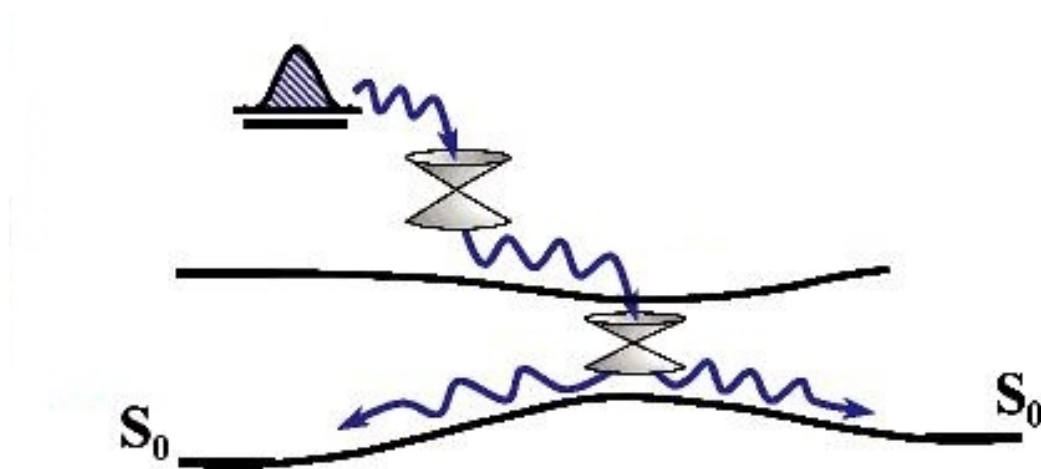


Theoretical Photochemistry WiSe 2018/19

Lecture 7



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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. **Interaction with light & what kind of spectroscopies?**
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?
11. Wavefunction propagation techniques

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

What do we need to calculate?

(1) PES's from electronic structure calculations:

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

(2) 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

(3) Spectroscopic signals:

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

Interaction with the electromagnetic field

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{int}}(t)$$

- semiclassical equations for the interaction with the field:

$$\hat{H}_{\text{int}}(t) = -E(r, t)\hat{\mu} = -E(r, t) \sum_{\alpha} \hat{\mu}_{\alpha} = -E(r, t) \sum_{\alpha} q_{\alpha} \hat{r}_{\alpha}$$

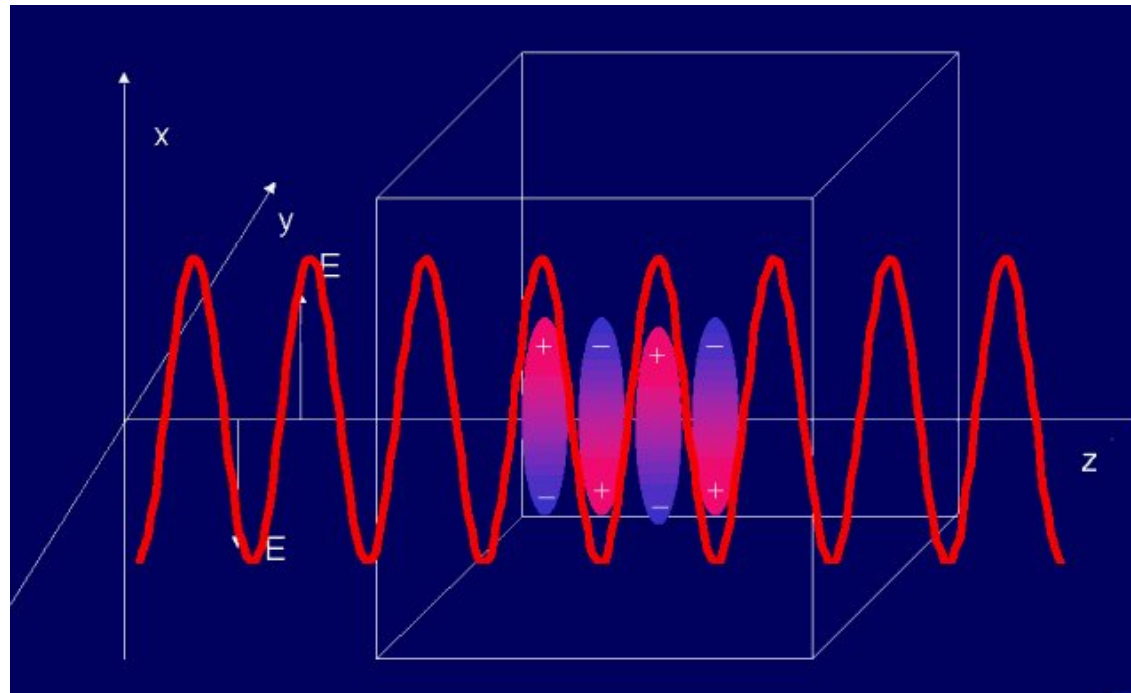
“back-of-the-envelope” derivation:

electromagnetic field E [N C⁻¹] = force per unit charge

e.g., force F_x for a field in x direction: $F_x = \sum_{\alpha} q_{\alpha} E_x = -(dV/dx)$

hence, the potential of interaction reads $V = -\sum_{\alpha} q_{\alpha} x E_x = -\sum_{\alpha} \mu_{\alpha} E_x$

