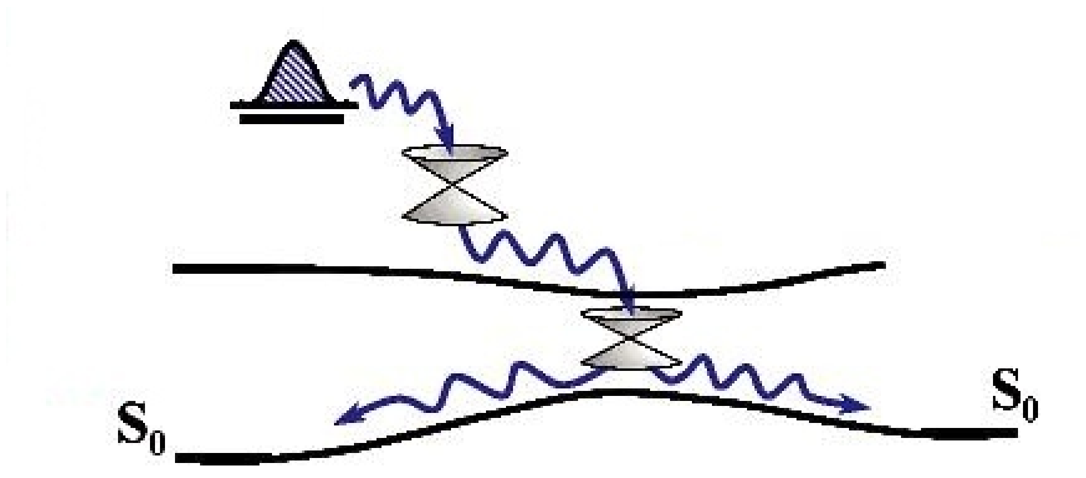
Theoretical Photochemistry WiSe 2017/18

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

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

- semiclassical equations for the interaction with the field:

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

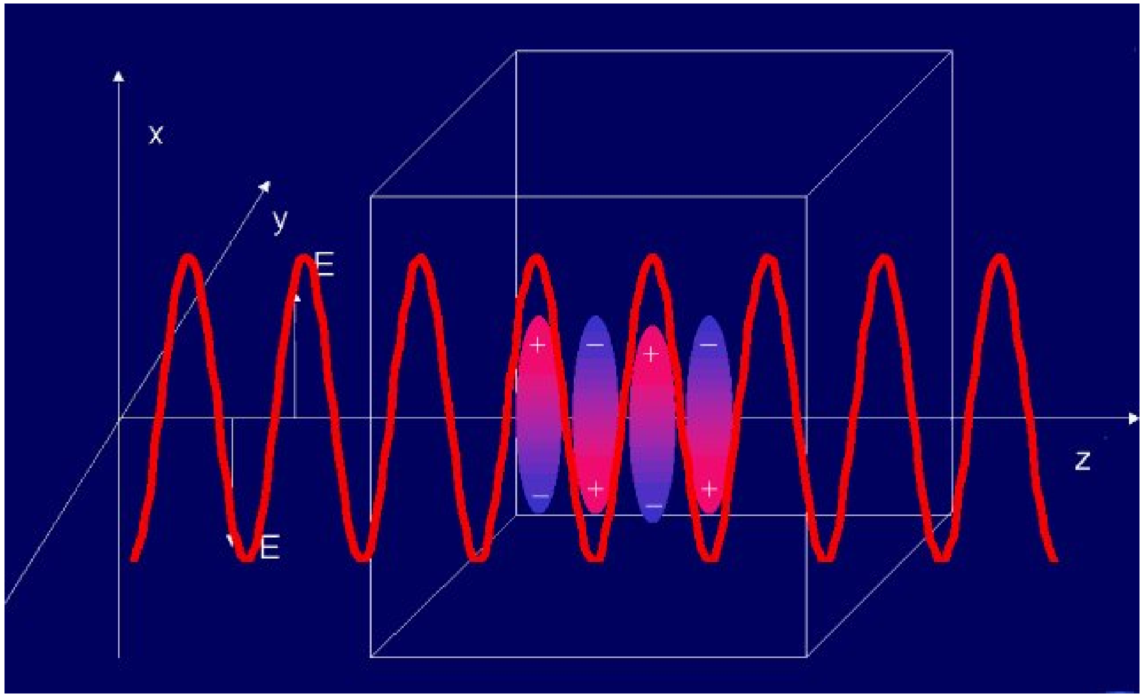
“back-of-the-envelope” derivation:

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



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

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

Absorption spectrum ("1st-Order Polarization")

