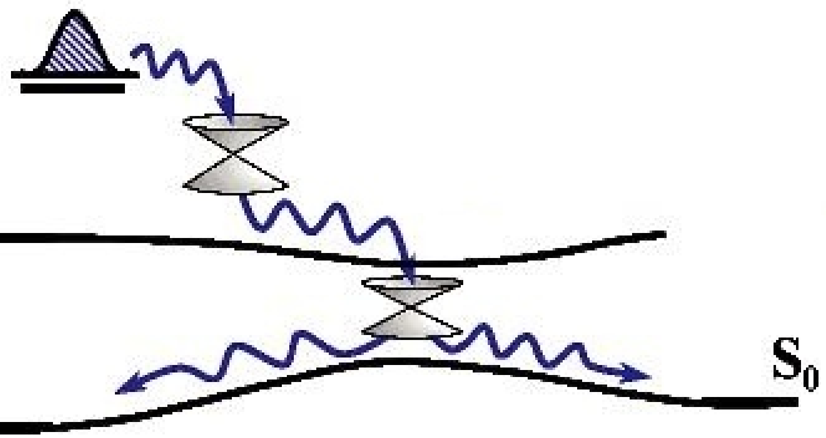
Theoretical Photochemistry WiSe 2017/18

Lecture 1



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http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. Photophysical Processes
2. The Born-Oppenheimer approximation
3. Wavepackets
4. Beyond Born-Oppenheimer – non-adiabatic transitions
5. The Franck-Condon picture of electronic transitions
6. Selection rules
7. What do we measure experimentally?
8. Conical intersections
9. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
10. Some electronic structure aspects
11. Dynamics: trajectories or wavefunctions?

12. **Wavefunction propagation techniques**
13. **Trajectory surface hopping techniques**
14. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
15. **Extended systems: Excitons, light-harvesting, etc.**
16. **Solvent/environmental effects**