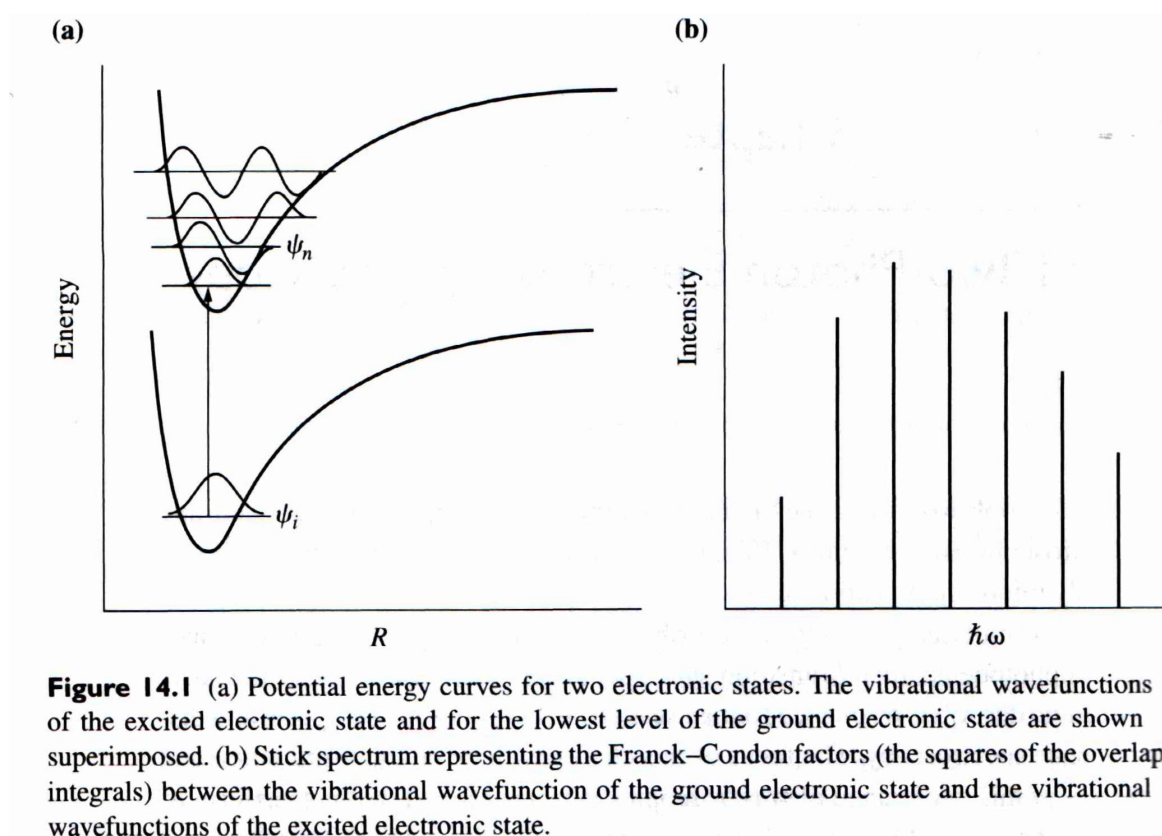
In general: Measure **polarisation** resulting from the interaction with an electromagnetic field



$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \dots = \epsilon_0 \left(\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}^2 + \chi^{(3)} \mathbf{E}^3 + \dots \right)$$

$\chi^{(n)}$ = n th order susceptibility

Absorption spectrum (“1st-Order Polarization”)



$$\sigma(\omega_I) = \frac{4\pi^2\omega_I}{3\hbar c} \sum_n |\langle \psi_n^E | \mu | \psi_i^G \rangle|^2 \delta(\omega_I - \omega_n)$$

Fermi's Golden Rule

Transition probability between quantum states that are subject to a perturbation

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

$$\text{e.g., } \hat{V}(t) = -\hat{\mu} E_0 (e^{i\omega t} + e^{-i\omega t}) \quad \text{“perturbation”}$$

Transition rate between two states $a \rightarrow b$
(in 2nd order perturbation theory):

$$\Gamma_{a \rightarrow b} = \frac{2\pi}{\hbar} |\langle \psi_b^{(0)} | \hat{\mu} | \psi_a^{(0)} \rangle|^2 \delta(E_b^0 - E_a^0 \pm \hbar\omega)$$

where $E_b^0 - E_a^0 = \hbar\omega_{ba}$ - **resonance condition!**

Perturbation Theory – Brief Primer

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

$\hat{H}_0$ = unperturbed Hamiltonian

$\hat{V}$ = perturbation Hamiltonian

λ = small parameter

Now expand

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

and insert into the Schrödinger Equation $\hat{H}\psi_n = E_n\psi_n \dots$

Perturbation Theory – Brief Primer, cont'd

. . . and insert into the Schrödinger Equation $\hat{H}\psi_n = E_n\psi_n$:

$$\begin{aligned}(\hat{H}_0 + \lambda\hat{V})(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \dots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \dots)\end{aligned}$$

Finally, sort according to contributions in λ^0 , λ^1 , λ^2 :

$$\begin{aligned}(\lambda^0) \dots \quad \hat{H}_0\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(0)} \\ (\lambda^1) \dots \quad \hat{H}_0\psi_n^{(1)} + \hat{V}\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \\ (\lambda^2) \dots \quad \hat{H}_0\psi_n^{(2)} + \hat{V}\psi_n^{(1)} &= E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}\end{aligned}$$

and obtain first-, second-order energies and wavefunctions . . .