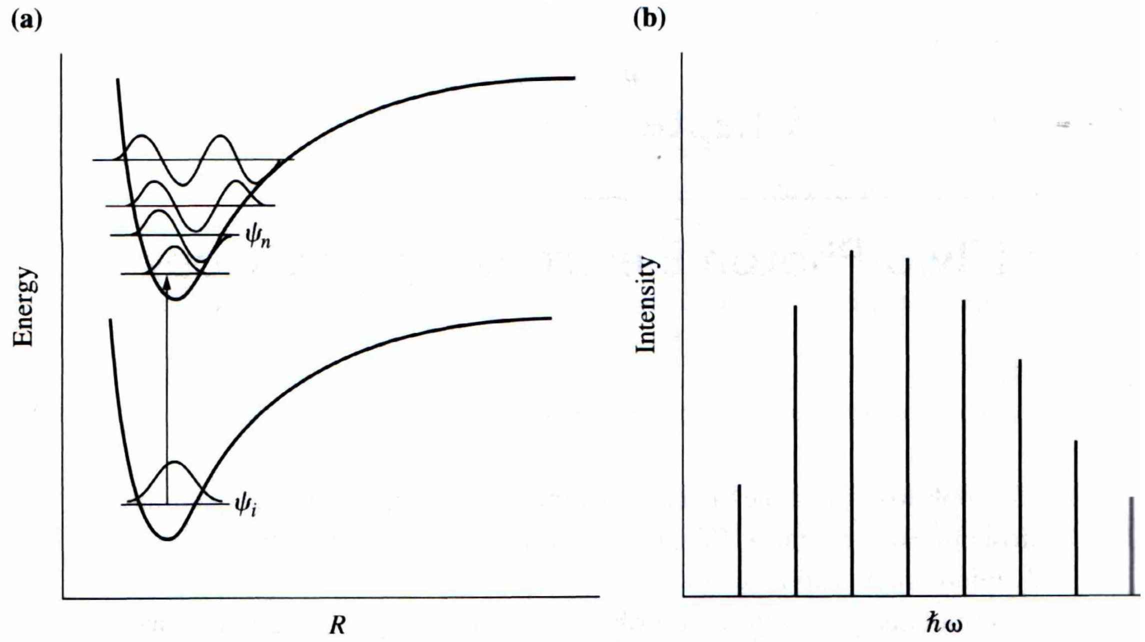


Figure 14.1 (a) Potential energy curves for two electronic states. The vibrational wavefunctions of the excited electronic state and for the lowest level of the ground electronic state are shown superimposed. (b) Stick spectrum representing the Franck–Condon factors (the squares of the overlap integrals) between the vibrational wavefunction of the ground electronic state and the vibrational wavefunctions of the excited electronic state.

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

Fermi's Golden Rule

Transition probability between quantum states that are subject to a perturbation

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

e.g., $\hat{V}(t) = -\hat{\mu}\, E_0\, (e^{i\omega t} + e^{-i\omega t})$ **"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

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

$\hat{H}_0$ = unperturbed Hamiltonian

$\hat{V}$ = perturbation Hamiltonian

λ = small parameter

Now expand

$$\begin{aligned} \psi_n &= \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \end{aligned}$$

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

Perturbation Theory – Brief Primer, cont'd

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

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

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

$$\begin{array}{lrcl} (\lambda^0)\ldots & \hat{H}_0\psi_n^{(0)} & = & E_n^{(0)}\psi_n^{(0)} \\ (\lambda^1)\ldots & \hat{H}_0\psi_n^{(1)} + \hat{V}\psi_n^{(0)} & = & E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \\ (\lambda^2)\ldots & \hat{H}_0\psi_n^{(2)} + \hat{V}\psi_n^{(1)} & = & E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(2)} \end{array}$$

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:

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

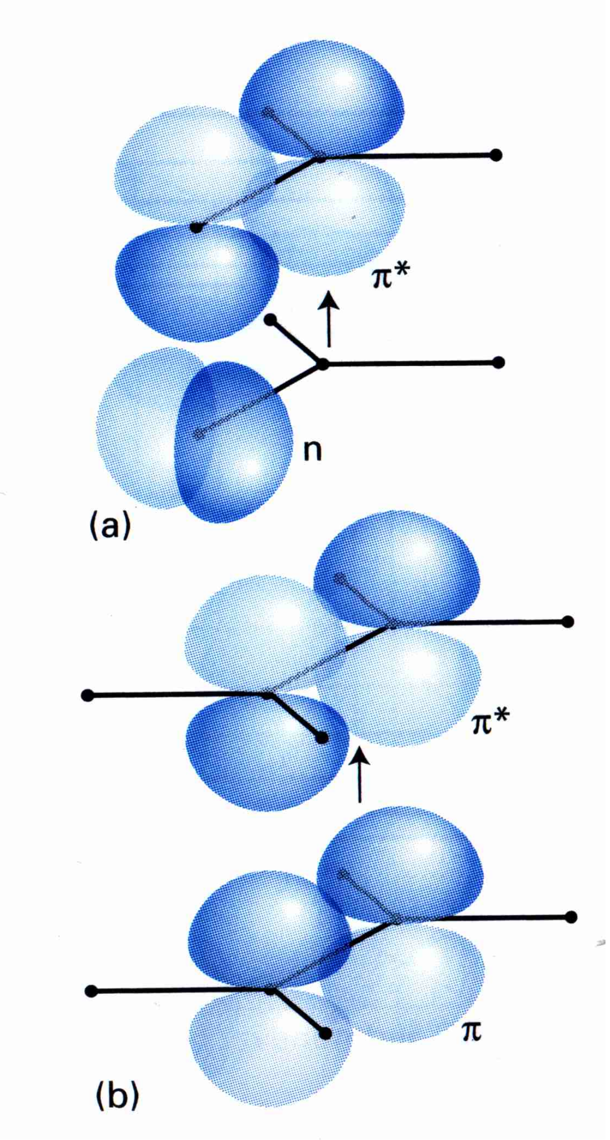
with the electronic matrix element $\mu_{EG} = \langle E | \hat{\mu} | G \rangle$ and the Franck-Condon factors $S_{ni} = \langle \psi_n | \psi_i \rangle$

