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# Of Molecules and Media

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June 19, 2014

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## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction
- ❖ Absorption
- ❖ Vibrations
- ❖ Stark

Media

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Exercises and  
Problems

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# *Molecules*

# What is a Molecule?

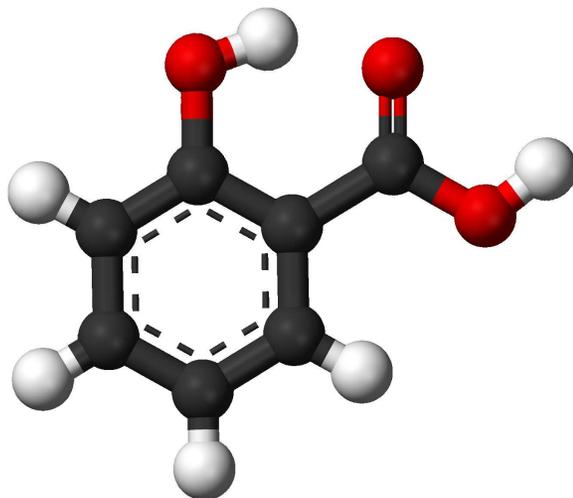
## Molecules

### ❖ Molecules

- ❖ Units
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- ❖ Stark

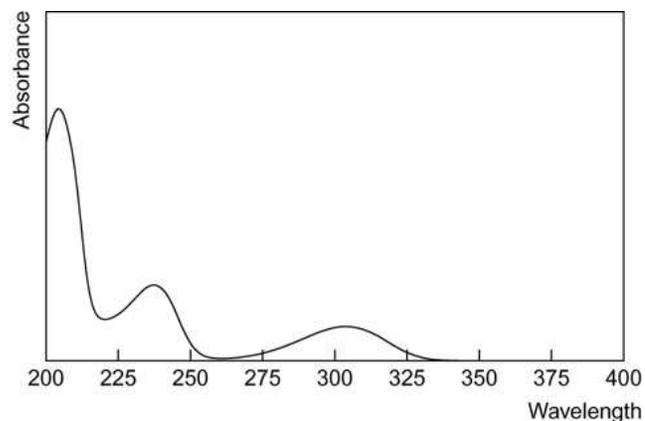
## Media

## Exercises and Problems



Quantum Chemists calculate:

- Positions of nuclei
- Electron density



Spectroscopists see:

- Peak positions
- Intensity profiles

# What is a Molecule? II

Molecules

❖ Molecules

❖ Units

❖ Hamiltonian

❖ Indole

❖ Interaction

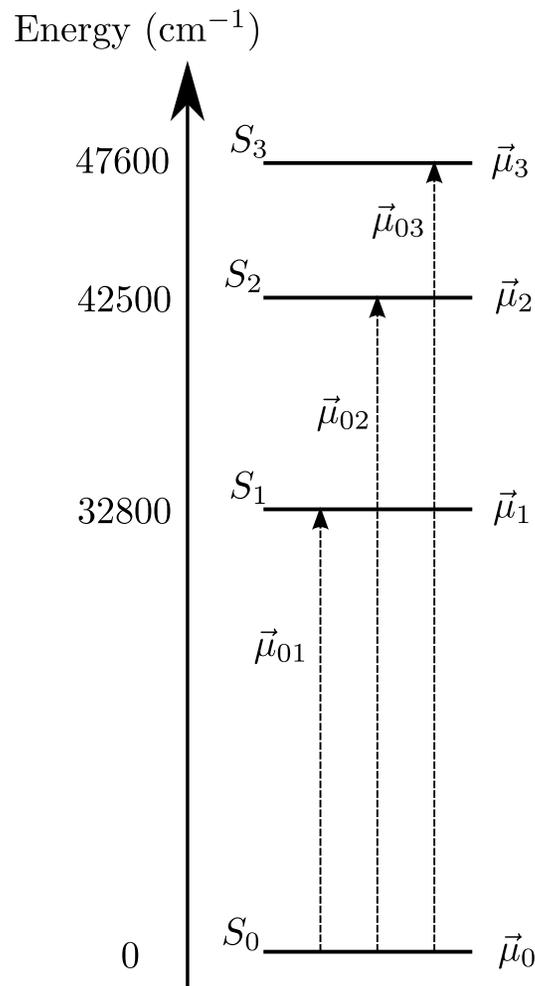
❖ Absorption

❖ Vibrations

❖ Stark

Media

Exercises and  
Problems



- Peak position  $\Rightarrow$  Energy difference

$$\lambda \text{ (in nm)} = \frac{10^7}{\nu \text{ (in cm}^{-1}\text{)}}$$

- Peak intensity  $\Rightarrow$  Oscillator strength

$$f = 4.319 \times 10^{-9} \int_{\text{band}} d\nu \epsilon(\nu)$$

$$\epsilon(\nu) \text{ in L mol}^{-1} \text{cm}^{-1}$$

- Peak Width = ?

# Units

## Molecules

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## Media

Exercises and  
Problems

The oscillator strength  $f$  is a dimensionless quantity, defined as the ratio of the absorption strength to the (hypothetical) absorption strength of a single harmonically oscillating electron. Oscillator strengths are between 0 and 1.

The transition dipole moment is related to the oscillator strength by the relation

$$\mu^2 = \frac{3e^2\hbar}{4\pi m_e\nu} \times f$$

where  $m_e$  is the mass and  $e$  the charge of the electron. This dipole moment is in Cm, a more common unit is the Debye (D). At 300 nm an oscillator strength of 1 corresponds to a transition dipole moment of  $\sim 5$  D.

# Hamiltonian, states, dipole moments

Molecules

❖ Molecules

❖ Units

❖ **Hamiltonian**

❖ Indole

❖ Interaction

❖ Absorption

❖ Vibrations

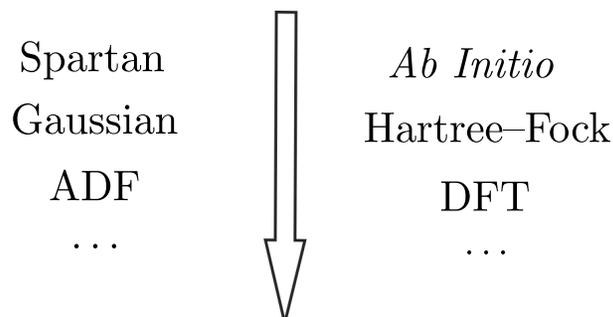
❖ Stark

Media

Exercises and  
Problems

Hamiltonian:

$$\mathcal{H} = \sum_{i \in e} \frac{p_i^2}{2m_e} + \sum_{i \in N} \frac{P_j^2}{2M_j} + V(\{\vec{r}\}, \{\vec{R}\})$$



$$\mathcal{H} |\text{state}\rangle = E_{\text{state}} |\text{state}\rangle$$

with

$$|\text{state}\rangle = |\text{electronic density; vibrations}\rangle$$

# Quantum Chemistry

## Molecules

❖ Molecules

❖ Units

❖ Hamiltonian

❖ Indole

❖ Interaction

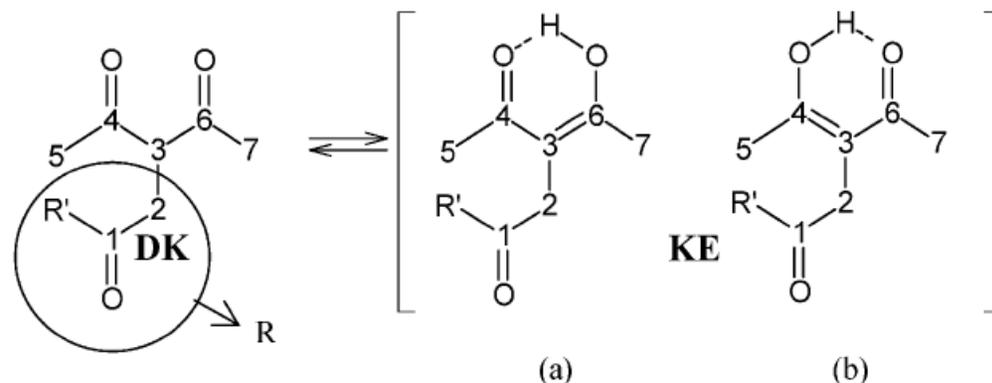
❖ Absorption

❖ Vibrations

❖ Stark

## Media

Exercises and  
Problems



**Table 1** Difference in free energy  $\Delta G^0$  (kcal mol<sup>-1</sup>) and relative di-ketonic fractions ( $f_{\text{DK}}$ ) calculated *in vacuo* using different models,  $\Delta G^0 = G_{(\text{DK})}^0 - G_{(\text{KE})}^0$

	$\Delta G^0$	$f_{\text{DK}}$
B3LYP/6-311G**	2.46	0.02
CBS-4M	-2.40	0.98
G3 MP2	0.15	0.44
CBS-QB3	0.22	0.41
CBS-4M//B3LYP/6-311G**	-1.13	0.87