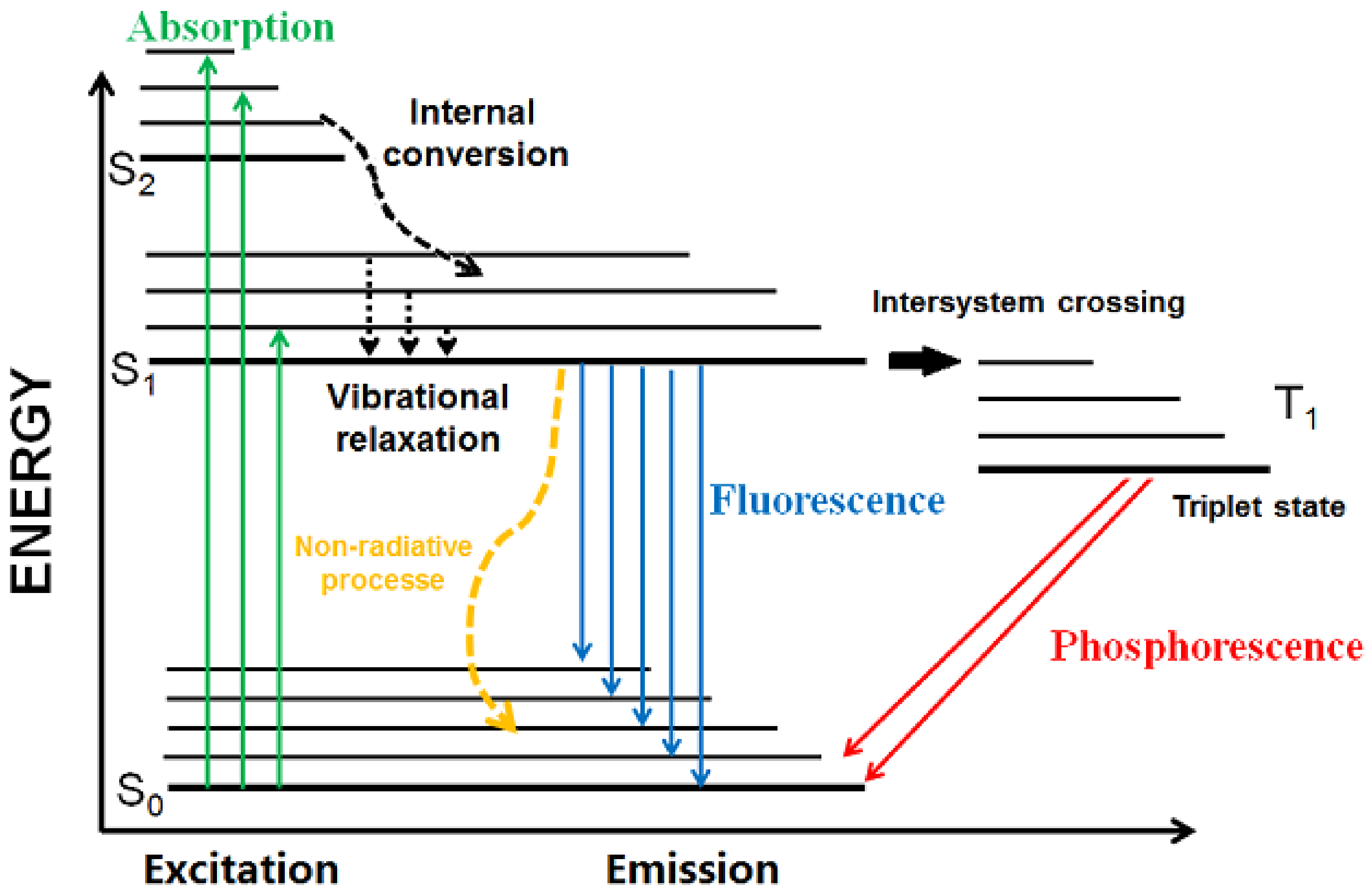
Literature

1. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press (2011).
2. D. Tannor, Introduction to Quantum Mechanics: A Time-Dependent Perspective, University Science Books (2006).
3. M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH-Wiley (1995).
4. I. N. Levine, Quantum Chemistry, 6th Edition, Pearson International Edition (2009).
5. F. Jensen, Introduction to Computational Chemistry, 2nd Edition, Wiley (2007).
6. C. J. Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd Edition, Wiley (2004).

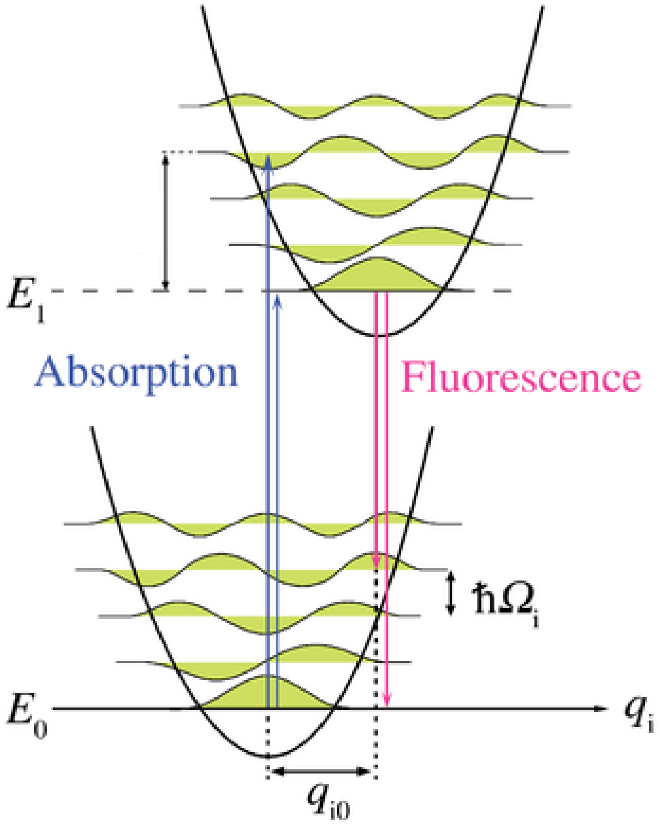
Introduction

1. Electronic excitation and what follows
2. What can we see experimentally?
3. Wavepackets
4. Born-Oppenheimer & beyond
5. What do we need to calculate?

Vibronic (=vibrational-electronic) state picture: Jablonski diagram



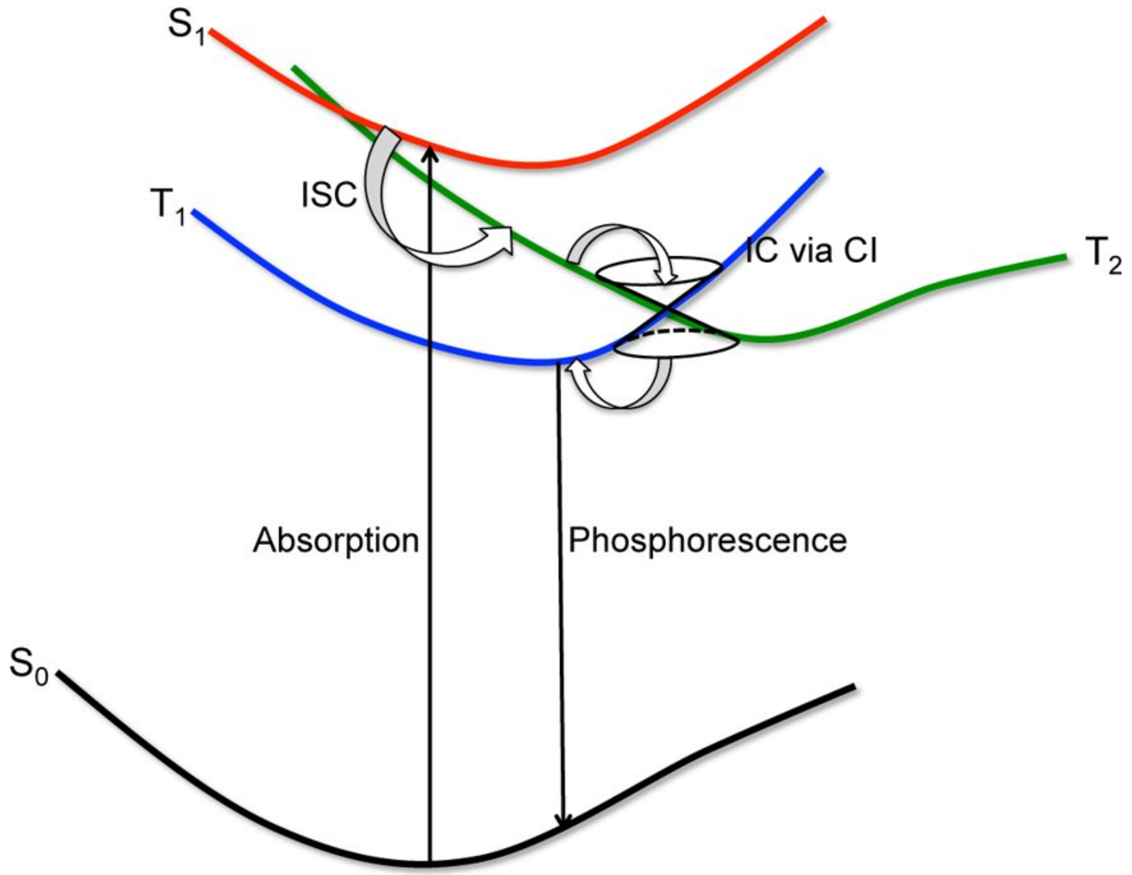
Vibronic (=vibrational-electronic) state picture + potential energy surfaces (PES)