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

$$n \sim O2p_y$$
$$\psi_{\pi^*} = c'\chi(C2p_x) + c\chi(O2p_x)$$

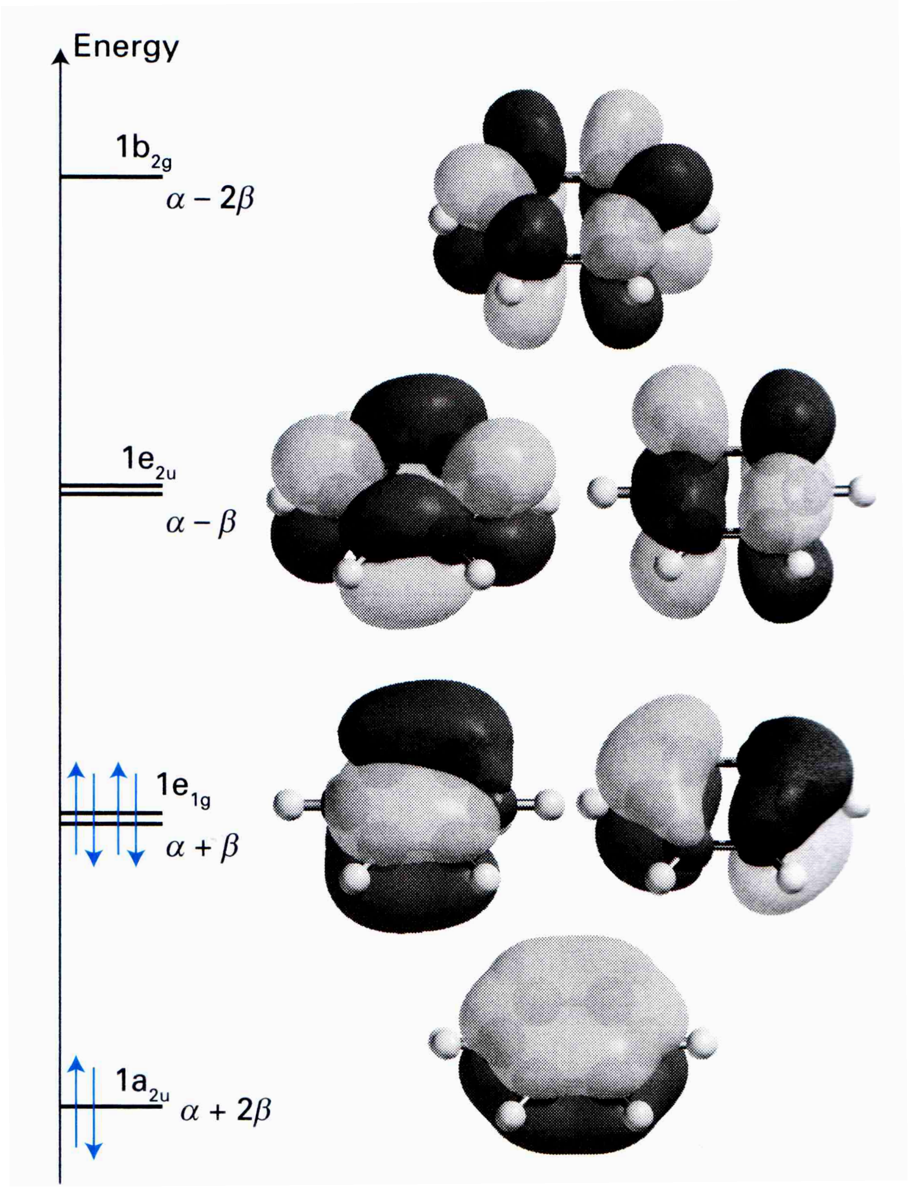
$$\langle \pi^* | \mu | n \rangle \sim c\langle Op_x | \mu | Op_y \rangle = 0$$

