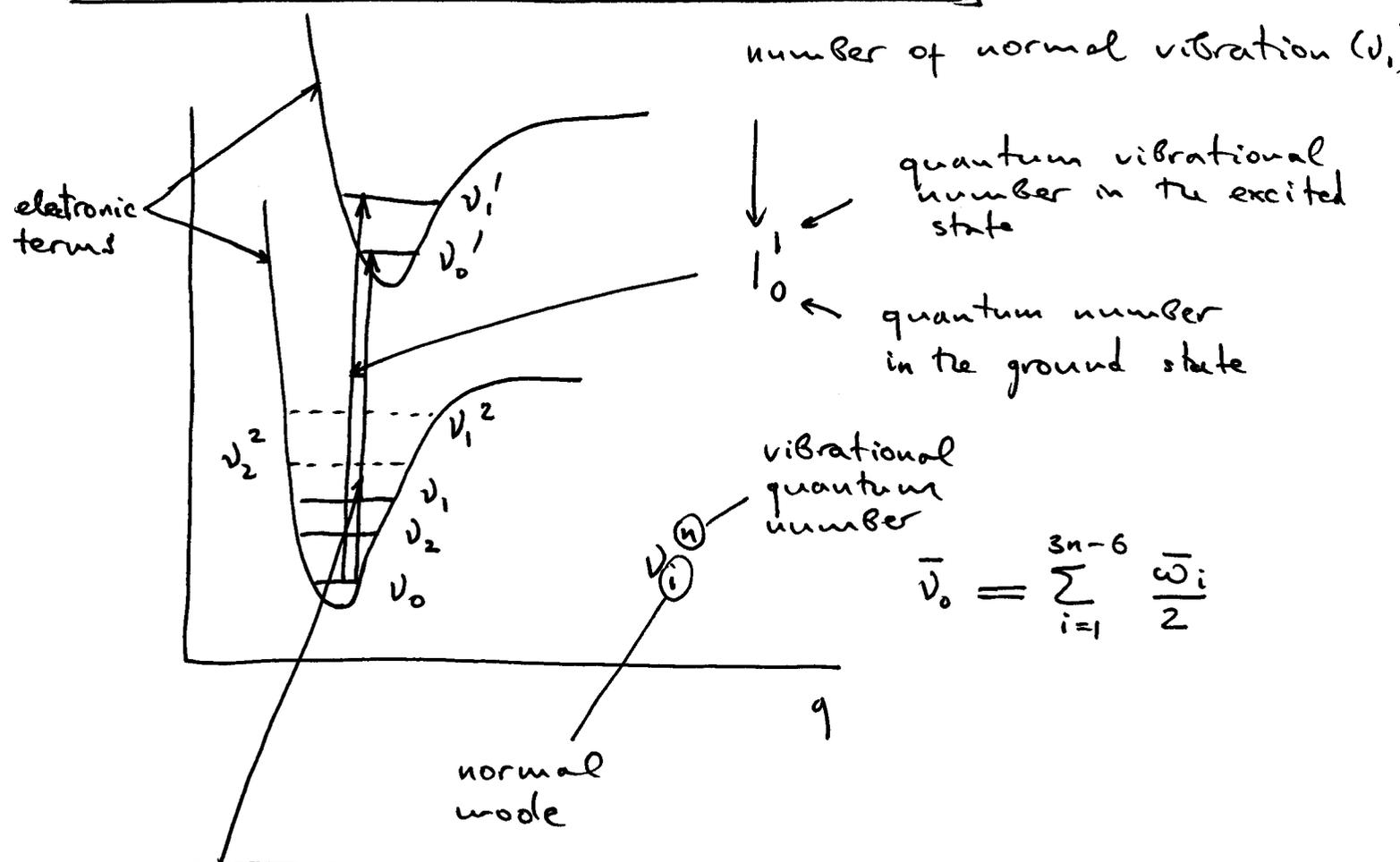
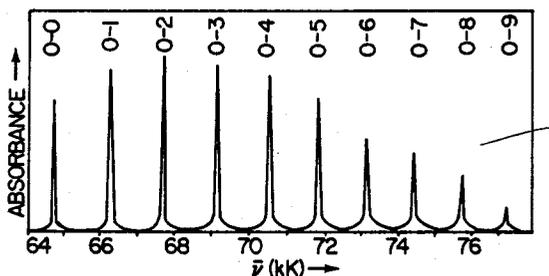


Transitions Between vibrational states



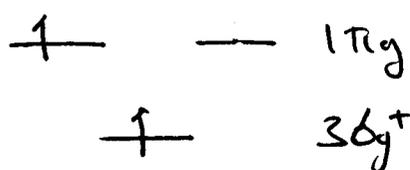
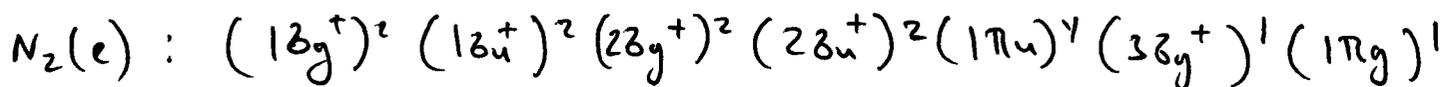
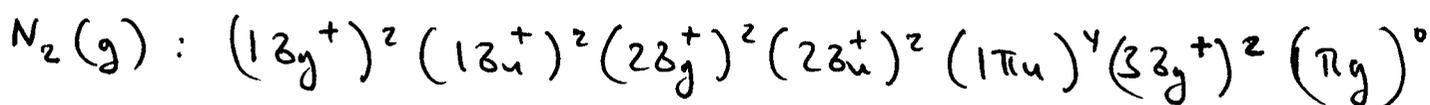
pure electronic transition, 0-0 transition

Transitions between different electronic terms involving vibrational excitations are called vibronic transitions.