excited state

ground state

Photochemical dynamics: potential energy surface (PES) picture



Example: benzaldehyde

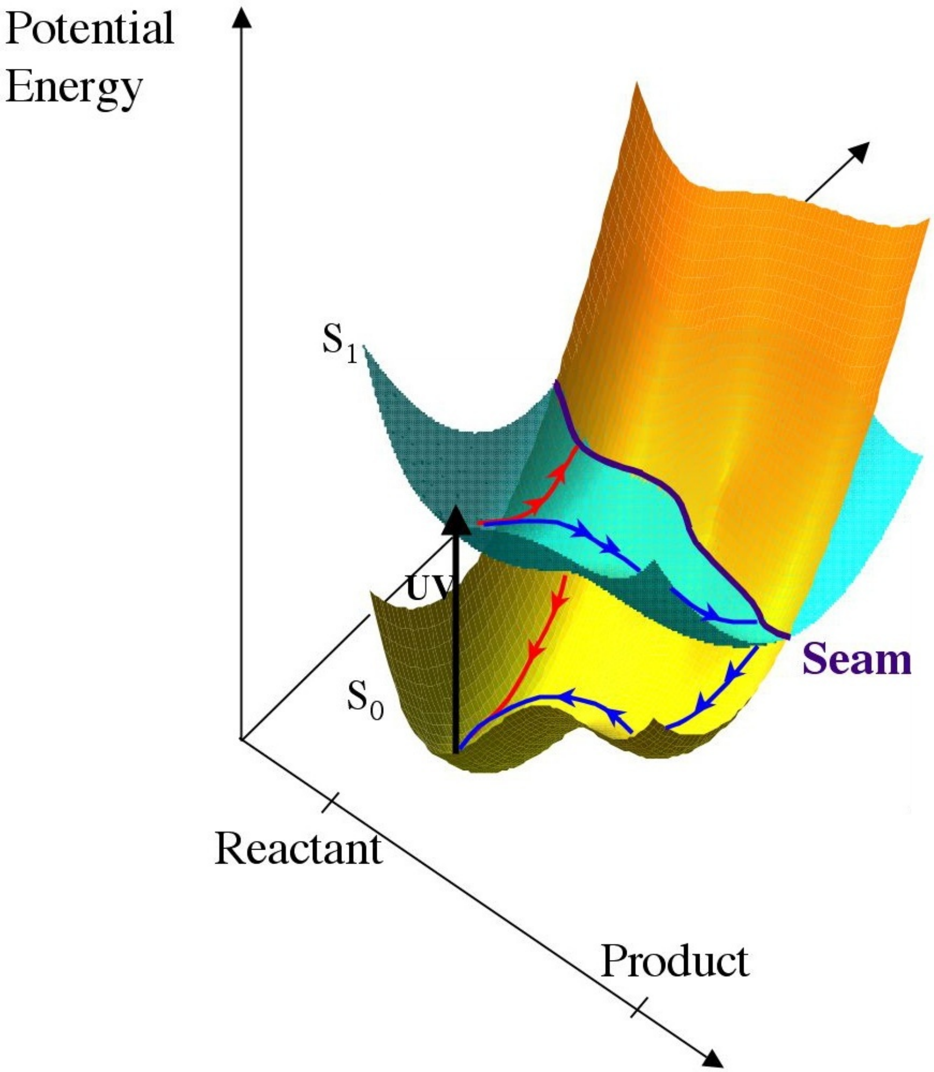
ISC = intersystem crossing

IC = internal conversion

CI = conical intersection

- ISC time scale: $\sim 10^{-9}$ s ("untypically" fast!)
- phosphoresence lifetime $\sim 2 \times 10^{-3}$ s