# Quantum Chemistry II

## Molecules

❖ Molecules

❖ Units

❖ Hamiltonian

❖ Indole

❖ Interaction

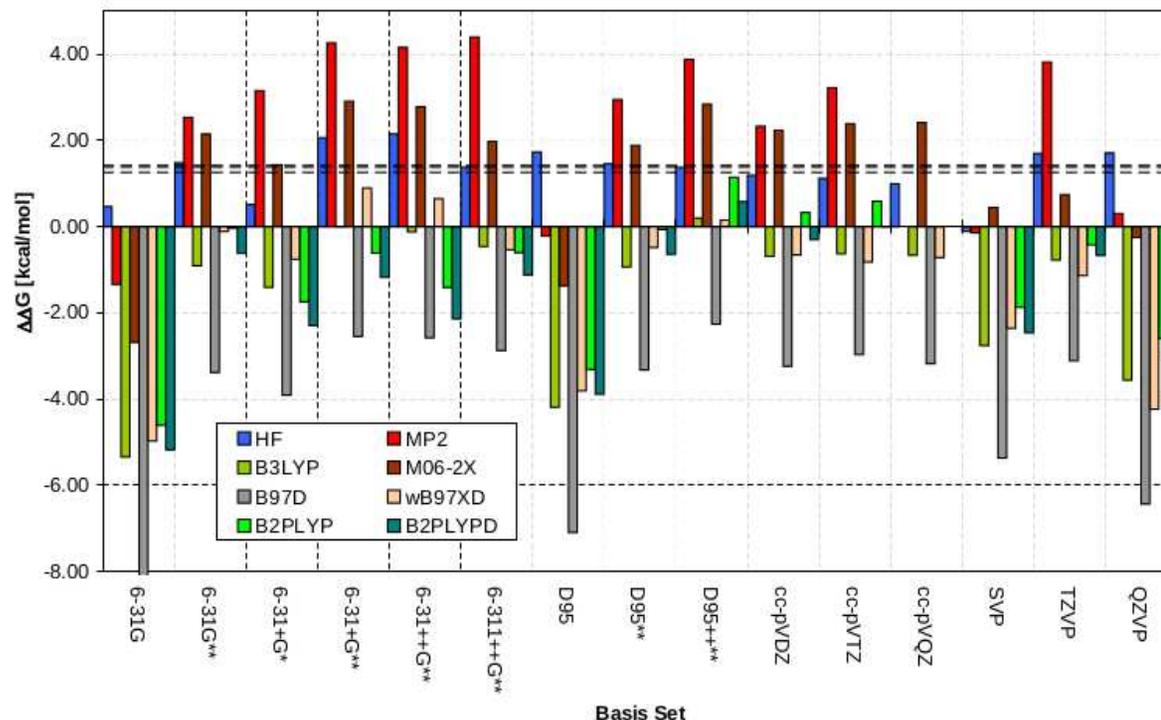
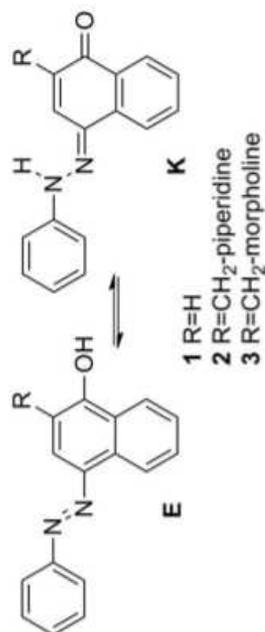
❖ Absorption

❖ Vibrations

❖ Stark

## Media

Exercises and Problems



“The problem is that if you have a real equilibrium this means a  $\Delta G$  value between -2 and +2 kcal/mol. Taking into account the real accuracy of the quantum chemistry of 1–2 kcal/mol, the results are meaningless in most cases. ”



# Hamiltonian, states, dipole moments II

## Molecules

❖ Molecules

❖ Units

❖ Hamiltonian

❖ Indole

❖ Interaction

❖ Absorption

❖ Vibrations

❖ Stark

## Media

Exercises and  
Problems

## Dipole Operator:

$$\hat{\vec{\mu}} = -e \sum_{i \in e} \vec{r}_i + \sum_{j \in N} q_j \vec{R}_j$$

- State dipole moment:

$$\vec{\mu}_i = \langle \text{state}_i | \hat{\vec{\mu}} | \text{state}_i \rangle$$

- Transition dipole moment:

$$\vec{\mu}_{ij} = \langle \text{state}_i | \hat{\vec{\mu}} | \text{state}_j \rangle$$

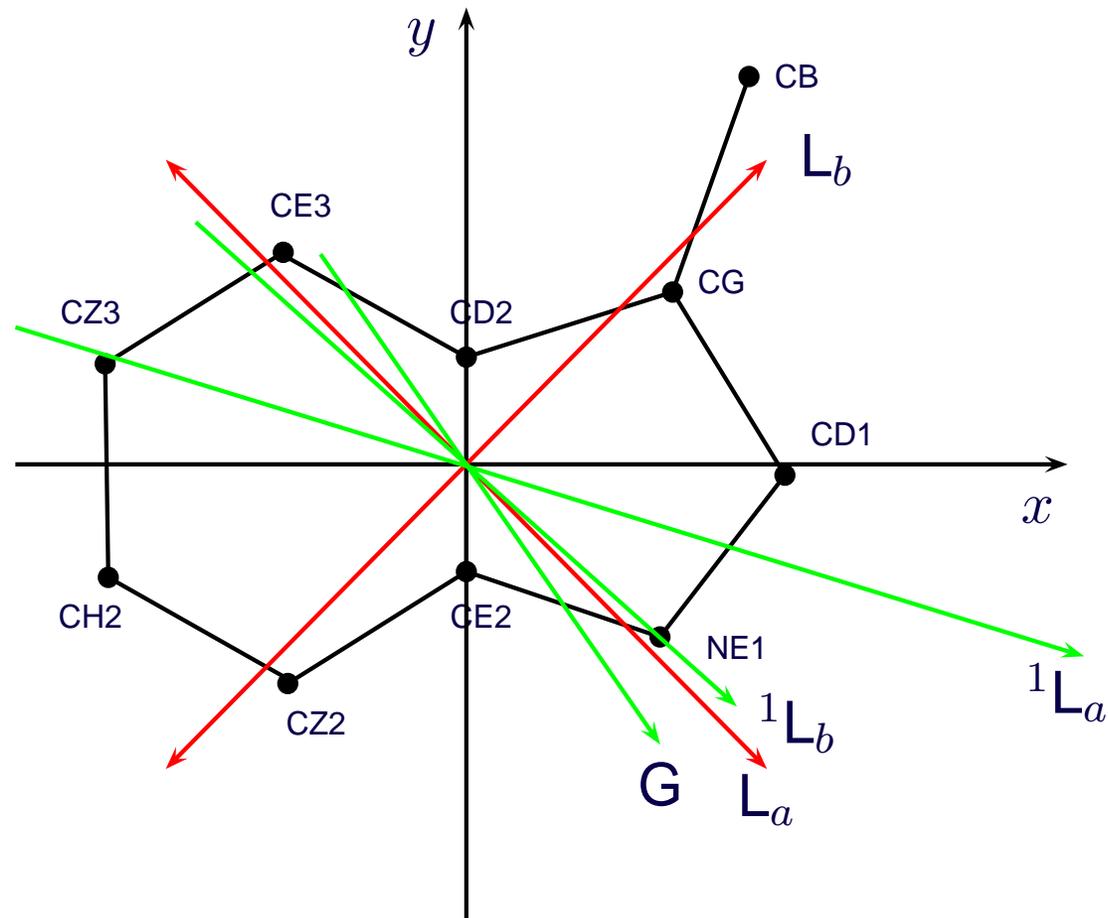
# Tryptophan (indole)

## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction
- ❖ Absorption
- ❖ Vibrations
- ❖ Stark

## Media

- Exercises and Problems



Red: transition dipole moments; Green: state dipole moments. Arrow length does *not* reflect magnitude.

# Interaction

## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction
- ❖ Absorption
- ❖ Vibrations
- ❖ Stark

## Media

- Exercises and Problems

## Interaction Hamiltonian with external fields:

$$\mathcal{H}_{\text{int}} = -\hat{\vec{\mu}} \cdot \vec{E}$$

- Linear and non-linear spectroscopies:

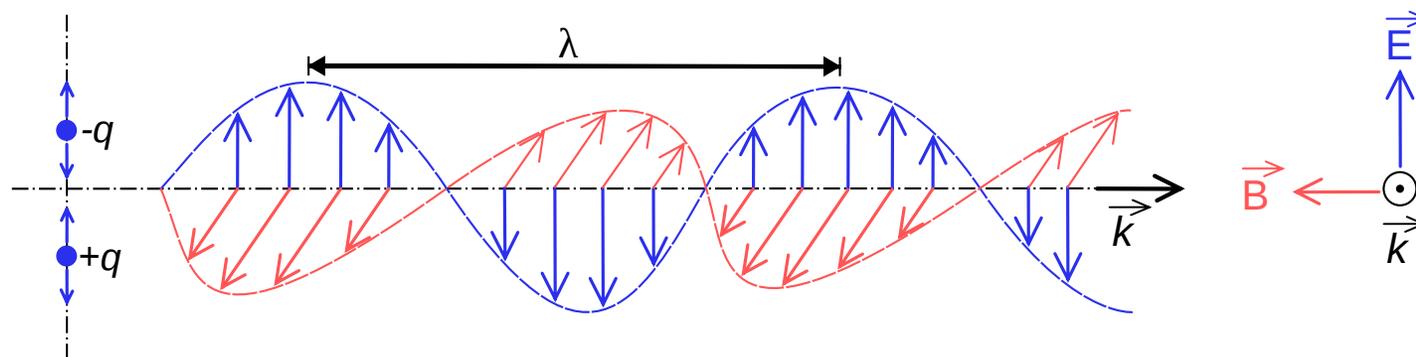
$$\vec{E}_{\text{light}}(t) = E_0 e^{-i\omega t + i\vec{k} \cdot \vec{r}} (\vec{e} + A e^{i\varphi} \vec{e}')$$

- Stark Spectroscopy: constant electric field in addition to the light field.
- “Quantum relaxation” (Redfield theory): randomly fluctuating electric fields.
- Polarization fields due to media; reaction field; QM/MM.

# Interaction with Light: Absorption

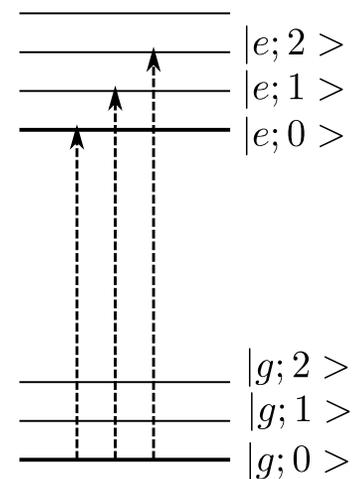
Interaction of a classical, oscillating, electric field, with a quantum molecule.