Second-Order Perturbation Theory

Putting the first- and second-order terms together then gives the results

$$E_n = E_n^{(0)} + \lambda V_{nn} - \lambda^2 \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}} + O(\lambda^3),$$

and

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle \left[1 - \frac{\lambda^2}{2} \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}^2} + O(\lambda^3) \right] \\ &+ \sum_{m \neq n} |m^{(0)}\rangle \left[-\lambda \frac{V_{mn}}{E_{mn}} + \lambda^2 \left(\sum_{m' \neq n} \frac{V_{mm'} V_{m'n}}{E_{mn} E_{m'n}} - \frac{V_{mn} V_{nn}}{E_{mn}^2} \right) + O(\lambda^3) \right]. \end{aligned}$$

Truncating the series, and setting $\lambda = 1$ then gives the approximations

$$E_n \approx E_n^{(0)} + V_{nn} - \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}},$$

and

$$|n\rangle \approx |n^{(0)}\rangle \left[1 - \frac{1}{2} \sum_{m \neq n} \frac{|V_{mn}|^2}{E_{mn}^2} \right] + \sum_{m \neq n} |m^{(0)}\rangle \left[-\frac{V_{mn}}{E_{mn}} + \sum_{m' \neq n} \frac{V_{mm'} V_{m'n}}{E_{mn} E_{m'n}} - \frac{V_{mn} V_{nn}}{E_{mn}^2} \right].$$

Transition dipole moment & oscillator strength

transition dipole moment:

$$\langle \psi_n^E | \mu | \psi_i^G \rangle \sim \mu_{EG} \langle \psi_n | \psi_i \rangle$$

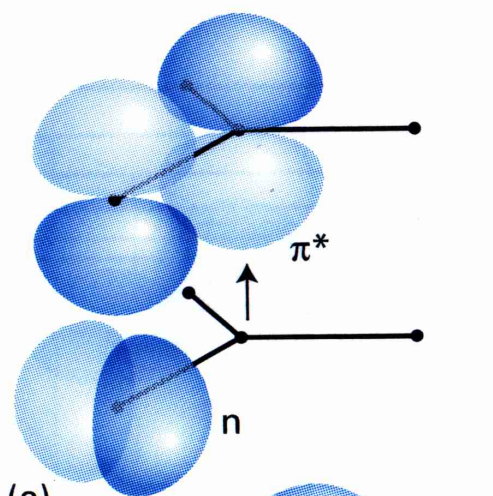
with the electronic matrix element $\mu_{EG} = \langle E | \hat{\mu} | G \rangle$ and the Franck-Condon factors $S_{ni} = \langle \psi_n | \psi_i \rangle$

oscillator strength:

(dimensionless quantity which measures the total area under the absorption band $\sigma(\omega_I) = \frac{4\pi^2\omega_I}{3\hbar c} \sum_n |\langle \psi_n | \mu | \psi_i \rangle|^2 \delta(\omega_I - \omega_n)$):

$$f = \left(\frac{4\pi m_e \omega_{EG}}{3e^2 \hbar} \right) |\mu_{EG}|^2$$

Dipole allowed and forbidden transitions



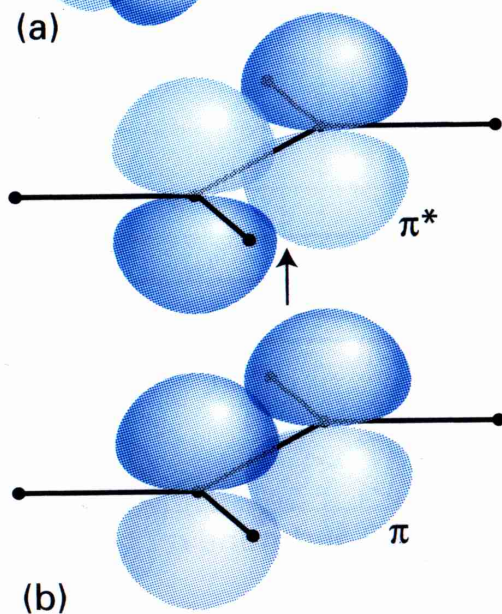
(a) carbonyl (C=O) group:
 $\pi^* \leftarrow n$ transition is **forbidden**