Radiationless return to the ground state



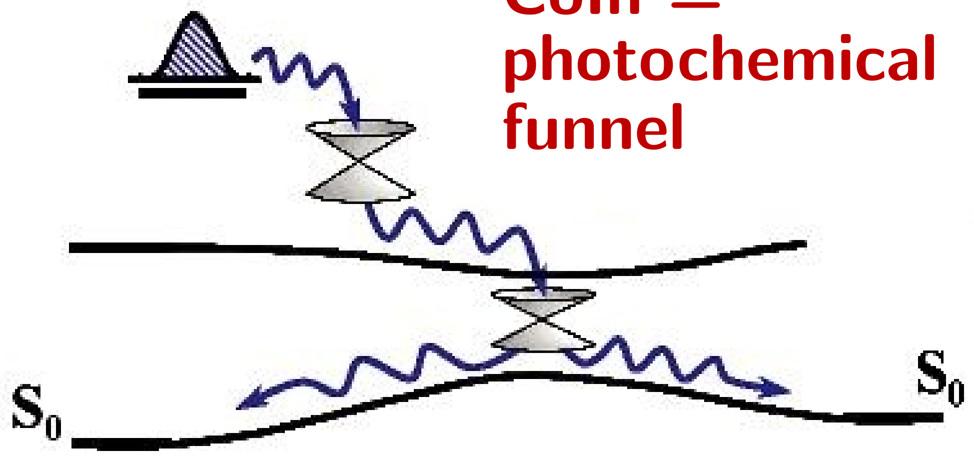
- e.g., excited-state lifetime of anthracene $\sim 10^{-13}$ s – ultrafast!

- by contrast, S_1 lifetime of pyrene is $\sim 10^{-6}$ s – here, deactivation occurs by fluorescence and intersystem crossing $(S \rightarrow T)$

- Kasha's Rule: luminescence observed exclusively from lowest excited state (S_1)

- intersystem crossing $(S \rightarrow T)$: typical time scale $\sim 10^{-7}$-10^{-11} s

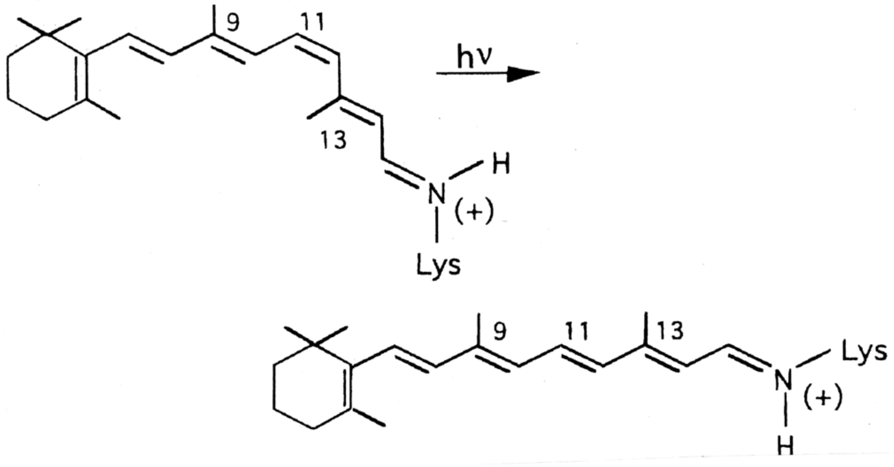
Conical intersections (CoIn's) as landmark topology