## Light



## Quantum molecule

$$\mathcal{H}_0 = \sum_{i \in \text{States}} E_i |i\rangle \langle i|$$



- Molecules
- ❖ Molecules
- ❖ Units
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- ❖ Interaction
- ❖ Absorption
- ❖ Vibrations
- ❖ Stark
- Media
- Exercises and Problems

# Interaction with Light: Absorption II

## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction

## ❖ Absorption

- ❖ Vibrations
- ❖ Stark

## Media

- Exercises and Problems

## Quantum Liouville Equation

$$\frac{\partial \rho(t)}{\partial t} = -i\hbar \left[ \mathcal{H}_0 - \hat{\vec{\mu}} \cdot \vec{E}(t), \rho(t) \right]$$

Solve to first order in the 'perturbation' gives the absorption spectrum of a single molecule:

$$A_0(\nu) = \frac{1}{\hbar} \sum_e \frac{\gamma \vec{\mu}_{ge} \vec{\mu}_{ge}^*}{(\nu - \nu_{eg})^2 + \gamma^2} \quad \vec{\mu}_{ge} = \langle g; 0 | \hat{\vec{\mu}} | e; i \rangle = \vec{\mu} \langle 0 | i \rangle$$

$|\langle 0 | i \rangle|^2$ : Franck–Condon factor;  $\gamma$ : homogeneous (lifetime) broadening.

Still to do: average over orientations and inhomogeneous broadening.

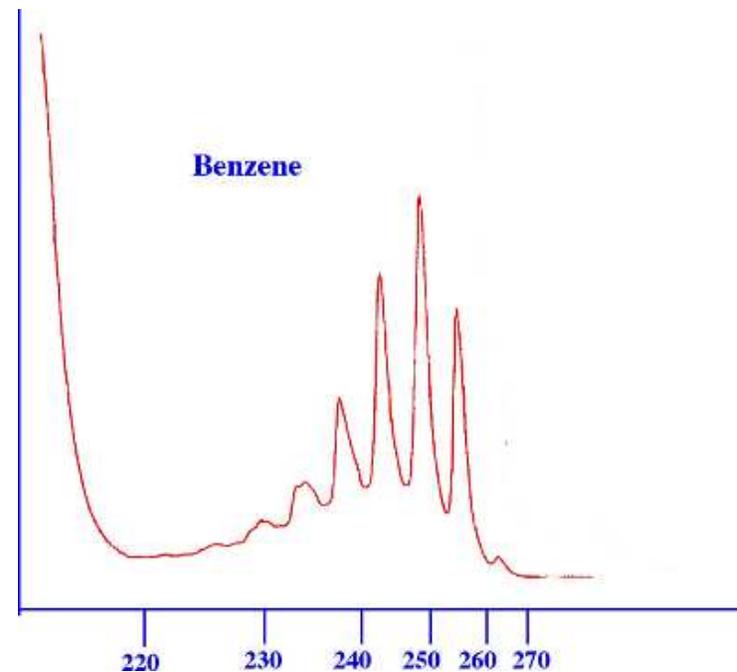
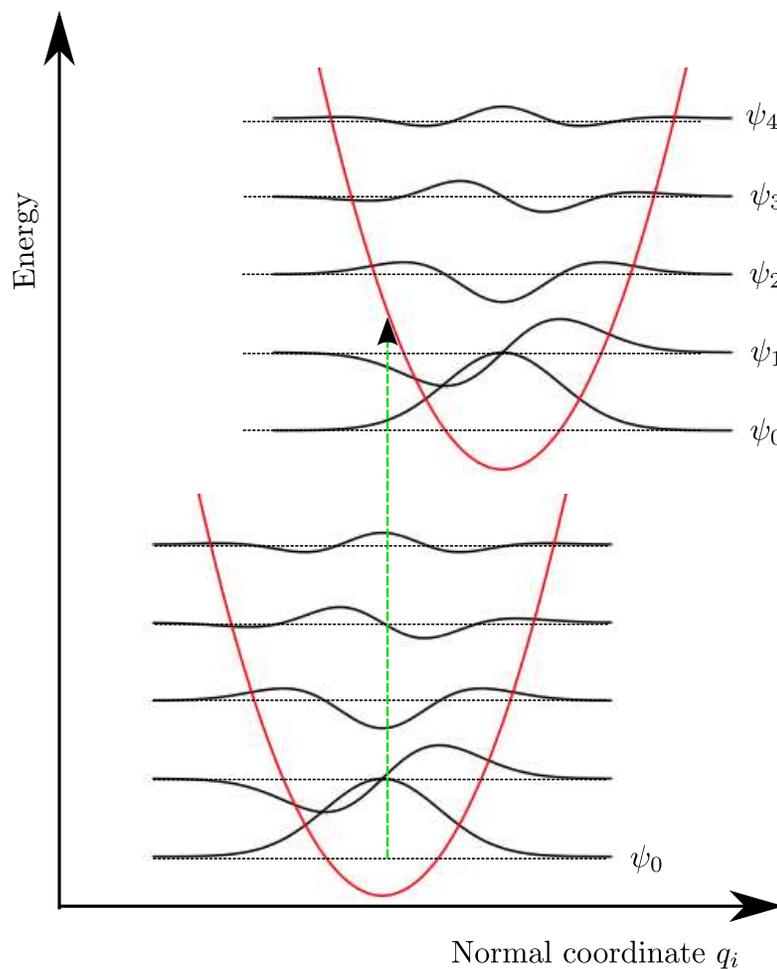
# Vibrations

## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction
- ❖ Absorption
- ❖ **Vibrations**
- ❖ Stark

## Media

- Exercises and Problems



Benzene has 30 vibrations. Why do we see so few, and why are the bands so sharp?

# Interaction with a static field

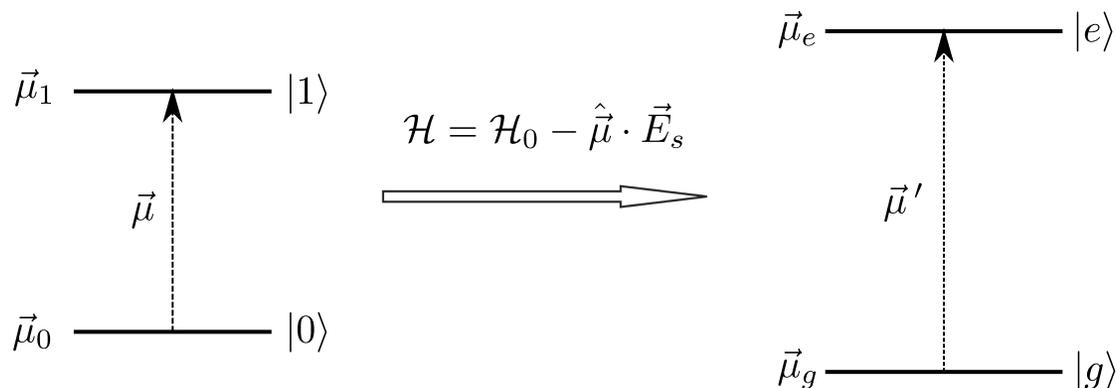
## Molecules

- ❖ Molecules
- ❖ Units
- ❖ Hamiltonian
- ❖ Indole
- ❖ Interaction
- ❖ Absorption
- ❖ Vibrations

## ❖ Stark

## Media

- Exercises and Problems



## A static electric field:

- Orients the molecules.
- Changes the absorption wavelength:

$$h\nu' = \sqrt{(h\nu - (\vec{\mu}_1 - \vec{\mu}_0) \cdot \vec{E}_s)^2 + 4(\vec{\mu} \cdot \vec{E}_s)^2}$$

- Changes the transition dipole moment.
- Changes the width.

# Stark Spectroscopy

## Molecules

- ❖ Molecules
- ❖ Units
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- ❖ Absorption
- ❖ Vibrations

## ❖ Stark

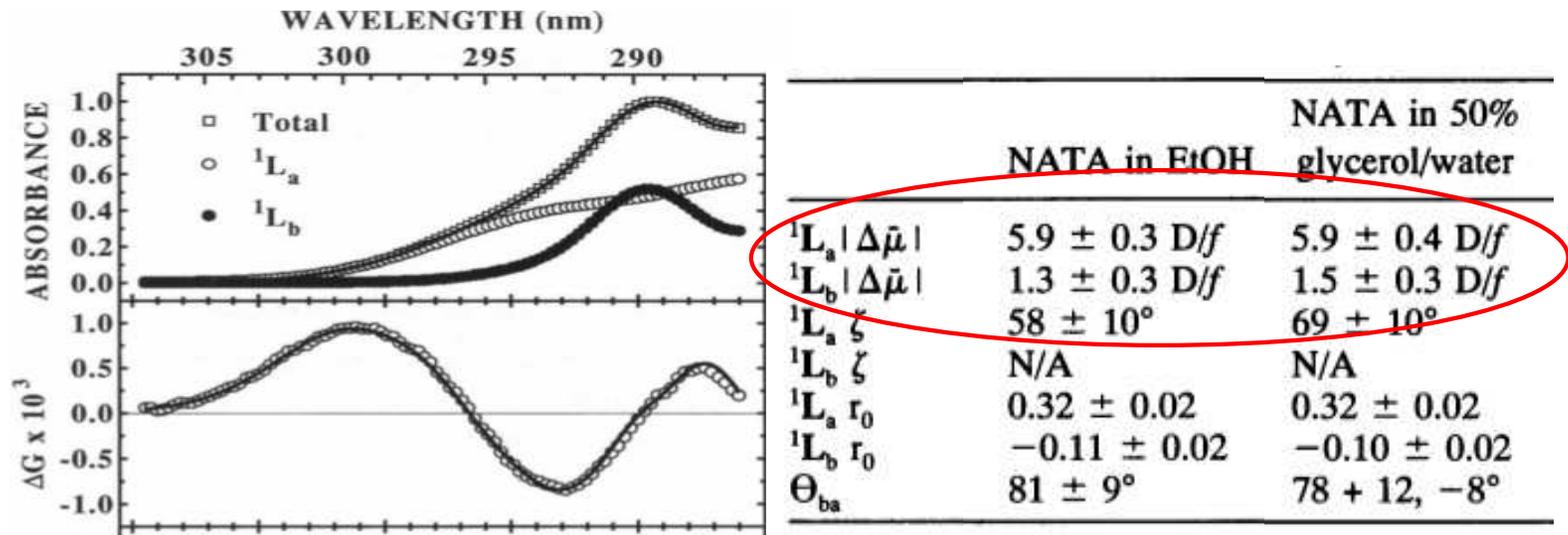
## Media

- Exercises and Problems

Changes are small: A 1D dipole in a 1 MV/cm field gives

$$\vec{\mu} \cdot \vec{E} \approx 16.8 \text{ cm}^{-1}$$

compare to  $h\nu \approx 20000 \text{ cm}^{-1}$ .