$$n \sim O2p_y$$

$$\psi_{\pi^*} = c'\chi(C2p_x) + c\chi(O2p_x)$$

$$\langle \pi^* | \mu | n \rangle \sim c \langle Op_x | \mu | Op_y \rangle = 0$$

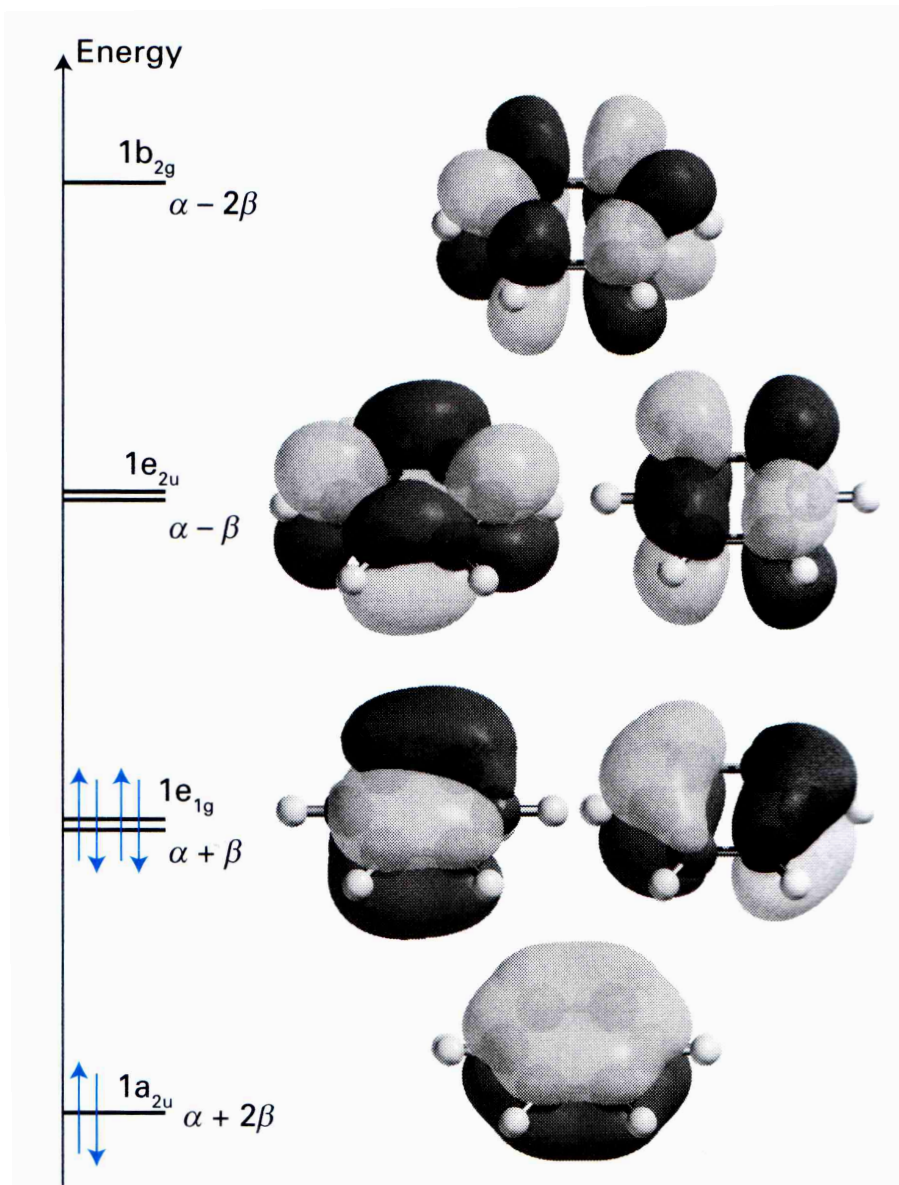
but: intensity borrowing possible



(b) ethene:
 $\pi^* \leftarrow \pi$ transition is **allowed**

transition to π^* induces twisting

Another case: Benzene (D_{6h})



three important bands in the UV:
 185 nm – symmetry-allowed, intense
 200 nm – symmetry-forbidden, weak
 260 nm – symmetry-forbidden, weak

ground state: $G(^1A_{1g})$

electric dipole operator:
 $A_{2u}(z) + E_{1u}(x, y)$

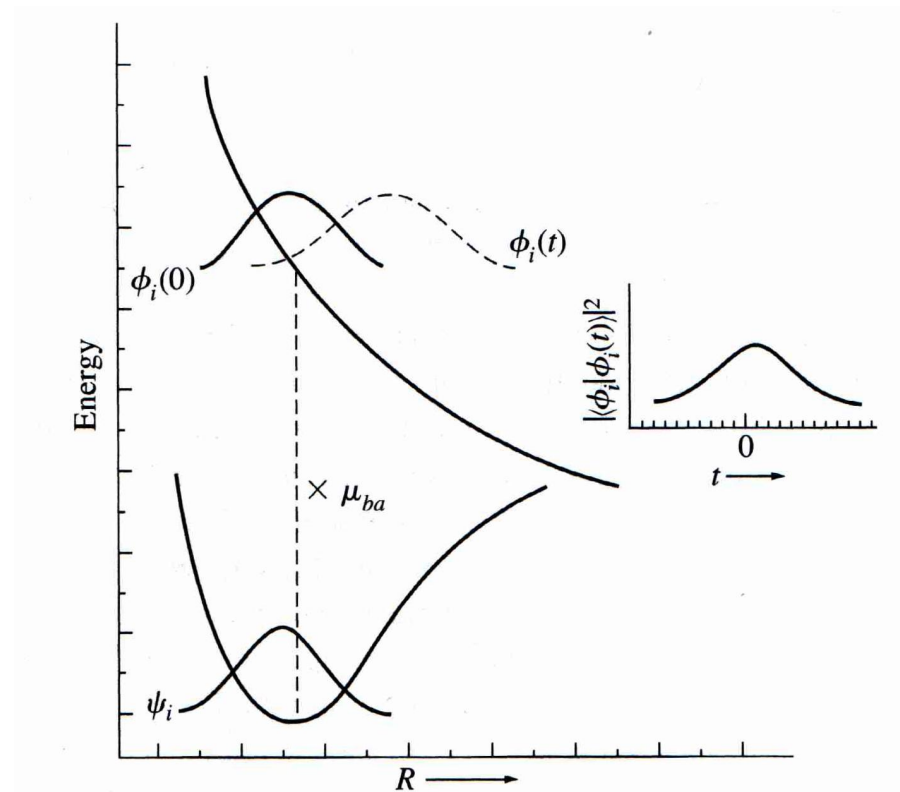
allowed transitions:

$E_{1u} \leftarrow ^1A_{1g}$ (185 nm)
 $^1A_{2u} \leftarrow ^1A_{1g}$

forbidden (but weak) transitions:

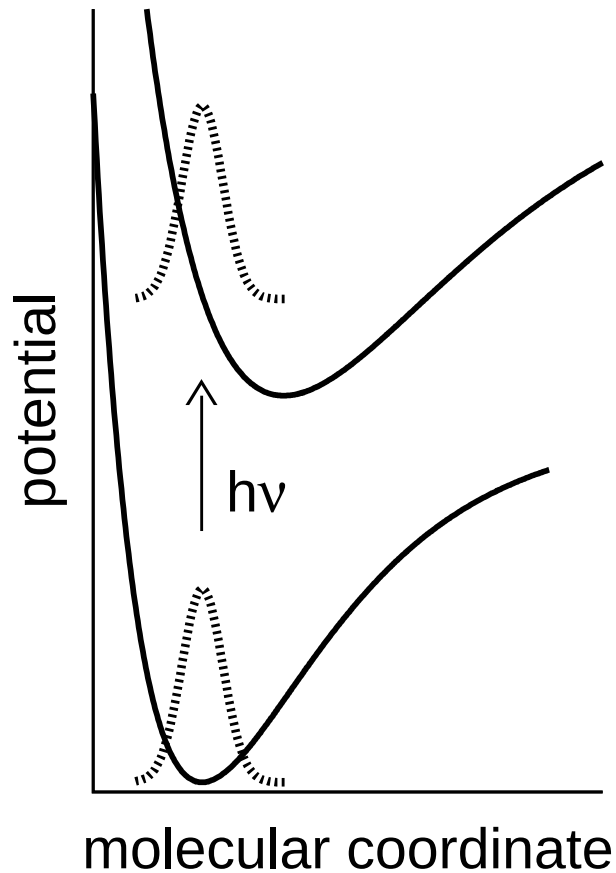
$^1B_{1u} \leftarrow ^1A_{1g}$ (200 nm)
 $^1B_{2u} \leftarrow ^1A_{1g}$ (260 nm)

Time-domain representation: Franck-Condon wavepacket



excited-state wavepacket: $|\phi_i(0)\rangle = \mu_{ba} |\psi_i(0)\rangle$

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!

Absorption spectrum: frequency and time-domain representation

$$\begin{aligned}\sigma(\omega_I) &= \frac{4\pi^2\omega_I}{3\hbar c} \sum_n |\langle\psi_n^E|\hat{\mu}|\psi_0^G\rangle|^2 \delta(\omega_I - \omega_n) \\ &= \frac{2\pi\omega_I}{3\hbar c} \int_{-\infty}^{\infty} dt \langle\phi_E(0)|\phi_E(t)\rangle e^{i\omega t}\end{aligned}$$

excited-state wavepacket: $|\phi_E(0)\rangle = \hat{\mu}|\psi_0^G\rangle$

autocorrelation function: $C(t) = \langle\phi_E(0)|\phi_E(t)\rangle$

The Fourier transform of $\langle\phi_E(0)|\phi_E(t)\rangle$ yields the absorption spectrum

Translate Fermi's Golden Rule rate to time-dependent picture

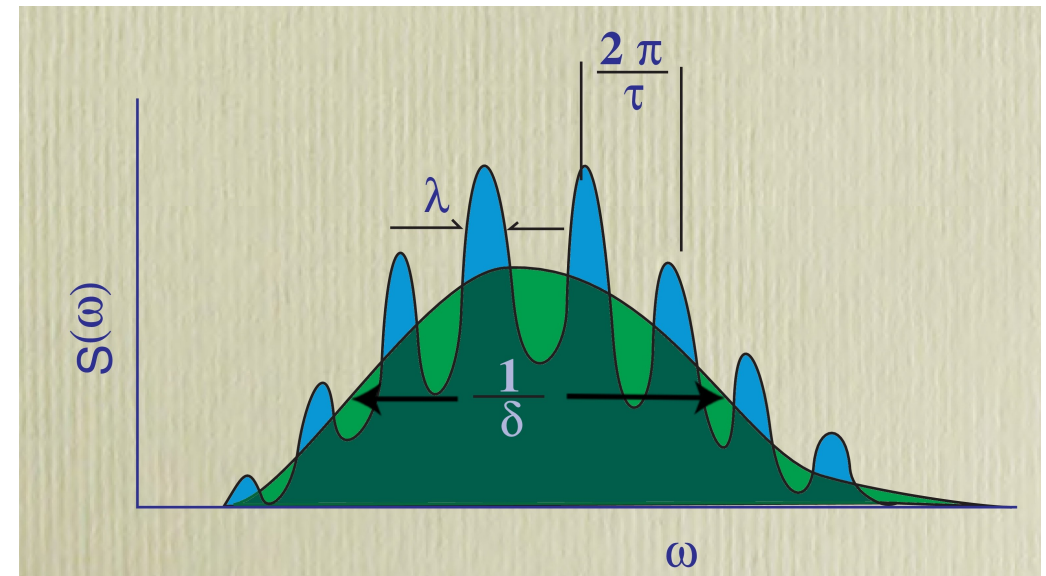
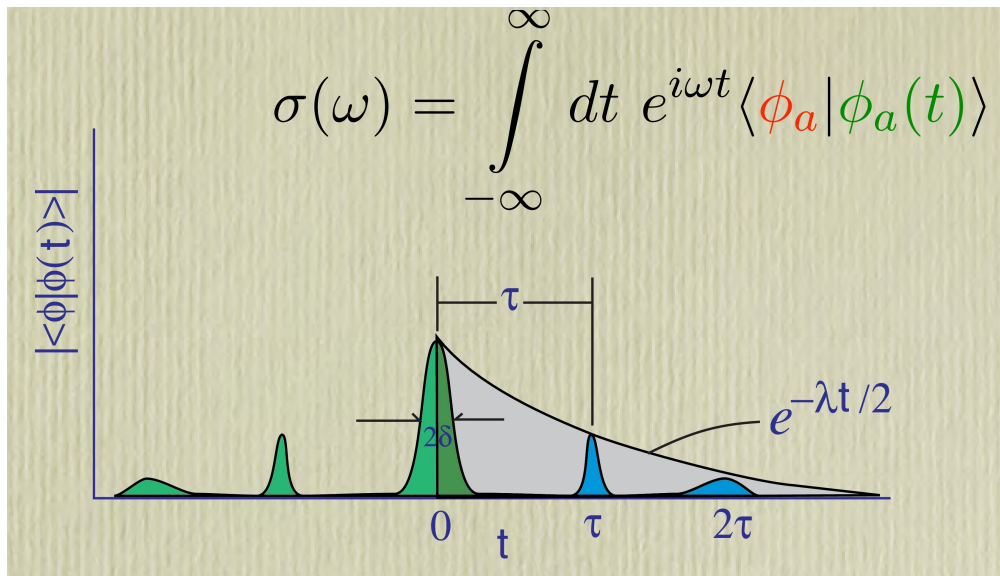
use **Fourier transform relation**

