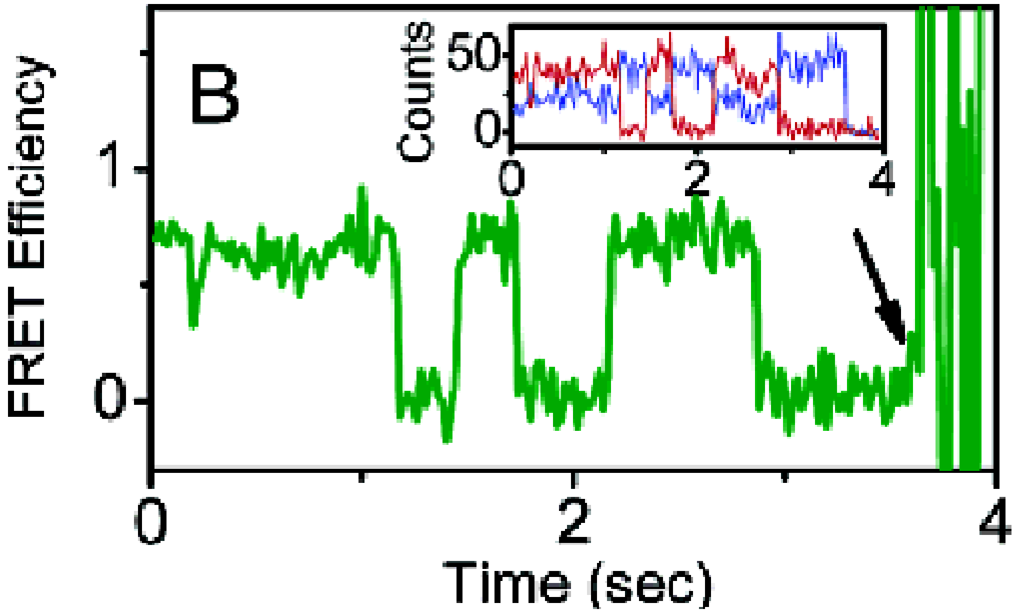
Förster Transfer

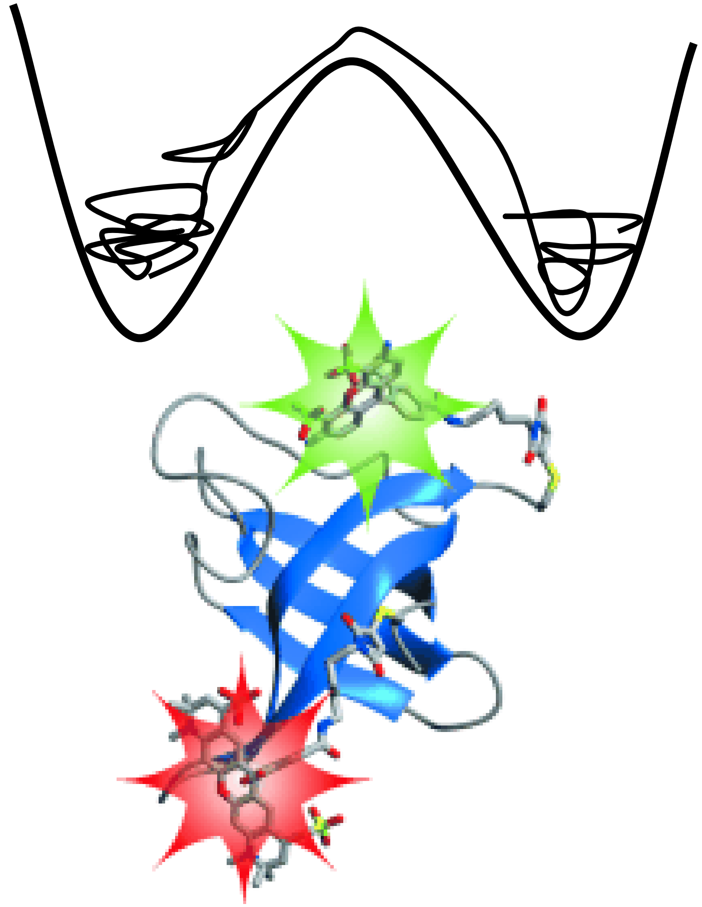




Schuler B, Single-molecule fluorescence spectroscopy of protein folding, ChemPhysChem 6 (2005) 1206-1220

Protein Folding: Single Molecule Spectroscopy





Two-State Folding Observed in Individual Protein Molecules

Rhoades, E.; Cohen, M.; **Schuler, B.;** Haran, G.;

J. Am. Chem. Soc.; **2004**; *126*; 14686-14687