${}^1L_a$  and  ${}^1L_b$  properties based on simultaneous fitting of absorption, fluorescence excitation anisotropy, and Stark spectroscopy.

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Molecules

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**Media**

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and  
Problems

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***Media***

# Dipoles and Dielectrics

Molecules

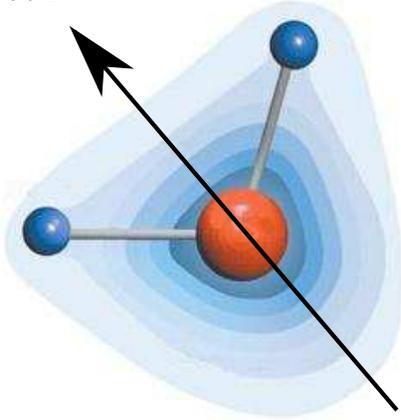
Media

❖ Dielectrics

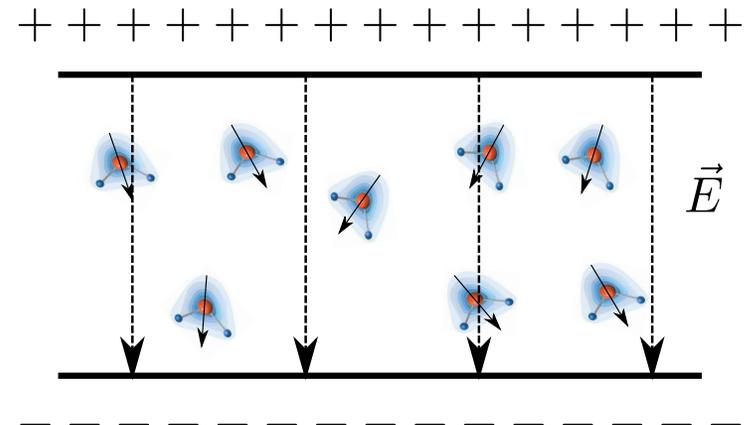
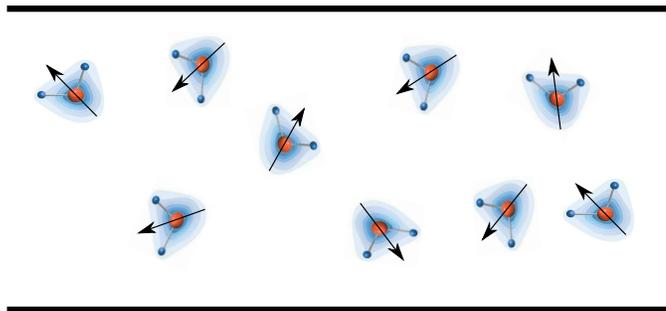
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
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- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

$$\mu = 1.86 \text{ D}$$



External fields align the dipoles:



- Dipole moments go from  $-q$  to  $q$
- Water has a dipole moment of 1.86 D.
- 1 D is displacement of an electron over 0.2 Å.

# Dielectric Constant

Molecules

Media

❖ Dielectrics

❖ Internal Field

❖ Interaction

❖ Reaction Field

❖ Stokes Shift

❖ ESIPT

❖ Dielectric Friction

❖ Dynamics

❖ conclusions

Exercises and Problems

Polarization is the average dipole moment of the system:

$$\vec{P} = \frac{1}{Q} \int d\vec{\Omega} \text{Tr} \left[ \hat{\vec{\mu}} e^{-\beta \mathcal{H}} \right]$$

To lowest order in the external field:

$$\vec{P} = \epsilon_0 (\epsilon_r - 1) \vec{E}$$

The relation between molecular dipole moment and dielectric constant  $\epsilon_r$  is exceedingly complex.

Compound	Dipole moment (D)	Polarizability ( $\text{\AA}^3$ )	Dielectric constant
water	1.85	1.48	78.5
methanol	1.71	3.23	32.6
acetonitril	3.46		34.6

# Dielectric Constant II

Molecules

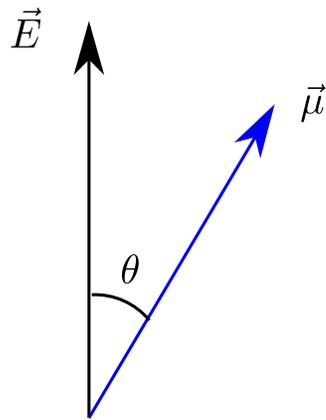
Media

❖ Dielectrics

- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

First attempt: Dilute gas of non-polarizable molecules.  
Average orientation in the external field:



$$\langle \cos \theta \rangle = \frac{\int_{-1}^1 d \cos \theta \cos \theta e^{\beta \mu E \cos \theta}}{\int_{-1}^1 d \cos \theta e^{\beta \mu E \cos \theta}} \approx \frac{\mu E}{3k_B T}$$

so that

$$\langle \vec{\mu} \rangle = \frac{\mu^2}{3k_B T} \vec{E}$$

Polarization:

$$\vec{P} = \frac{N}{V} \langle \vec{\mu} \rangle = \frac{N}{V} \frac{\mu^2}{3k_B T} \vec{E} = \epsilon_0 (\epsilon_r - 1) \vec{E}$$

So that

$$\epsilon_r - 1 = \frac{N \mu^2}{3 \epsilon_0 k_B T V}$$

# Internal Field

Molecules

Media

❖ Dielectrics

❖ Internal Field

❖ Interaction

❖ Reaction Field

❖ Stokes Shift

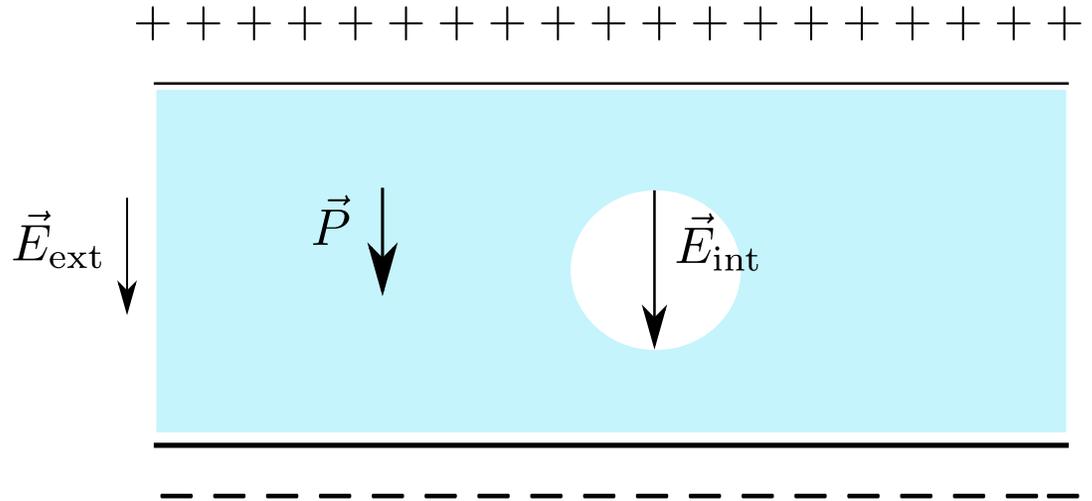
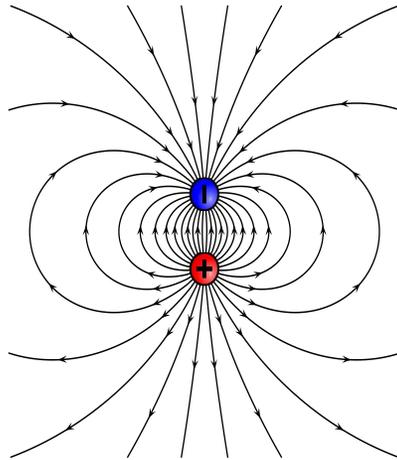
❖ ESIPT

❖ Dielectric Friction

❖ Dynamics

❖ conclusions

Exercises and Problems



Lorentz Cavity Field:

$$\vec{E}_{\text{int}} = \vec{E}_{\text{ext}} + \frac{1}{3\epsilon_0} \vec{P} = \frac{\epsilon_r + 2}{3} \vec{E}_{\text{ext}}$$

Debye:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\mu^2}{9\epsilon_0 k_B T V}$$

# Dipole–dipole interaction

Molecules

Media

❖ Dielectrics

❖ Internal Field

❖ Interaction

❖ Reaction Field

❖ Stokes Shift

❖ ESIPT

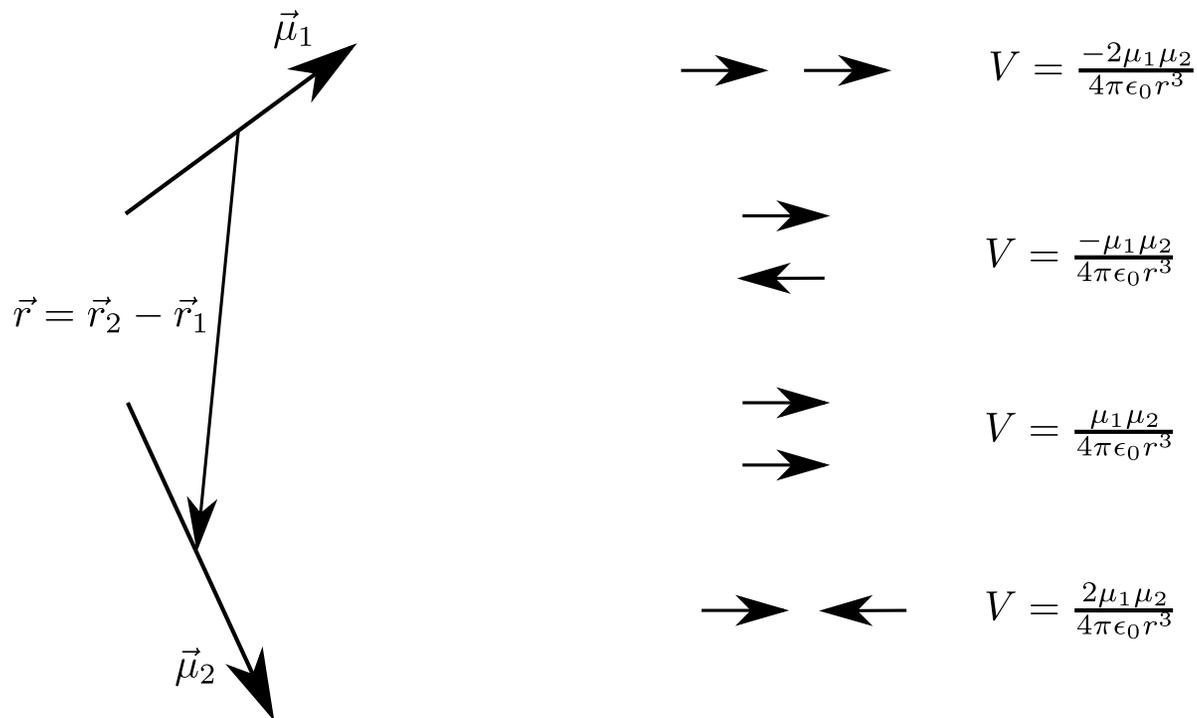
❖ Dielectric Friction

❖ Dynamics

❖ conclusions

Exercises and Problems

$$V_{dd} = \frac{1}{4\pi\epsilon_0 r^3} \vec{\mu}_1 \cdot \left( 1 - 3 \frac{\vec{r}\vec{r}}{r^2} \right) \cdot \vec{\mu}_2$$