$$\delta(\omega - \omega_n) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - \omega_n)t}$$

such that

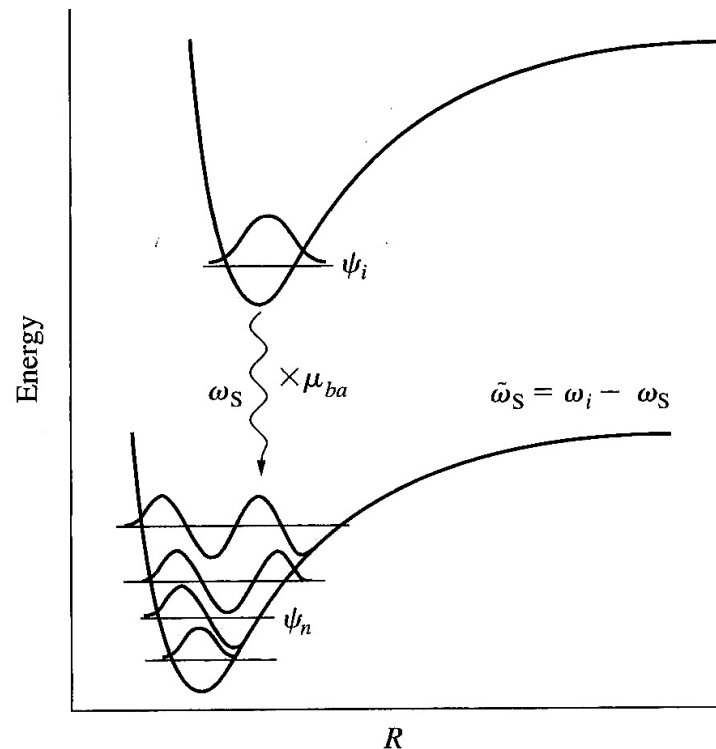
$$\begin{aligned}\sigma &= \frac{4\pi^2\omega_I}{3\hbar c} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \sum_n e^{i(\omega - \omega_n)t} \langle \psi_0^G | \hat{\mu} | \psi_n^E \rangle \langle \psi_n^E | \hat{\mu} | \psi_0^G \rangle \\ &= \frac{2\pi\omega_I}{3\hbar c} \int_{-\infty}^{\infty} dt \sum_n e^{i\omega t} \langle \psi_0^G | \hat{\mu} | e^{-i\omega_n t} \psi_n^E \rangle S_{n0} \\ &= \frac{2\pi\omega_I}{3\hbar c} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \phi_E(0) | \phi_E(t) \rangle\end{aligned}$$

Time-frequency correspondence



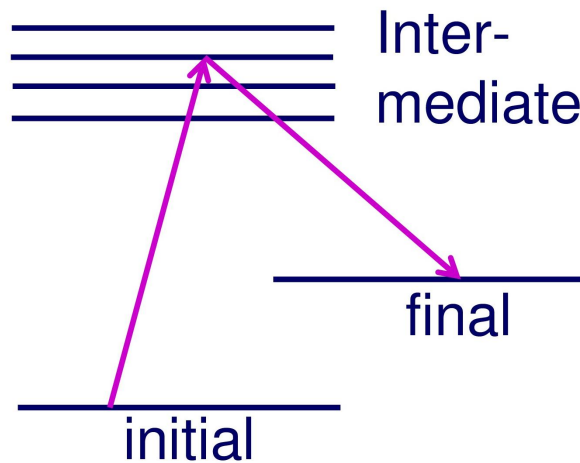
- **recurrences** of the autocorrelation function generate the vibrational fine structure of the spectrum!