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

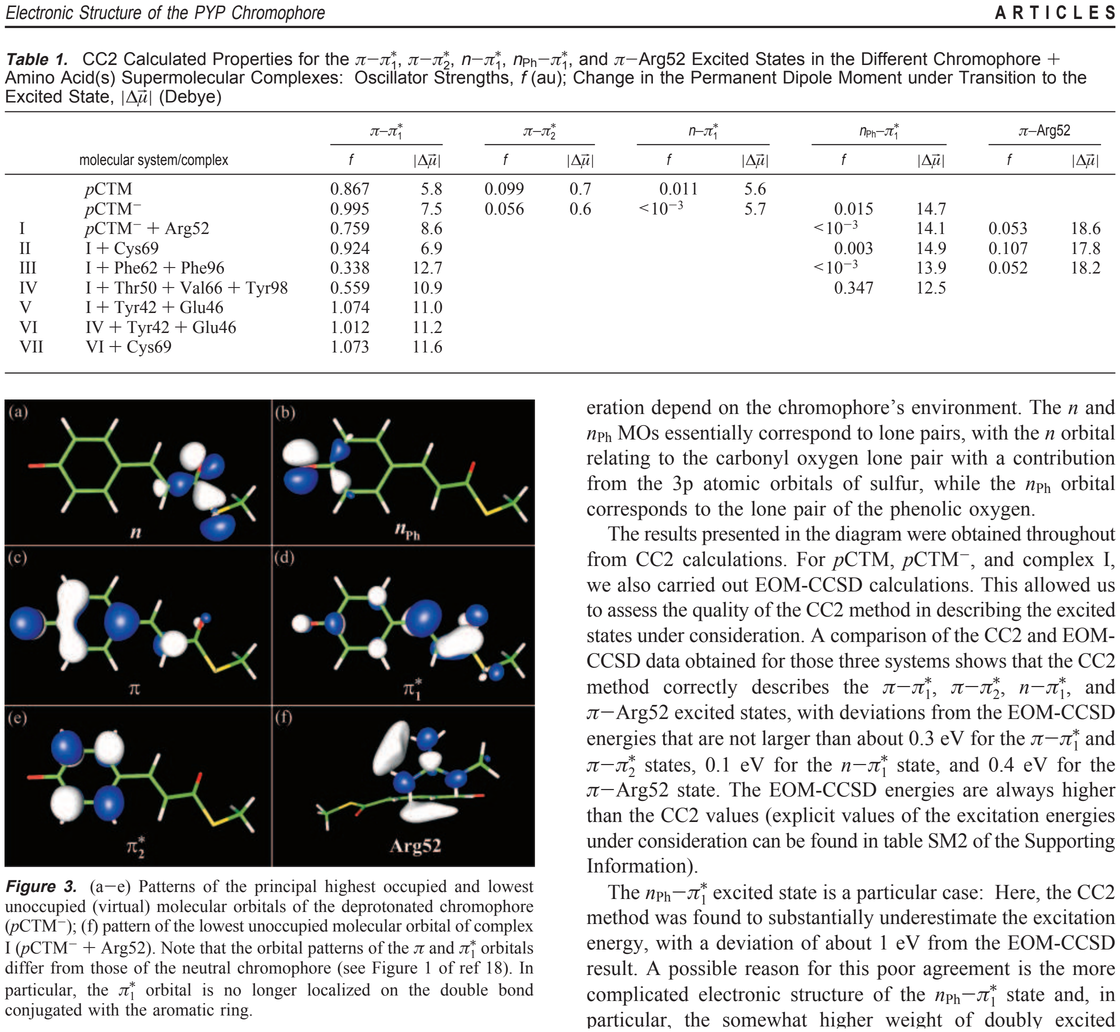
ground state: G($^1A_{1g}$)

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)**

PYP chromophore



Electronic Structure of the PYP Chromophore **ARTICLES**

Table 1. CC2 Calculated Properties for the $\pi-\pi_1^*$, $\pi-\pi_2^*$, $n-\pi_1^*$, $n_{Ph}-\pi_1^*$, and $\pi-$Arg52 Excited States in the Different Chromophore + Amino Acid(s) Supermolecular Complexes: Oscillator Strengths, *f* (au); Change in the Permanent Dipole Moment under Transition to the Excited State, $|\Delta\vec{\mu}|$ (Debye)

		$\pi-\pi_1^*$		$\pi-\pi_2^*$		$n-\pi_1^*$		$n_{Ph}-\pi_1^*$		$\pi-$Arg52	
	molecular system/complex	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$	*f*	$\lvert\Delta\vec{\mu}\rvert$
	*p*CTM	0.867	5.8	0.099	0.7	0.011	5.6				
	*p*CTM⁻	0.995	7.5	0.056	0.6	$<10^{-3}$	5.7	0.015	14.7		
I	*p*CTM⁻ + Arg52	0.759	8.6					$<10^{-3}$	14.1	0.053	18.6
II	I + Cys69	0.924	6.9					0.003	14.9	0.107	17.8
III	I + Phe62 + Phe96	0.338	12.7					$<10^{-3}$	13.9	0.052	18.2
IV	I + Thr50 + Val66 + Tyr98	0.559	10.9					0.347	12.5		
V	I + Tyr42 + Glu46	1.074	11.0								
VI	IV + Tyr42 + Glu46	1.012	11.2								
VII	VI + Cys69	1.073	11.6								