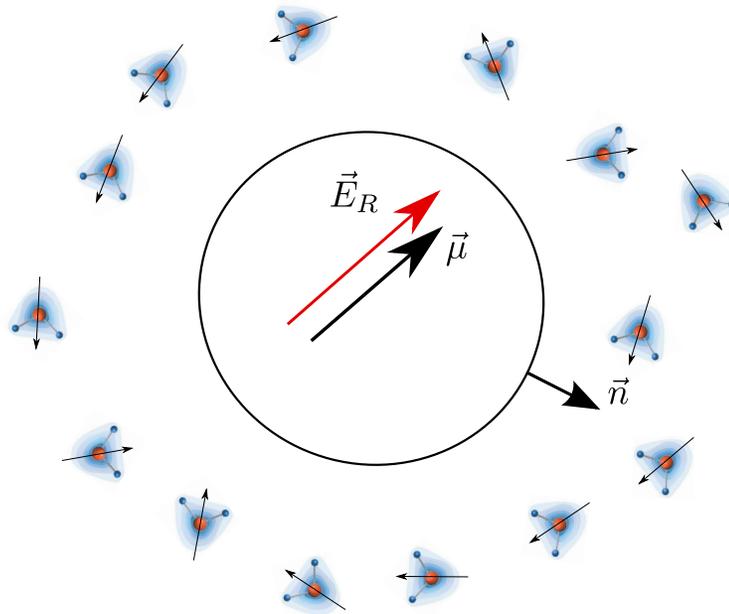
$$\frac{\mu^2}{4\pi\epsilon_0 r^3} = 5.035 \text{ cm}^{-1} \quad \text{for} \quad \mu = 1 \text{ D}, r = 1 \text{ nm}$$

# Onsager's Reaction Field

Molecules

Media

- ❖ Dielectrics
  - ❖ Internal Field
  - ❖ Interaction
  - ❖ **Reaction Field**
  - ❖ Stokes Shift
  - ❖ ESIPT
  - ❖ Dielectric Friction
  - ❖ Dynamics
  - ❖ conclusions
- Exercises and Problems



Maxwell equations:

$$\vec{\nabla} \times \vec{E} = 0$$

$$\vec{\nabla} \cdot \vec{D} = \rho$$

$$\vec{n} \cdot \vec{D}_{\text{in}} = \vec{n} \cdot \vec{D}_{\text{out}}$$

$$\vec{n} \times \vec{E}_{\text{in}} = \vec{n} \times \vec{E}_{\text{out}}$$

Reaction field:

$$\vec{E}_R = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r - 1)}{2\epsilon_r + 1} \vec{\mu}$$

Internal field due to Onsager:

$$\vec{E}_{\text{int}} = \frac{3\epsilon_r}{2\epsilon_r + 1} \vec{E}_{\text{ext}}$$

# Dielectric Constant IV

Molecules

Media

- ❖ Dielectrics
  - ❖ Internal Field
  - ❖ Interaction
  - ❖ **Reaction Field**
  - ❖ Stokes Shift
  - ❖ ESIPT
  - ❖ Dielectric Friction
  - ❖ Dynamics
  - ❖ conclusions
- Exercises and Problems

Reaction fields can be quite strong, and the energy of a dipole in its own reaction field,  $U_R = -\vec{\mu} \cdot \vec{E}_R$ , quite large. For a 6 D dipole in a cavity with 0.5 nm radius in water the field is  $1.4 \times 10^9 \text{V/m}$ , and the energy is  $U_R \approx -1450 \text{ cm}^{-1}$

Onsager's result for the relation between dielectric constant and molecular dipole moment:

$$\frac{(2\epsilon_r + 1)(\epsilon_r - 1)}{\epsilon_r} = \frac{N\mu^2}{\epsilon_0 k_B T V}$$

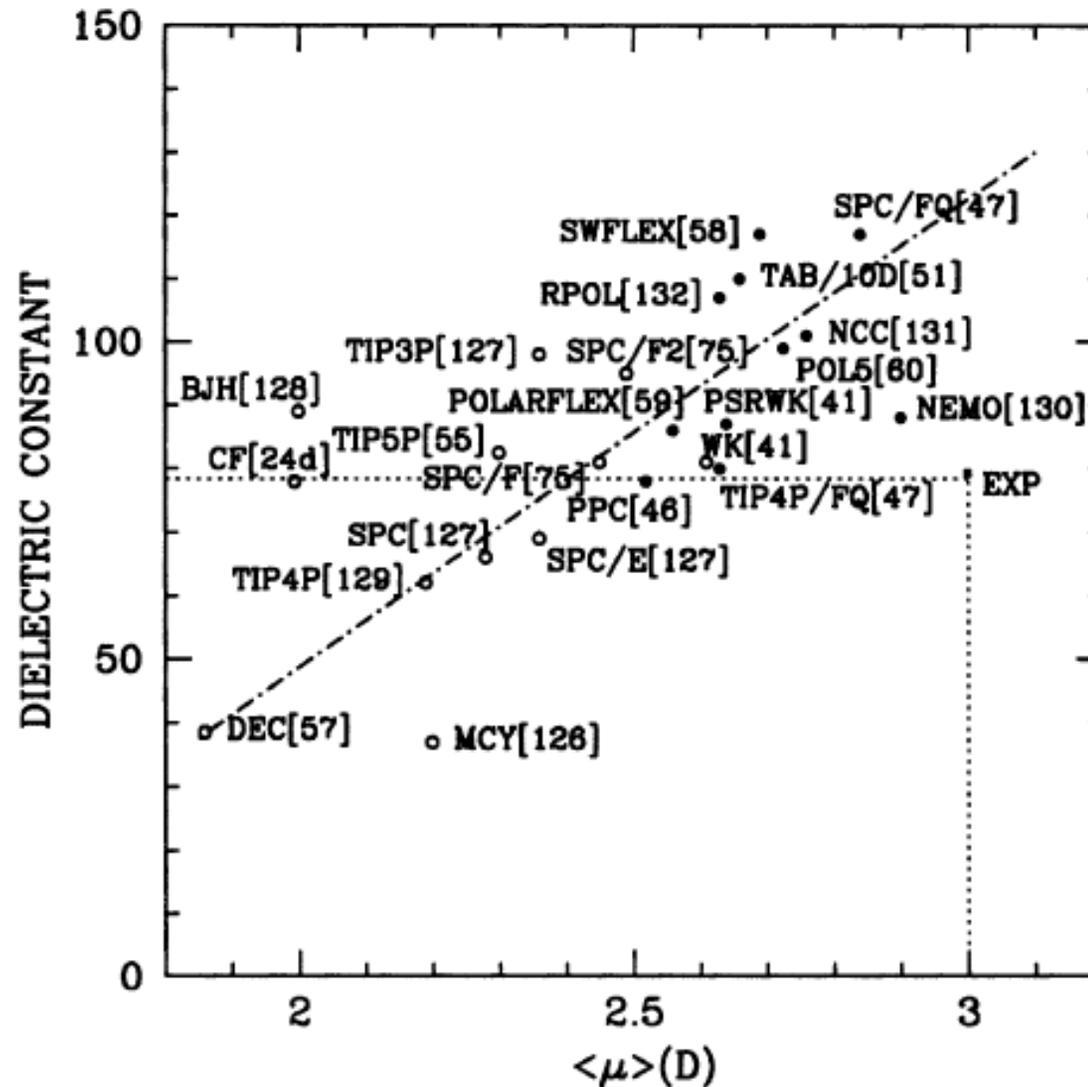
# Dielectric Constant, $V$

Molecules

Media

- ❖ Dielectrics
  - ❖ Internal Field
  - ❖ Interaction
  - ❖ **Reaction Field**
  - ❖ Stokes Shift
  - ❖ ESIPT
  - ❖ Dielectric Friction
  - ❖ Dynamics
  - ❖ conclusions
- Exercises and Problems

Results of calculations (MD/MC):