Emission spectra



- emission spectrum: very similar description – but distinguish **stimulated** vs. **spontaneous** emission: Einstein coefficients $A_{fi}^{\text{sp}} = (8\pi h \nu_{fi}^3 / c^3) B_{fi}^{\text{st}}$
- emission spectrum is **red-shifted** as compared to absorption

Second-Order Processes

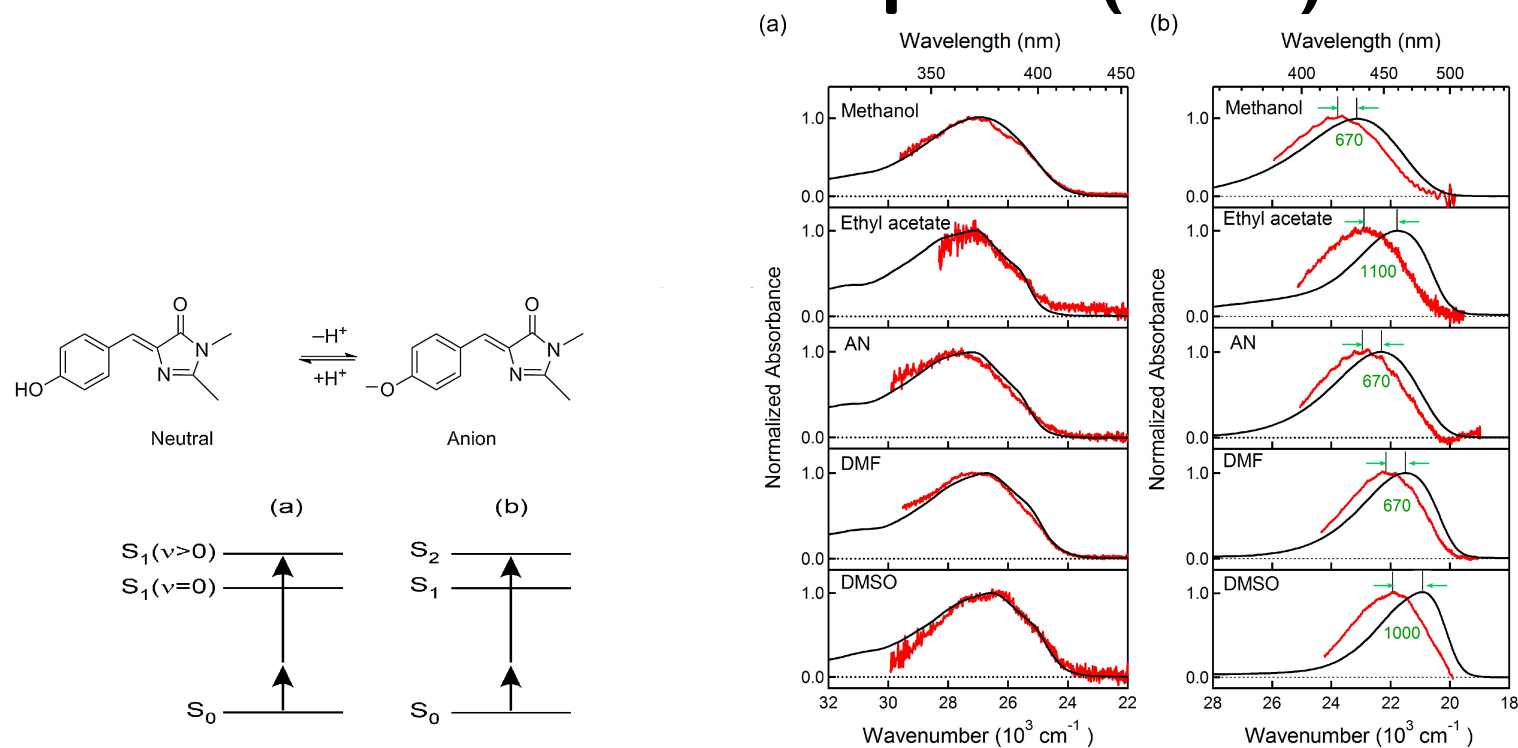


second-order perturbation theory:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

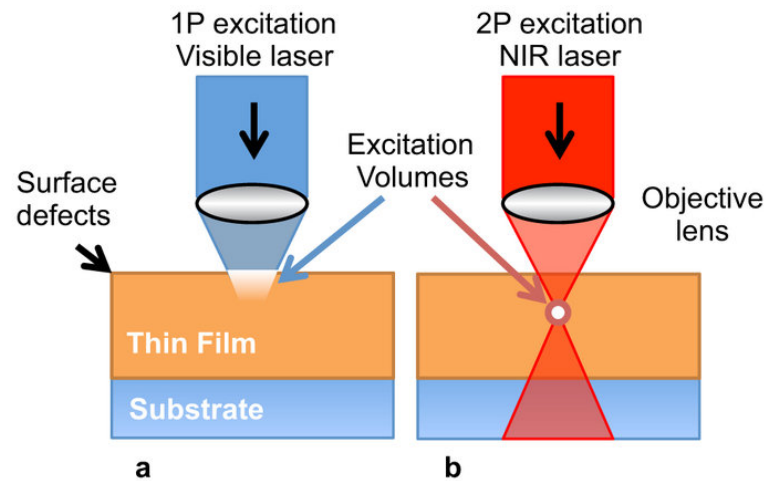
$$\begin{aligned} (\hat{H}_0 + \lambda \hat{V})(|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \dots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^{(2)} E_n^{(2)} + \dots)(|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \dots) \end{aligned}$$

Two-Photon Absorption (TPA)



- TPA is **quadratically** proportional to the intensity of the incident light
- localized excitation in a small volume: useful for materials & biosystems!