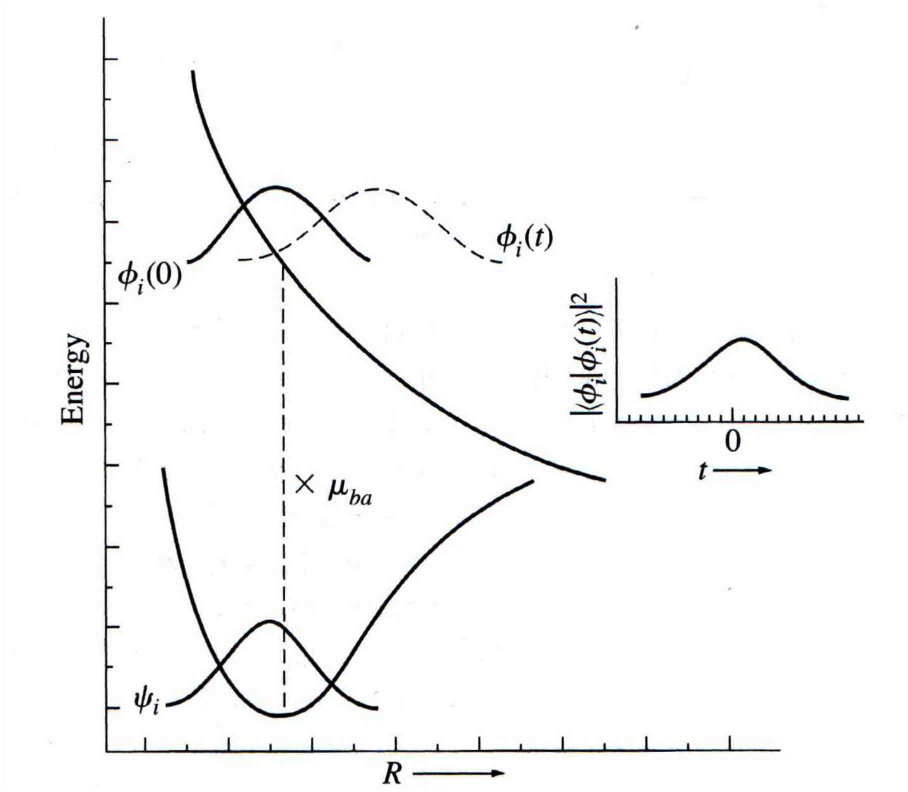
Figure 3. (a−e) Patterns of the principal highest occupied and lowest unoccupied (virtual) molecular orbitals of the deprotonated chromophore (*p*CTM⁻); (f) pattern of the lowest unoccupied molecular orbital of complex I (*p*CTM⁻ + Arg52). Note that the orbital patterns of the π and π_1^* orbitals differ from those of the neutral chromophore (see Figure 1 of ref 18). In particular, the π_1^* orbital is no longer localized on the double bond conjugated with the aromatic ring.

eration depend on the chromophore's environment. The *n* and n_{Ph} MOs essentially correspond to lone pairs, with the *n* orbital relating to the carbonyl oxygen lone pair with a contribution from the 3p atomic orbitals of sulfur, while the n_{Ph} orbital corresponds to the lone pair of the phenolic oxygen.

The results presented in the diagram were obtained throughout from CC2 calculations. For *p*CTM, *p*CTM⁻, and complex I, we also carried out EOM-CCSD calculations. This allowed us to assess the quality of the CC2 method in describing the excited states under consideration. A comparison of the CC2 and EOM-CCSD data obtained for those three systems shows that the CC2 method correctly describes the $\pi-\pi_1^*$, $\pi-\pi_2^*$, $n-\pi_1^*$, and $\pi-$Arg52 excited states, with deviations from the EOM-CCSD energies that are not larger than about 0.3 eV for the $\pi-\pi_1^*$ and $\pi-\pi_2^*$ states, 0.1 eV for the $n-\pi_1^*$ state, and 0.4 eV for the $\pi-$Arg52 state. The EOM-CCSD energies are always higher than the CC2 values (explicit values of the excitation energies under consideration can be found in table SM2 of the Supporting Information).

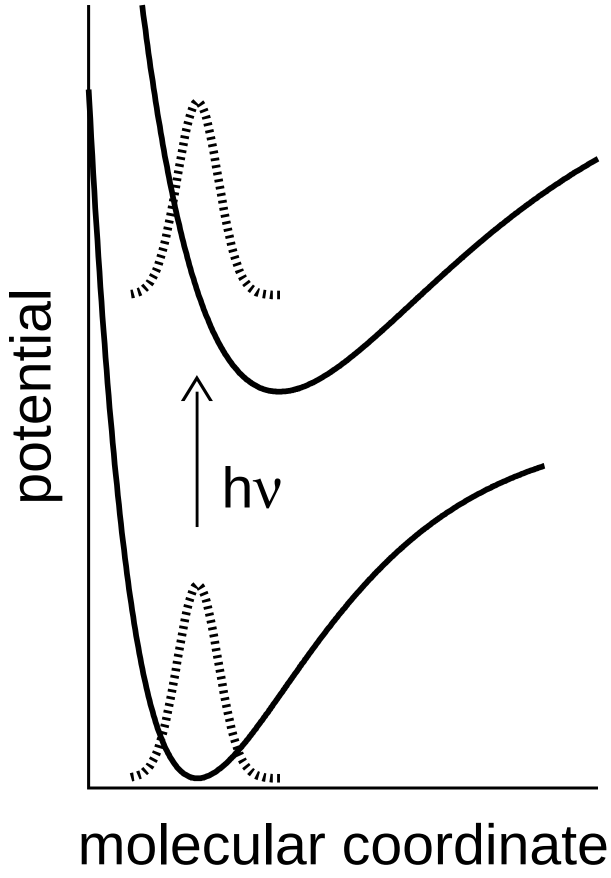
The $n_{Ph}-\pi_1^*$ excited state is a particular case: Here, the CC2 method was found to substantially underestimate the excitation energy, with a deviation of about 1 eV from the EOM-CCSD result. A possible reason for this poor agreement is the more complicated electronic structure of the $n_{Ph}-\pi_1^*$ state and, in particular, the somewhat higher weight of doubly excited