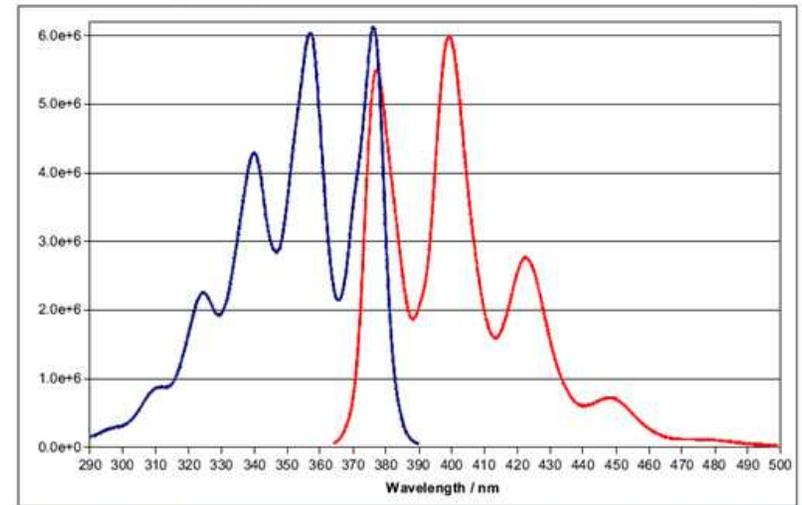
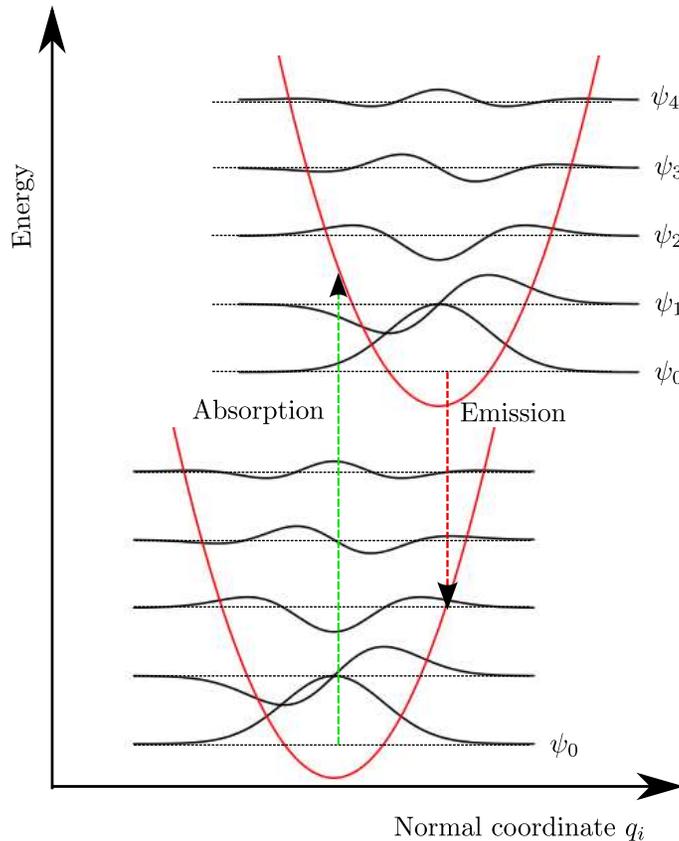
# Vibrational Stokes Shift

Molecules

Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems



Anthracene in Cyclohexane,  $10^{-5}M$ , degassed

- Transition energies: Absorption  $\nu_0 + n\nu_s$ , emission  $\nu_0 - n\nu_s$ .
- Oscillator strengths:  $\mu^2 |\langle 0 | n \rangle|^2$ .

# Solvent Dependent Stokes Shift

Molecules

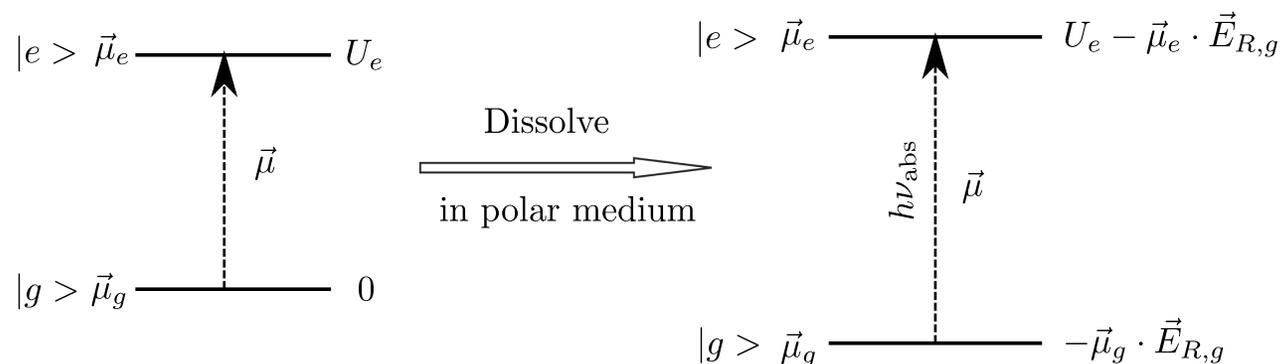
Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ **Stokes Shift**
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

## Absorption

First approximation:



Reaction field:

$$\vec{E}_{R,g} = \frac{2(\epsilon_r - 1)}{4\pi\epsilon_0 a^3 (2\epsilon_r + 1)} \vec{\mu}_g \equiv A_0 \mu_g$$

Absorption frequency:

$$h\nu_{\text{abs}} = U_e - \Delta\vec{\mu} \cdot \vec{E}_{R,g} = h\nu_0 - A_0 \Delta\vec{\mu} \cdot \vec{\mu}_g$$

# Solvent Dependent Stokes Shift II

Molecules

Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field

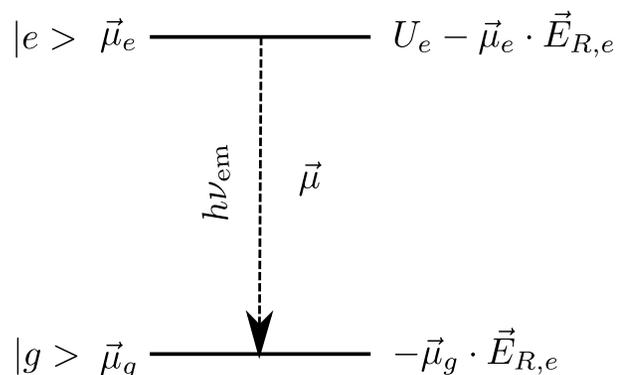
❖ Stokes Shift

- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

## Relaxed Emission

Reaction field in equilibrium with the new (excited state) dipole moment:



$$h\nu_{em} = h\nu_0 - A_0 \Delta\vec{\mu} \cdot \vec{\mu}_e$$

## Lippert–Mataga (without polarizability)

$$\Delta\nu = \frac{1}{4\pi\epsilon_0 a^3 h} \frac{2(\epsilon - 1)}{2\epsilon + 1} |\Delta\vec{\mu}|^2$$

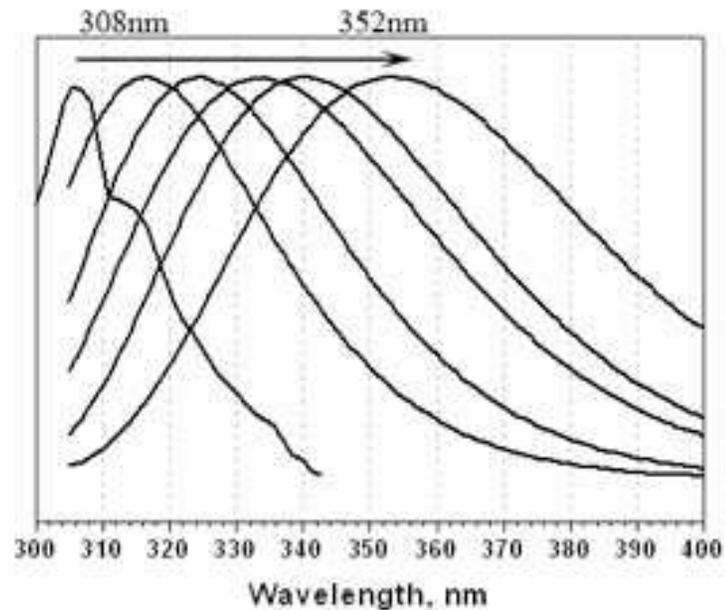
# Tryptophan

Molecules

Media

- ❖ Dielectrics
  - ❖ Internal Field
  - ❖ Interaction
  - ❖ Reaction Field
  - ❖ Stokes Shift
  - ❖ ESIPT
  - ❖ Dielectric Friction
  - ❖ Dynamics
  - ❖ conclusions
- Exercises and Problems

Emission is from  ${}^1L_a$ , with  $|\Delta\vec{\mu}| \approx 6 \text{ D} \Rightarrow$  sensitive to environment.



For tryptophan shifts range from  $1400\text{--}5400 \text{ cm}^{-1}$ , depending on polarity of the environment.

Molecules

Media

❖ Dielectrics

❖ Internal Field

❖ Interaction

❖ Reaction Field

❖ Stokes Shift

❖ ESIPT

❖ Dielectric Friction

❖ Dynamics

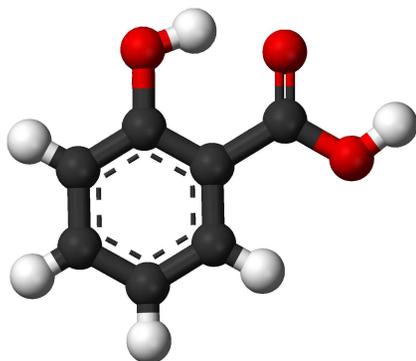
❖ conclusions

Exercises and Problems

Larger Stokes shifts, sometimes more than  $10000\text{ cm}^{-1}$ , are also reported:

**TABLE 1: Spectroscopic Data of the Salicylic Anion ( $2\text{ }\mu\text{M}$ ) in Various Solvents at  $296\text{ K}^a$**

solvent	$E_T(30)$ (kcal/mol)	$\pi^*$	$\alpha$	$\beta$	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Delta$ ( $\text{cm}^{-1}$ )	$\varphi$	$\tau_F$ (ns)
DMSO	45	0.98	0.00	0.76	296	391	8208	0.19	5.61
DMFA	43.8	0.88	0.00	0.69	296	389	8077	0.20	5.71
ACN	46	0.73	0.25	0.44	296	389	8077	0.24	6.56
2-PrOH	48.6	0.48	0.76	0.95	296	398	8658	0.23	6.30
EtOH	51.9	0.54	0.83	0.77	297	405	8978	0.25	6.71
EG	56.3	0.88	0.90	0.52	297	406	9039	0.25	6.56
MeOH	55.5	0.60	0.93	0.69	297	405	8978	0.26	6.78
H <sub>2</sub> O	63.1	1.09	1.17	0.47	296	407	9214	0.16	4.3
TFE	59.5	0.73	1.51	0.00	296	412	9512	0.18	5.58
D <sub>2</sub> O					296	407	9214	?	5.05



Usual cause: excited state reactions, e.g. Intramolecular Excited State Proton Transfer (ESIPT).