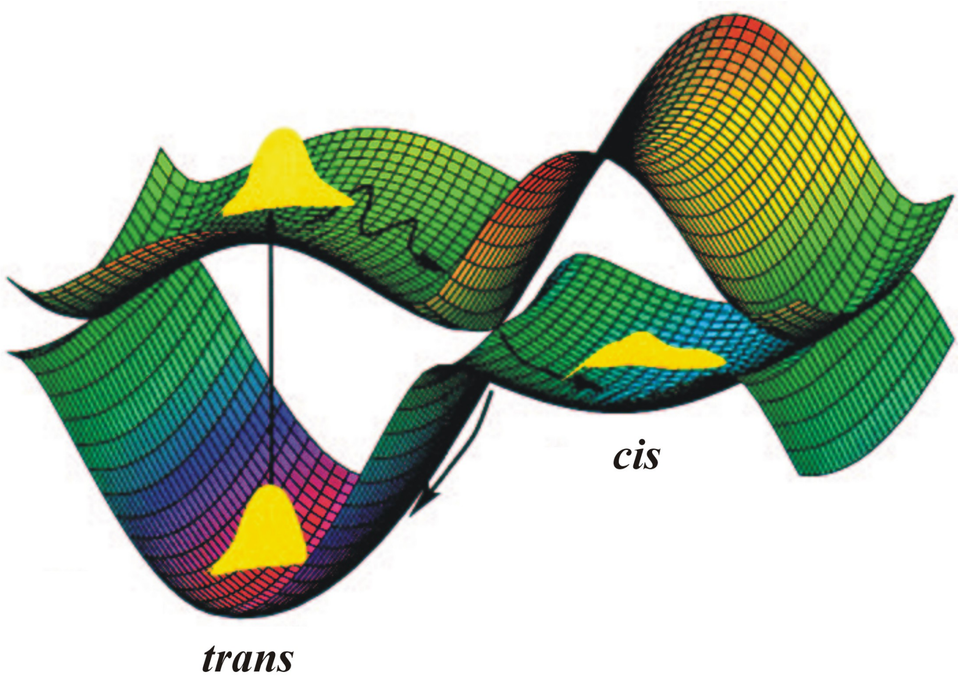


adapted from: Schultz et al., J. Am. Chem. Soc. 125, 8098 (2003)

- Conical intersection topologies are highly anharmonic
- Extreme breakdown of the Born-Oppenheimer approximation
- The electronic decay at a CoIn is ultrafast (femtosecond to picosecond scale)
- CoIn's are ubiquitous (Truhlar/Mead: "Principle of non-rareness of CoIn's")
- Polyatomic molecules; Jahn-Teller effect in solids

Ultrafast photo-isomerization of retinal





S. Hahn and G. Stock, J. Phys. Chem. B 104, 1146 (2000).

- primary process of vision
- relevant coordinates: twist + skeletal stretch + . . .
- excited-state decay in the protein: ∼ 200 fs / in solution phase: ∼ 5 ps

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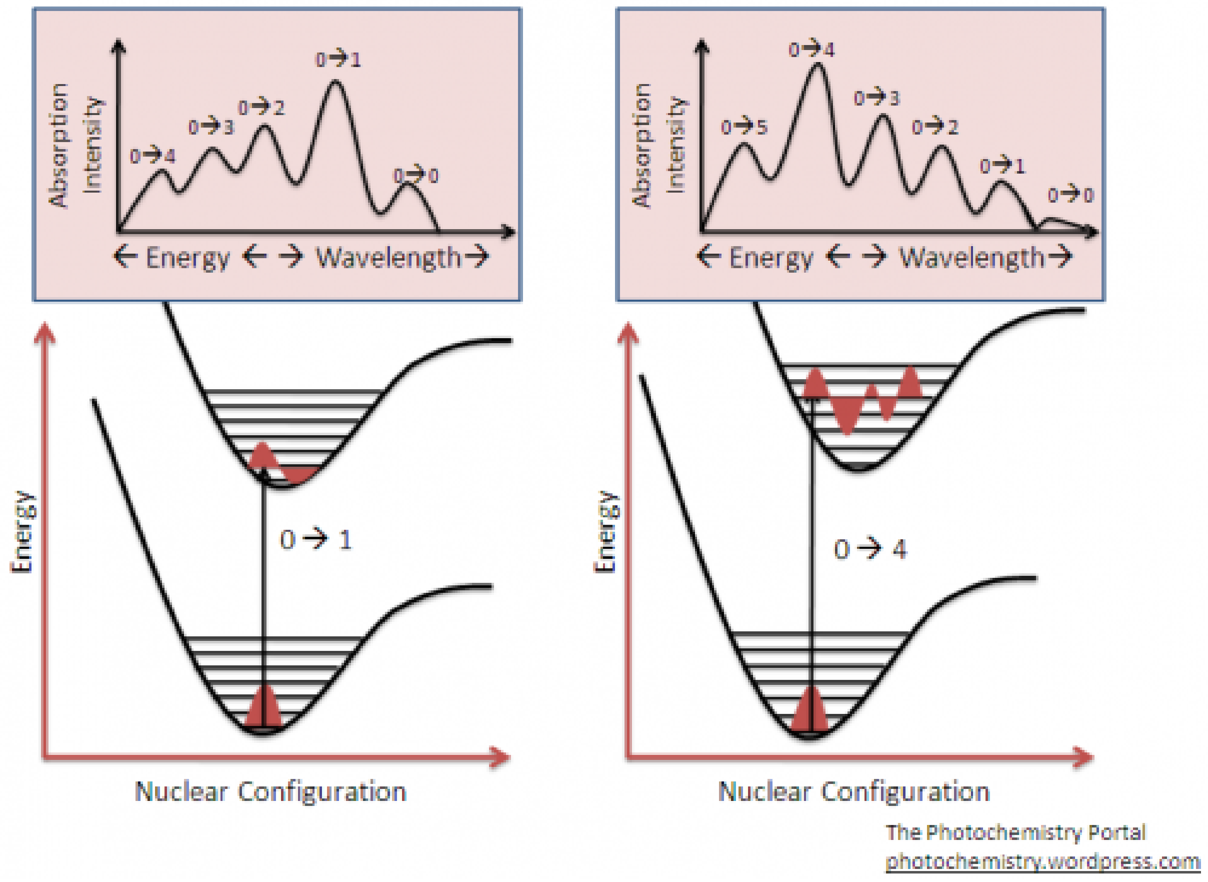
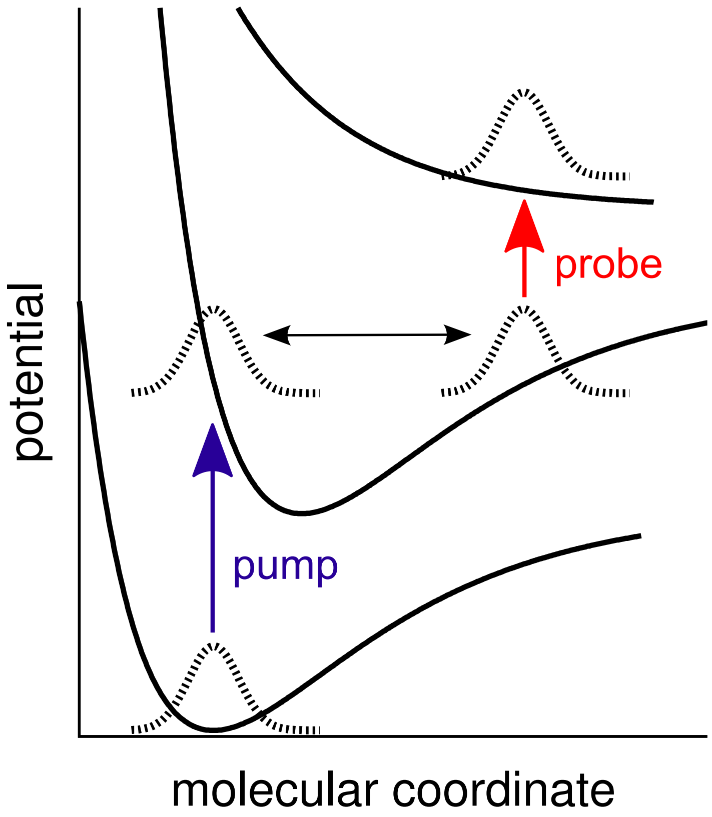
Franck-Condon absorption spectrum