Time-domain representation: Franck-Condon wavepacket



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

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

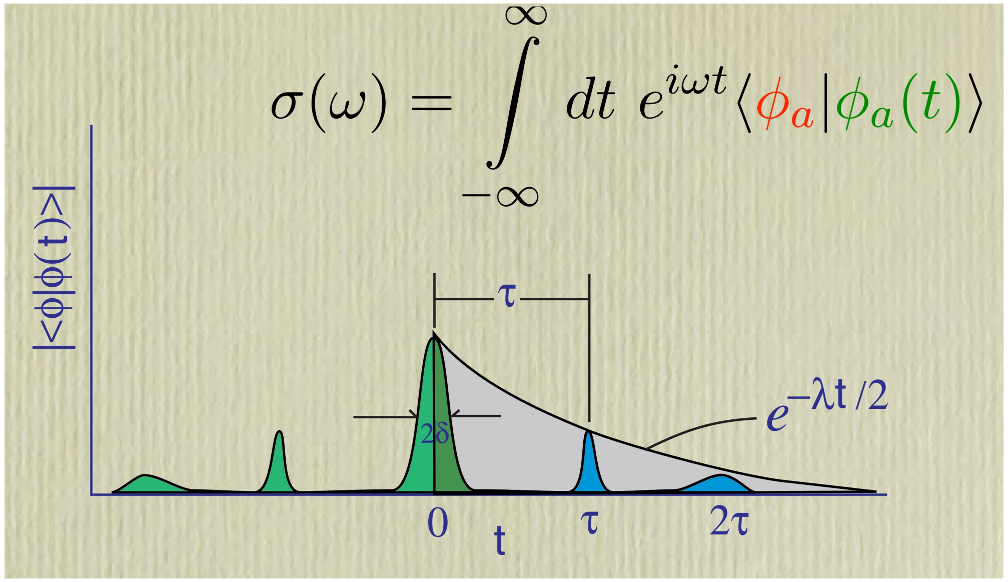
use Fourier transform relation

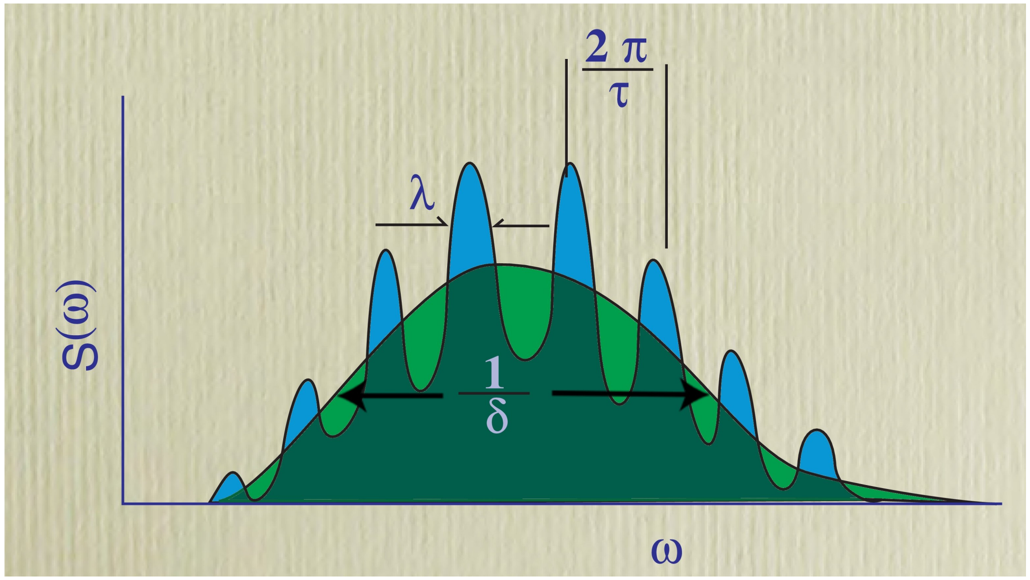
$$\delta(\omega - \omega_n) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i(\omega-\omega_n)t}$$