# ESIPT II

## Molecules

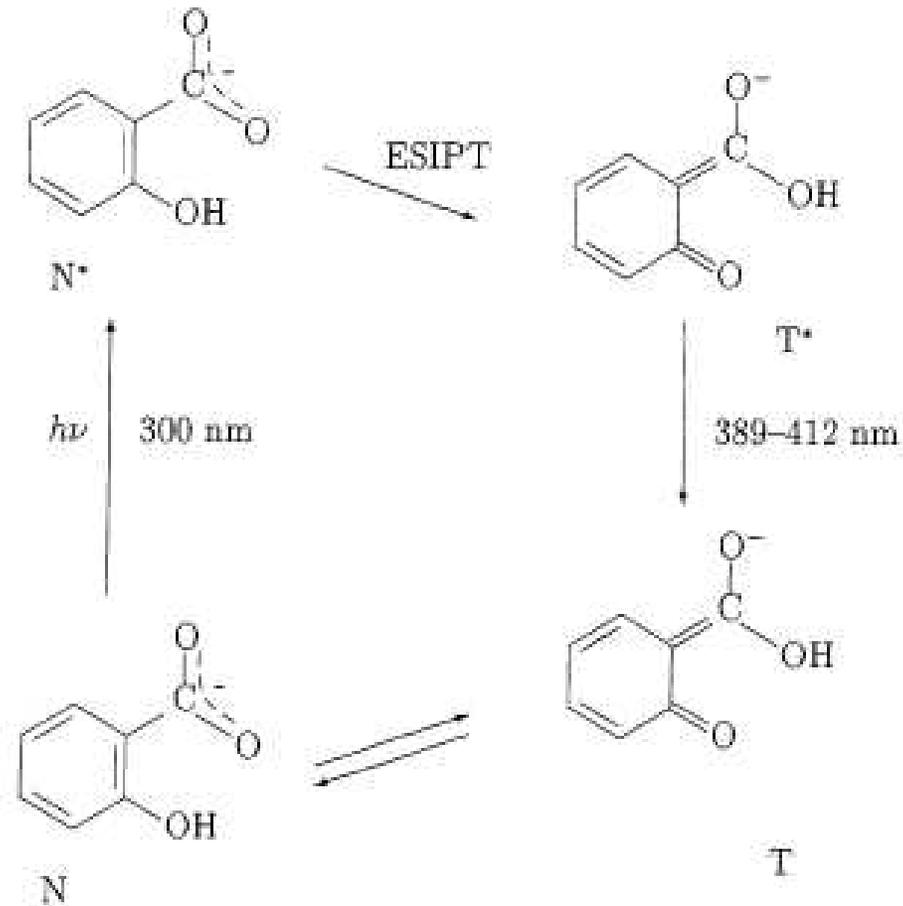
## Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift

## ❖ ESIPT

- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

## Exercises and Problems



# Dielectric Friction

## Molecules

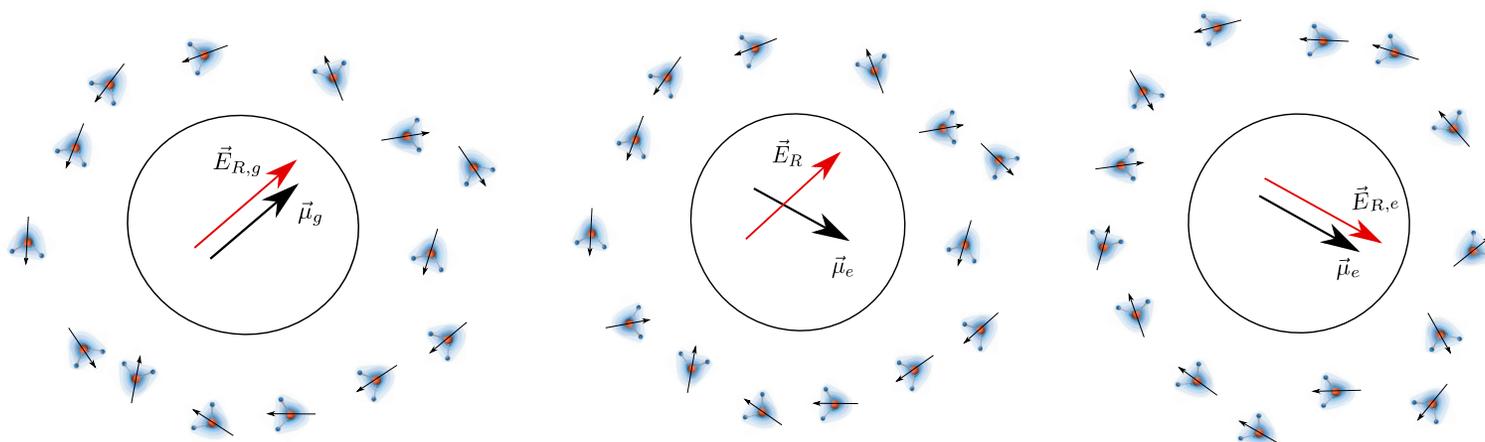
## Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ES IPT

## ❖ Dielectric Friction

- ❖ Dynamics
- ❖ conclusions

## Exercises and Problems



A rotating dipole experiences *dielectric friction* because the surrounding solvent dipoles need to adjust themselves to the new situation. Since this friction also applies to the solvent dipoles themselves the theory of dielectric relaxation is rather complicated.

Debye: 
$$\epsilon_r(\omega) = \frac{\epsilon_r - i\omega\tau_D}{1 - i\omega\tau_D}$$

$\tau_D$ : rotational correlation time of the solvent dipole, Debye relaxation time.

# Dielectric Friction II

Molecules

Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

Onsager's solution is still valid:

$$\vec{E}_R(\omega) = A(\omega)\vec{\mu}(\omega)$$

with

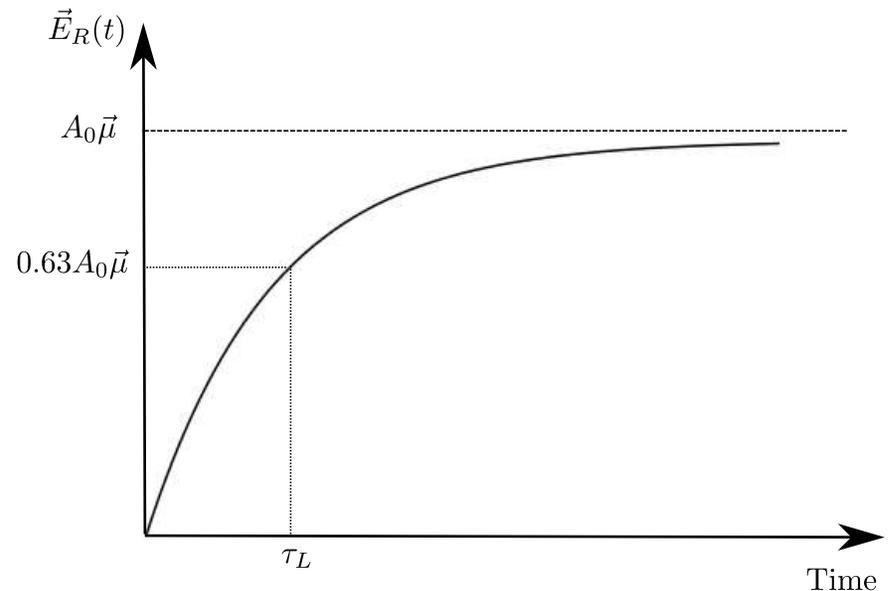
$$A(\omega) = \frac{1}{4\pi\epsilon_0 a^3} \frac{2(\epsilon_r(\omega) - 1)}{2\epsilon_r(\omega) + 1} = \dots = \frac{A_0}{1 - i\omega\tau_L} \quad (1)$$

Longitudinal relaxation time:

$$\tau_L = \frac{3\tau_D}{2\epsilon_r + 1}$$

Turn on  $\vec{\mu}$  at  $t = 0$ :

$$\vec{E}_R(t) = \vec{\mu} \int_0^t A(t - \tau)$$



# Dielectric Friction III

Molecules

Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ES IPT

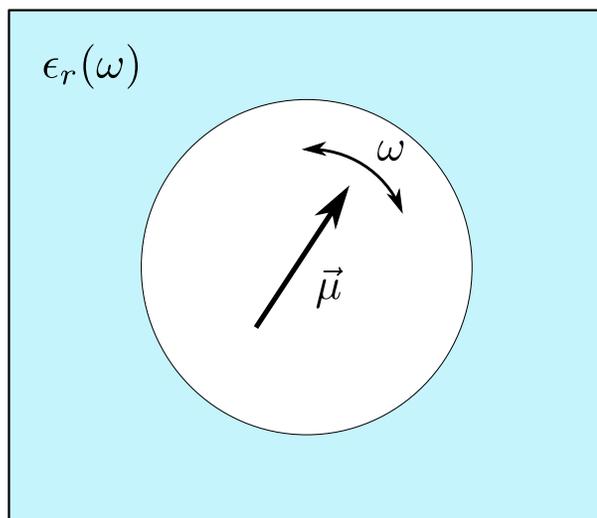
❖ Dielectric Friction

- ❖ Dynamics
- ❖ conclusions

Exercises and Problems

## Nee and Zwanzig: friction on a rotating dipole

$$\zeta(\omega) = \frac{A(\omega) - A_0}{i\omega} = \frac{A_0\tau_L}{1 - i\omega\tau_L}$$



- $\omega \rightarrow \infty \Rightarrow \zeta \rightarrow 0$ : solvent cannot keep up.
- $\omega \rightarrow 0 \Rightarrow \zeta \rightarrow A_0\tau_L$ : solvent needs to be dragged along.

Dielectric friction plays a role in isomerization reaction kinetics, electron, and proton transfer. Whenever charges are moved or dipoles rotated, there is dielectric friction.