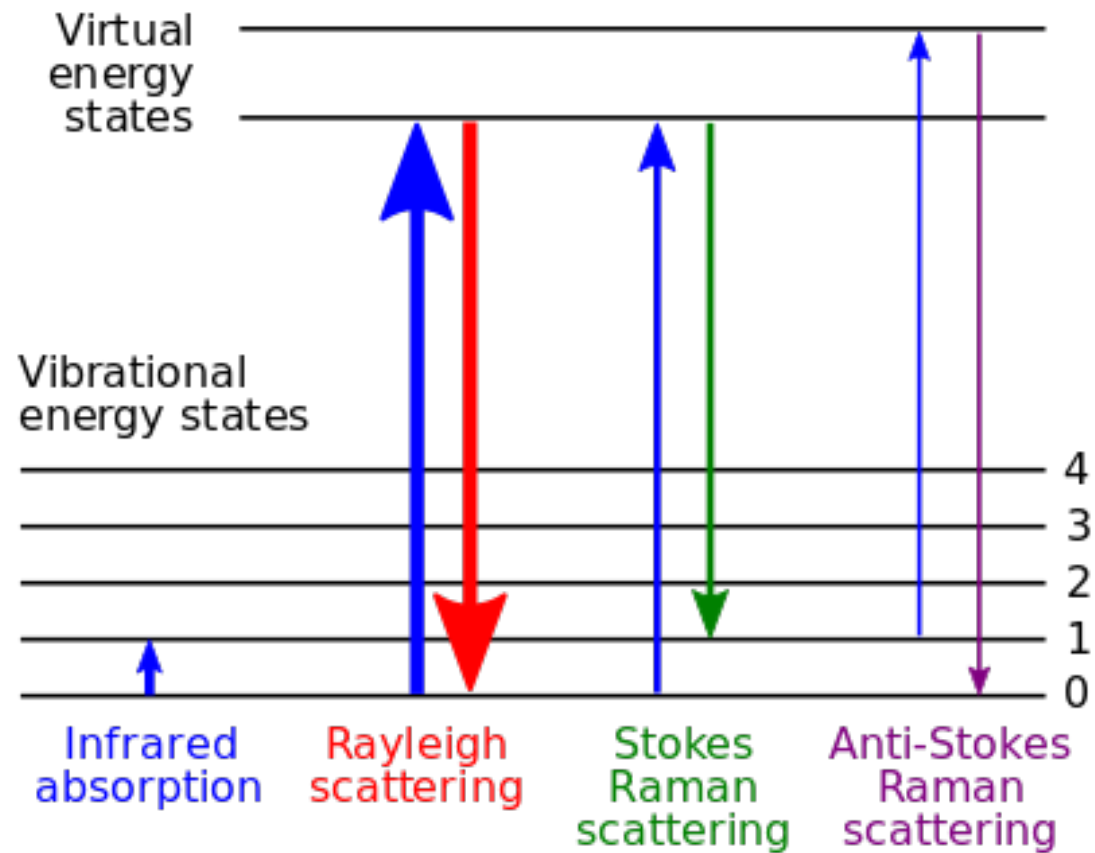
Two-Photon Absorption (TPA)



- localized excitation in a small volume: useful for materials & biosystems!

Raman Spectroscopy

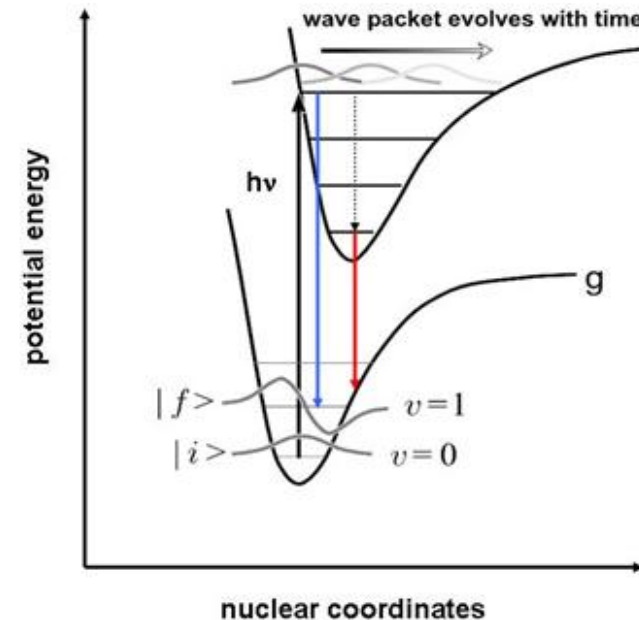
(“Inelastic Scattering of a photon by a molecule”)



Raman Spectroscopy (Off-resonant Raman Scattering)

Kramers-Heisenberg-Dirac (2nd order perturbation) theory:

$$\begin{aligned}
 I_{ab}(\omega) &= \left| \sum_m \frac{\langle \chi_b | \hat{\mu} | m \rangle \langle m | \hat{\mu} | \chi_a \rangle}{E_a + \hbar\omega - E_m + i\epsilon} \right|^2 \\
 &= \left| \sum_m \frac{\langle \phi_b | m \rangle \langle m | \phi_a \rangle}{E_a + \hbar\omega - E_m + i\epsilon} \right|^2 \\
 &= \left| \int_0^\infty dt e^{i\omega t} \langle \phi_b | \phi_a(t) \rangle \right|^2 \\
 &= |\langle \phi_b | R_\omega^a \rangle|^2
 \end{aligned}$$



R_ω^a = “Raman wave function” Lee, Heller, J. Chem. Phys. 71, 4777 (1979)

$I_{ab}(\omega)$ relates to polarizability!