such that

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

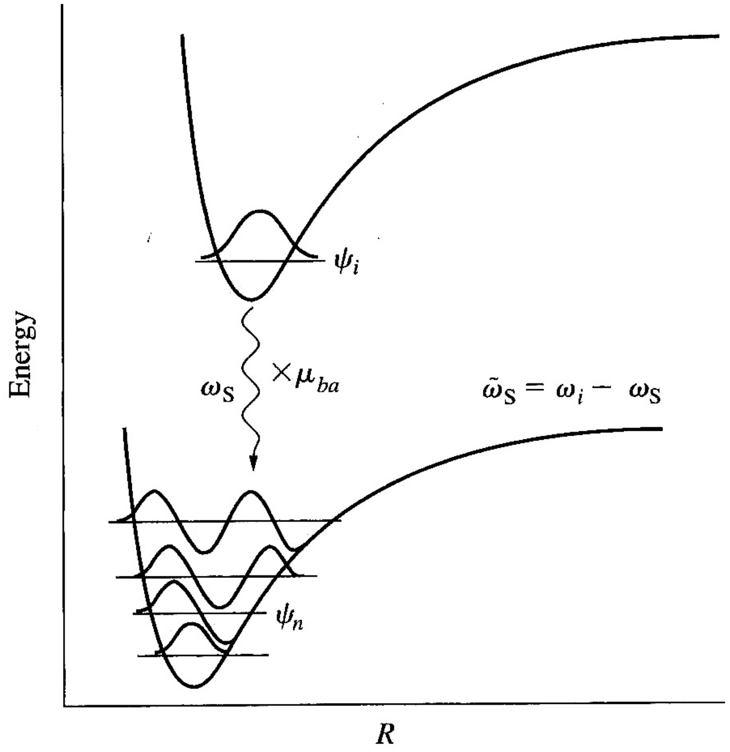
Time-frequency correspondence





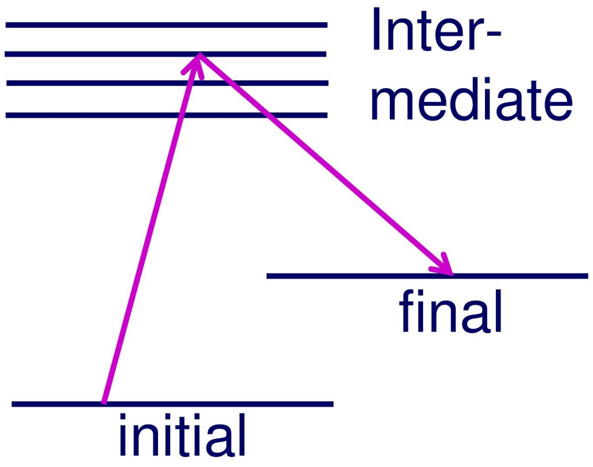
- **recurrences of the autocorrelation function generate the vibrational fine structure of the spectrum!**

Emission spectra



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

Second-Order Processes

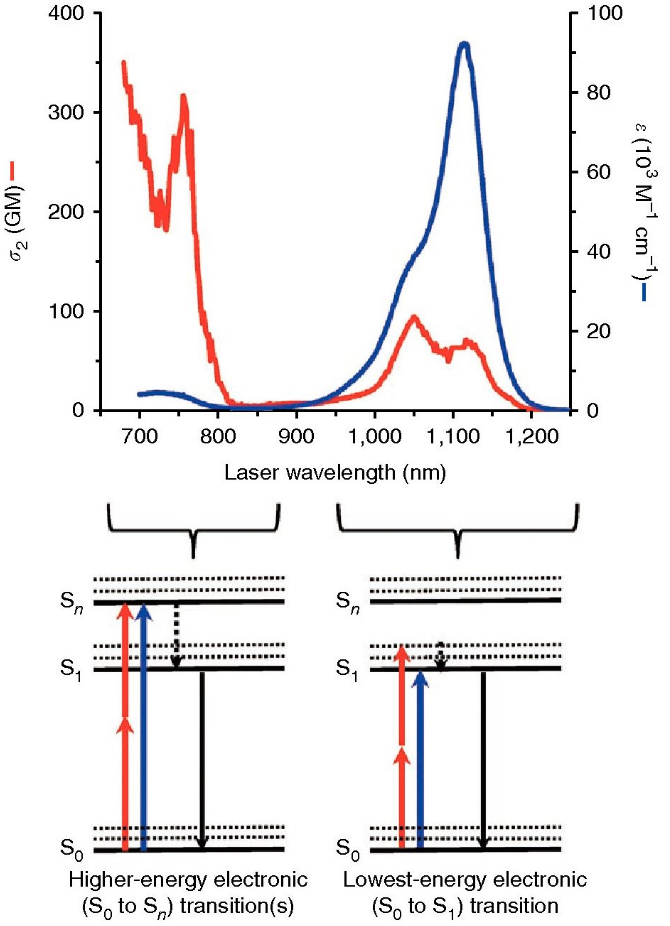


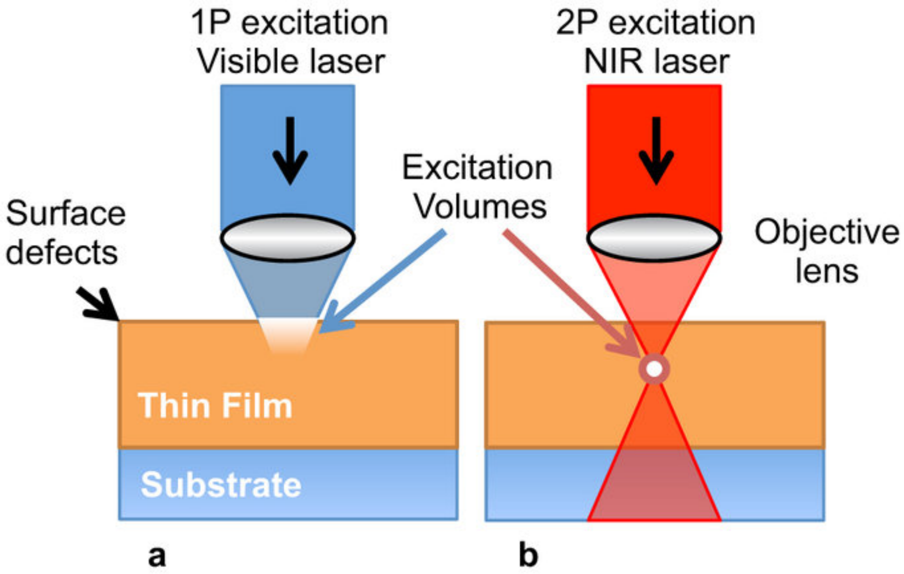
second-order perturbation theory:

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

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

Two-Photon Absorption (TPA)

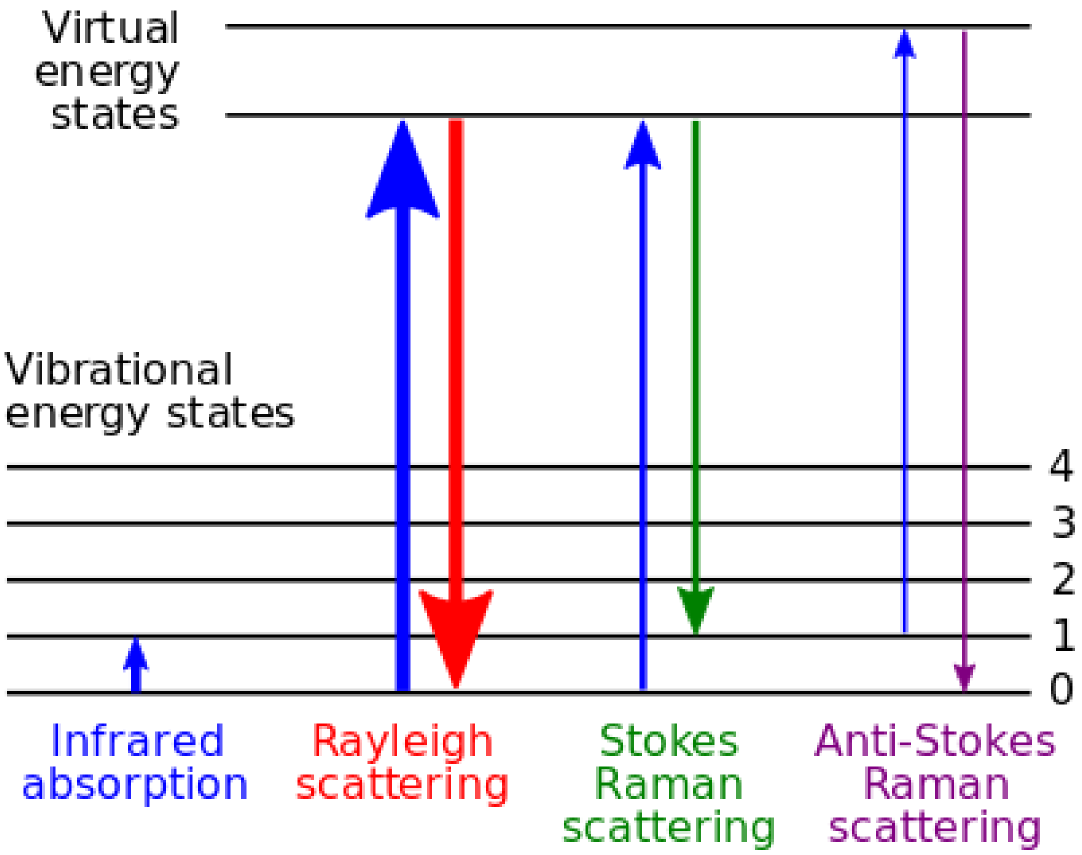




- **TPA is quadratically proportional to the intensity of the incident light**
- **localized excitation in a small volume: useful for materials & biosystems!**

Raman Spectroscopy

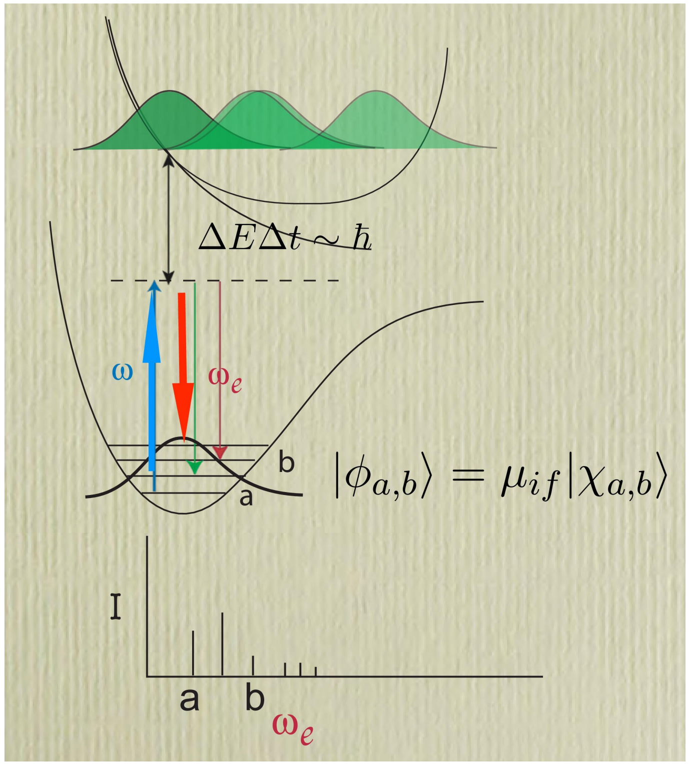
("Inelastic Scattering of a photon by a molecule")



Raman Spectroscopy
(Off-resonant Raman Scattering)

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

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



R^a_ω = "Raman wave function" Lee, Heller, J. Chem. Phys. 71, 4777 (1979)

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