The Photochemistry Portal
photochemistry.wordpress.com

- **transitions between quantized vibronic states**

Time-resolved Spectroscopy



- e.g., pump-probe spectroscopy: sequence of ultrashort ($\sim$ 10-50 fs) UV/Vis pulses
- vary the time delay between the pulses

Watching the dissociation of ICN

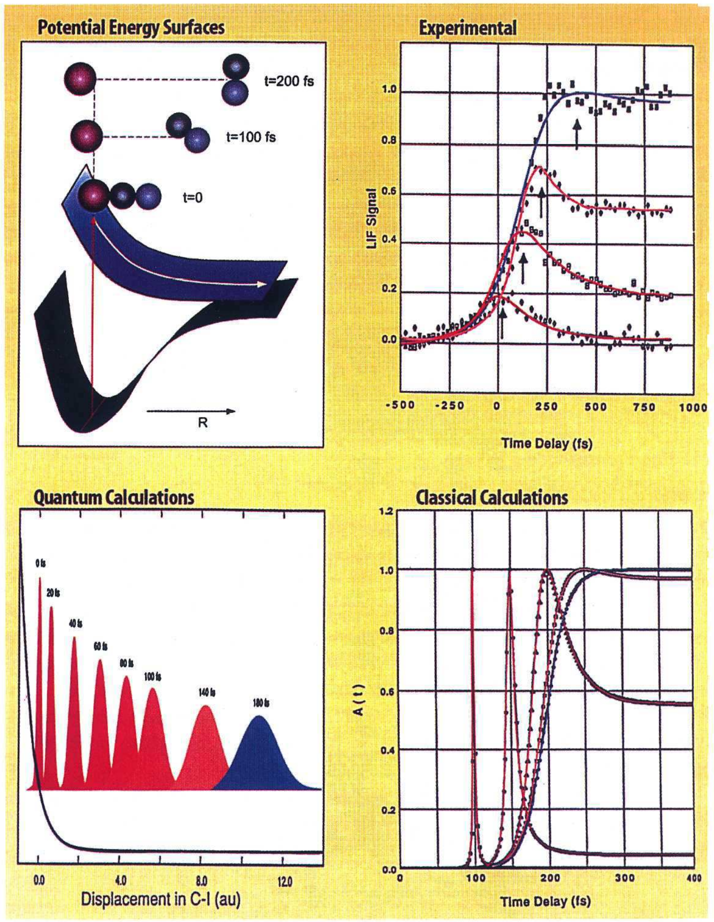


Figure 14. Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown (see text). [Ref. B1, B4, B6, B14, B16, B18, B19, B28, 55]