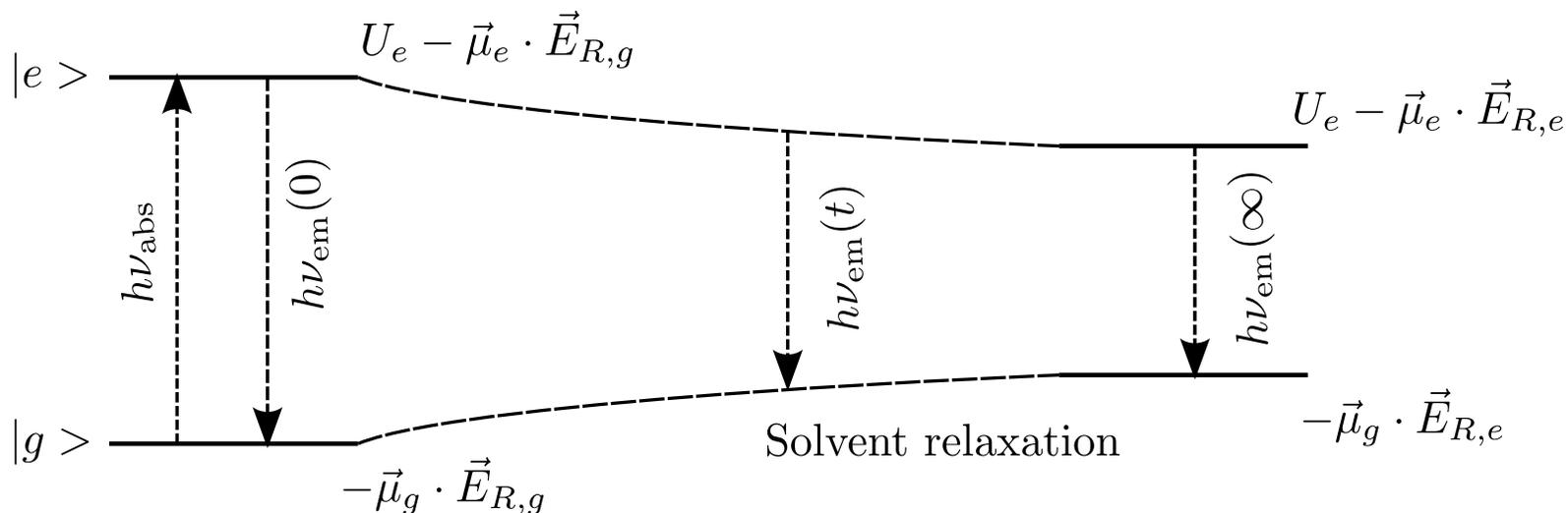
# Dynamical Stokes Shift

Molecules

Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

Exercises and Problems



$$\Delta(t) = \frac{\nu_{\text{em}}(t) - \nu_{\text{em}}(\infty)}{\nu_{\text{em}}(0) - \nu_{\text{em}}(\infty)} = \frac{\zeta(t)}{\zeta(0)}$$

$\zeta(t)$  is the time-dependent friction [Fourier transform of  $\zeta(\omega)$ ] on the *difference dipole moment*  $\Delta\vec{\mu} = \vec{\mu}_e - \vec{\mu}_g$ .

# Dynamical Stokes Shift II

## Molecules

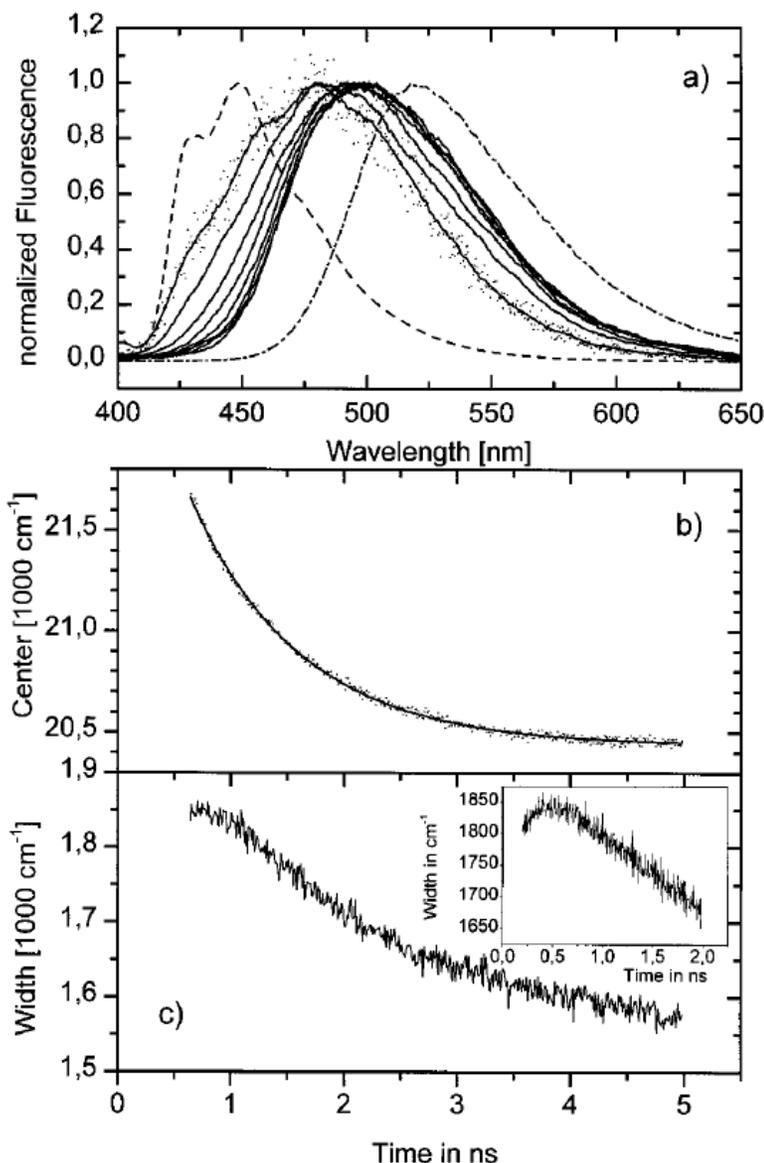
## Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction

## ❖ Dynamics

- ❖ conclusions

## Exercises and Problems



(a) Fluorescence spectra of C153 in a hexane/EtOH mixture at  $x_P = 0.029$  at different times ( $\Delta t = 0.6$  ns). For the first time step raw data are shown by the dots. The solid lines are the result of smoothing the raw data. Steady-state spectrum in hexane (dashed line) and in pure EtOH (dot-dashed line); (b) center of the band (dots) and monoexponential fit (solid line); (c) width of the band; inset shows data taken with higher time resolution.

# Remarks and Conclusions

## Molecules

## Media

- ❖ Dielectrics
- ❖ Internal Field
- ❖ Interaction
- ❖ Reaction Field
- ❖ Stokes Shift
- ❖ ESIPT
- ❖ Dielectric Friction
- ❖ Dynamics
- ❖ conclusions

## Exercises and Problems

- Molecules and Media are both collections of dipoles.
- Molecules must be treated quantum mechanically: we have state and transition dipole moments.
- Media are treated classically: we have dipole moments and polarizability (ignored in this lecture, but not irrelevant).
- Polarization is not the only relevant property of media that influences spectroscopy: protons can also play an important role, *viz.* Kamlet–Taft parameters.
- Interaction between molecules and media is a very complex topic. For those who want to know more: come to Finland in august: [www.jyu.fi/summerschool](http://www.jyu.fi/summerschool).

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Molecules

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Media

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Exercises and  
Problems

- ❖ Exercises
- ❖ Problems
- ❖ Literature

# *Exercises and Problems*

# Exercises

Molecules

Media

Exercises and  
Problems

❖ Exercises

❖ Problems

❖ Literature

1. Show that Debye's expression (on slide 21) leads to a critical temperature  $T_c$  below which the system has a macroscopic permanent dipole moment. What would  $T_c$  be for water? Do these so-called electrets exist?
2. Show that Onsager's solution, on slide 24, does not suffer from the problem given in 1.
3. In which direction does the polarity increase in the figure of slide 29?
4. Derive Eq. (1). Explain how the field can relax much faster (for water about 50 times) than the solvent dipoles rotate.
5. For a rainy afternoon: rederive all expressions for the dielectric constant in these slides taking the polarizability of the solvent molecules into account.
6. And, while you're at it, derive the Lippert–Mataga expression including polarizability. Remember that polarizability adjusts instantaneously to a new situation.
7. Why is it a good idea to use a dilute solution of ethanol in hexane to do experiments in, as in the Cichos reference?

# Problems

Molecules

Media

Exercises and  
Problems

❖ Exercises

❖ **Problems**

❖ Literature

As far as I know these topics have not yet been addressed in the literature, so they might make a good subject for a report.

1. What are the essential differences between the way polarization and magnetization is treated. In magnetization  $T_c$  (see exercise 1) is called the Curie temperature. Why is there no Onsager in the field of magnets who makes this temperature go away. In the mean time (since Onsager) electrets were discovered, so where is Onsager wrong?
2. The Stark field is most of the time much weaker than the Onsager reaction field. Nevertheless in Stark spectroscopy the perturbation is made on the quantum level, whereas for the reaction field we first make the molecule a classical system with dipole moment and polarizability (dipolar spring). Derive a self-consistent equation for a quantum system in equilibrium with its reaction field. Explore the solutions of this non-linear equation.
3. Explain the behavior of the width in Cichos' experiment.

# Literature

Molecules

Media

Exercises and  
Problems

❖ Exercises

❖ Problems

❖ Literature

1. S.K. Cushing, M. Li, F. Huang, and N. Wu, Origin of Strong Excitation Wavelength Dependent Fluorescence of Graphene Oxide, *ACS NANO*, (2014), **8**, 1002–1013.
2. N. Amdurski, Y. Erez, and D. Huppert, Molecular Rotors: What Lies Behind the High Sensitivity of the Thioflavin-T Fluorescent Marker, *Acc. Chem. Res.*, (2012), **45**, 1549–1557
3. A. Ajdarzadeh, C. Consani, O. Bräm, A. Tortschanoff, A. Cannizzo, and M. Chergui, Ultraviolet transient absorption, transient grating and photon echo studies of aqueous tryptophan, *Chem. Phys.*, (2013), **422**, 47–52.