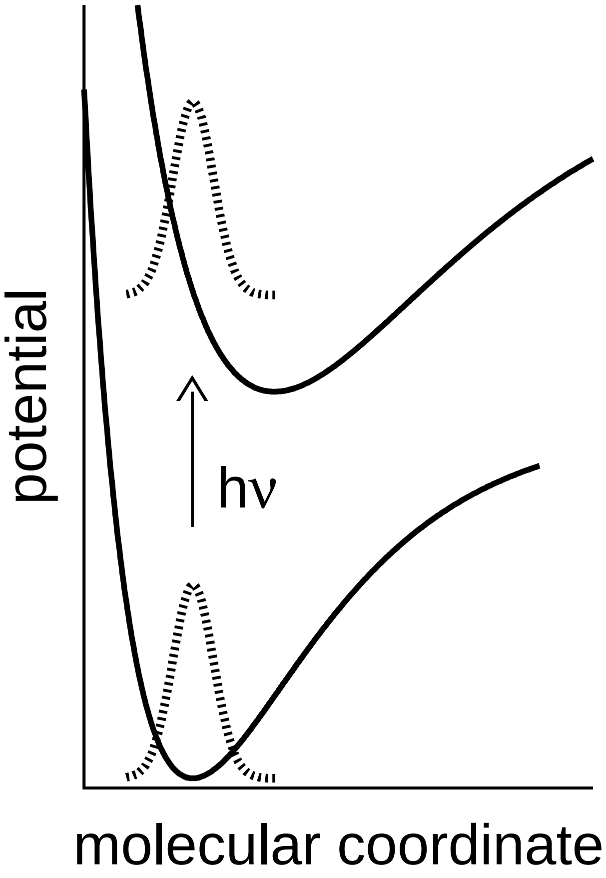
Pump-probe spectroscopy:

$\mathbf{ICN}^* \longrightarrow \mathbf{I + CN}$

(Zewail & co (1987))

- **dissociation described by outgoing wavepacket**

Franck-Condon transition – wavepacket picture



ground-state wavefunction:

$$|\psi^{(0)}(x,t_0)\rangle = \chi_G^{(0)}(x,t_0)|G\rangle$$

act with the dipole moment operator on $\psi^{(0)}$:

$$\begin{aligned}\hat{\mu}|\psi^{(0)}\rangle &= \mu_{EG}(|E\rangle\langle G| + |G\rangle\langle E|)|\psi^{(0)}\rangle \\ &= \mu_{EG}\,\chi_G^{(0)}(x,t_0)|E\rangle \\ &\equiv |\Phi_E(x,t_0)\rangle\end{aligned}$$

$|\Phi_E(x,t)\rangle$ = excited-state wavepacket

non-stationary state!

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Quantum dynamics – basics

- Wavepackets correspond to coherent superposition states

$$\Psi(x,t) = \sum_n a_n \varphi_n(x) \exp\left(-\frac{i}{\hbar} E_n t\right)$$

- For example, for a harmonic oscillator:

$$\begin{aligned} \varphi_n(x) &= N_n H_n(y) \exp(-y^2/2) \quad ; \quad y = (m\omega/\hbar)^{1/2} x \quad ; \quad N_n = (1/2^n n! \pi^{1/2})^{1/2} \\ E_n &= \hbar\omega(n + 1/2) \end{aligned}$$

- For a given eigenstate φ_n, all observables are independent of time (i.e., the state is *stationary*)

- A coherent superposition of at least two eigenstates is required to observe a time dependence of the observables, e.g., $\langle x \rangle (t)$.

Quantum dynamics – basics / cont'd

- The time evolution of the wavepacket $\Psi(x,t)$ is given in terms of the time-dependent Schrödinger equation (TDSE):

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi$$

- Particular solution, for eigenstates:

$$\Psi(x,t) = \varphi_n(x)\mathrm{exp}\left(-\frac{i}{\hbar}E_n t\right)$$

- Examples which allow for analytical solutions: particle-in-a-box, free particle wavepacket, Gaussian wavepackets

- In general, we need to integrate the time-dependent Schrödinger equation numerically – in that case, the knowledge of the eigenstates is not necessary

Eigenstate solution: “separation of variables”

- assume that solutions of the TDSE exist which can be written in product form,

$$\Psi(x,t) = \psi(x)\chi(t)$$

- such that $\partial\Psi/\partial t = \dot{\chi}(t)\psi(x)$, and

$$i\hbar\frac{\dot{\chi}(t)}{\chi(t)} = \frac{(-\frac{\hbar^2}{2m}\nabla^2 + V)\psi(x)}{\psi(x)}$$

- since the l.h.s. is only a function of t and the r.h.s. is only a function of x, both must be equal to the same constant, E. Therefore,

$$\begin{aligned} i\hbar\dot{\chi}(t) &= E\chi(t) \\ (-\frac{\hbar^2}{2m}\nabla^2 + V)\psi(x) &= E\psi(x) \end{aligned}$$

- The first equation can be integrated to give $\chi(t) = \chi_0 \exp(-iEt/\hbar)$

Superposition states & time-dependent observables

- First, use the particular solution $\Psi(x,t) = \psi_E(x)\exp(-iEt/\hbar)$ to calculate time-dependent expectation values, e.g.,

$$\begin{aligned}\langle x\rangle_t &= \int dx\,\Psi^*(x,t)\,x\,\Psi(x,t) = \int dx\,\psi_E^*(x)e^{iEt/\hbar}\,x\,\psi_E(x)e^{-iEt/\hbar} \\ &= \int dx\,\psi_E^*(x)x\,\psi_E(x) \longrightarrow \text{no time-dependence!}\end{aligned}$$

- Next, try a linear combination:

$$\Psi(x,t) = a\,\psi_E(x)\exp(-iEt/\hbar) + b\,\psi_{E'}(x)\exp(-iE't/\hbar)$$

$$\begin{aligned}\langle x\rangle_t &= |a|^2\int dx\;x\,|\psi_E(x)|^2 + |b|^2\int dx\;x\,|\psi_{E'}(x)|^2 \\ &\quad +2\mathrm{Re}(a^*b)\int dx\;x\,\psi_E^*(x)\psi_{E'}(x)e^{-i(E'-E)t/\hbar}\end{aligned}$$

The time dependence is in the interference term!

Wavepackets = most general TDSE solutions

- As we have seen, a coherent superposition of eigenstates (= wavepacket) is required in order to have time dependence in any observable

- The general solution of the TDSE thus reads as follows:

$$\Psi(x,t) = \sum_{n=1}^{\infty} a_n\, \psi_n(x) \exp\Big(-\frac{i}{\hbar} E_n t\Big) \qquad \text{(discrete spectrum)}$$

– where $(\psi_n(x), E_n)$ are obtained by solving the time-independent SE

– the a_n's are obtained from the initial condition: $a_n = \int dx\, \psi_n^*(x) \Psi(x,0)$

- For a continuous spectrum, we get analogously:

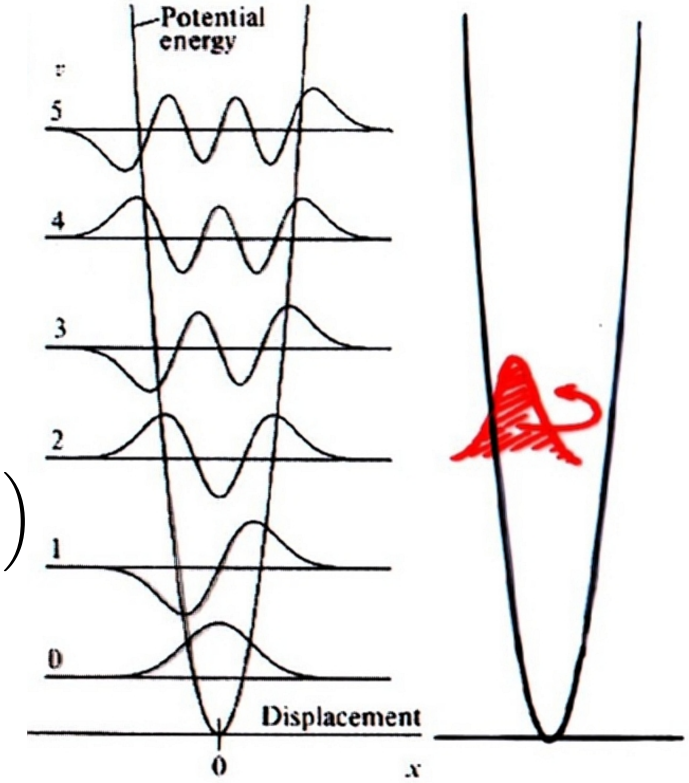
$$\Psi(x,t) = \int_0^{\infty} dE\, a(E) \psi_E(x) \exp\Big(-\frac{i}{\hbar} E t\Big) \qquad \text{(continuous spectrum)}$$

Gaussian wavepacket in a harmonic potential

- $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \qquad k = m\omega^2$

- time-evolving wavepacket:

$$\Psi(x,t) = \sum_n a_n \varphi_n(x) \exp\Big(-\frac{i}{\hbar}\hbar\omega(n+1/2)t\Big)$$



- wavepacket at time $t = mT$
where $T = 2\pi/\omega$ is the classical period:

$$\begin{aligned}\Psi(x,t=mT) &= \sum_n a_n \varphi_n(x) \exp\Big(-\frac{i}{\hbar}\hbar\omega(n+1/2)mT\Big) \\ &= \exp(-i2\pi m(n+1/2))\Psi(x,0) = (-1)^m \Psi(x,0)\end{aligned}$$

- the wavepacket oscillates with the classical period T!

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4. **Born-Oppenheimer & beyond** ⟶ **next lecture!**
5. **What do we need to calculate?**

What do we need to calculate?

(1) Franck-Condon excitation & beyond:

- Franck-Condon wavepackets
- transition dipole moment, oscillator strength
- absorption spectra, nonlinear optical spectroscopy . . .

(2) PES's from electronic structure calculations:

- calculate Potential Energy Surfaces (PES)
- calculate non-adiabatic couplings
- possibly "diabatize" (= transform to a diabatic representation)

(3) Dynamics (once the PES's are known):

- wavepacket simulations on non-adiabatically coupled PES's
- or simplified descriptions of the dynamics: classical trajectories, Gaussian wavepackets