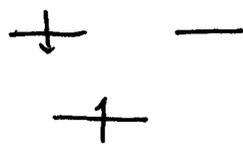


Homework. On the spectrum above the spacing between 0-0 and 0-1 transitions is 2.8 kK and the spacing between 0-8 and 0-9 is ~~0.6~~ 2.4 kK. Determine $\bar{\omega}_e$ and $\bar{\omega}_e x_e$.

Electronic configuration:



triplet state



singlet state

Wave function:

$$\Psi = \psi_v \psi_e \psi_s$$

Born-Oppenheimer approximation

vibrational wave function

electronic orbital wave function

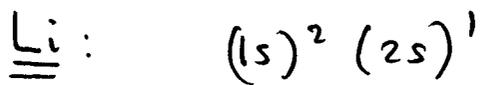
electron spin wave function

Pauli principle

The total many-electron wave function must be antisymmetric with respect to exchange of two electrons

$\Psi^* \Psi = |\Psi|^2$ does not change by exchange $1 \leftrightarrow 2$

$$P_{12} \Psi(1, 2, 3, \dots, n) = -\Psi(2, 1, 3, \dots, n)$$



Hartree approximation

$$\Psi_{es}(\text{Li}) = (100\alpha|1) (100\beta|2) (200\alpha|3)$$

n e m_e m_s

$\alpha \rightarrow \frac{1}{2}, \uparrow$
$\beta \rightarrow -\frac{1}{2}, \downarrow$

Antisymmetric wave function:

$$\Psi_{es}(\text{Li}) = \frac{1}{\sqrt{6}} \left[(100\alpha|1)(100\beta|2)(200\alpha|3) + (100\beta|1)(200\alpha|2)(100\alpha|3) \right. \\ \left. + (200\alpha|1)(100\alpha|2)(100\beta|3) - (200\alpha|1)(100\beta|2)(100\alpha|3) \right. \\ \left. - (100\alpha|1)(200\alpha|2)(100\beta|3) - (100\beta|1)(100\alpha|2)(200\alpha|3) \right]$$

Slater determinant:

$$\Psi_{es}(Li) = \frac{1}{\sqrt{3!}} \begin{vmatrix} (100\alpha|1) & (100\alpha|2) & (100\alpha|3) \\ (100\beta|1) & (100\beta|2) & (100\beta|3) \\ (200\alpha|1) & (200\alpha|2) & (200\alpha|3) \end{vmatrix}$$

(shortcut notation)

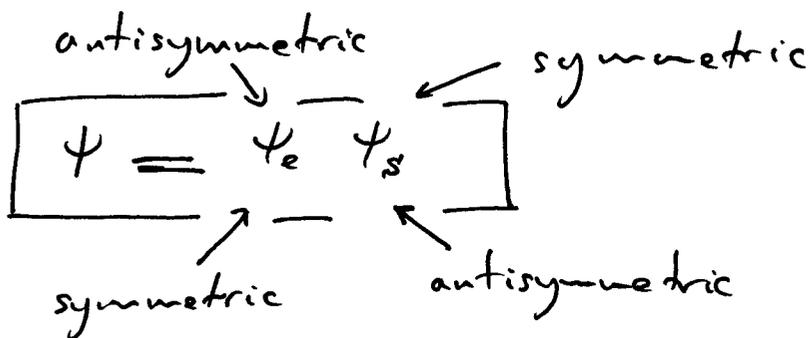
$$\Psi_{es}(Li) = \frac{1}{\sqrt{3!}} \left| (100\alpha|1) (100\beta|2) (200\alpha|3) \right|$$

Properties: For an $N \times N$ Slater determinant

$$\Psi_N = \frac{1}{\sqrt{N!}} \left| \Psi_1(1) \Psi_2(2) \dots \Psi_N(N) \right|$$

* $\Psi_N = 0$ if $\Psi_i(i) = \Psi_j(j)$

* $\Psi_N \rightarrow -\Psi_N$ by exchange of two electrons



Spin wave functions

Orthonormal relations: $\langle \alpha | \alpha \rangle = \int \alpha^*(1) \alpha(1) d\tau_1 = 1$

$\langle \beta | \beta \rangle = \int \beta^*(1) \beta(1) d\tau_1 = 1$

$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$

Homework: Calculate

$$\langle \alpha(1) \beta(2) \alpha(4) \alpha(3) | \alpha(4) \beta(3) \beta(2) \alpha(1) \rangle$$

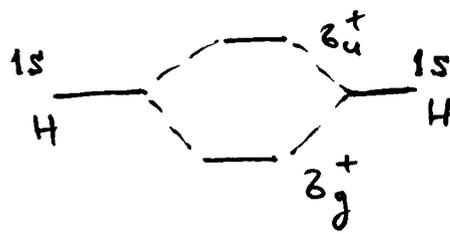
Spin wave functions of two electrons:

$$\left. \begin{aligned} \Psi &= \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) + \beta(1) \alpha(2)] \\ \psi &= \alpha(1) \alpha(2) \\ \Psi &= \beta(1) \beta(2) \end{aligned} \right\} \text{symmetric}$$

$$\Psi' = \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) - \beta(1) \alpha(2)] \left. \right\} \text{antisymmetric}$$

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \frac{1}{2} \langle \alpha(1) \beta(2) + \beta(1) \alpha(2) | \alpha(1) \beta(2) + \beta(1) \alpha(2) \rangle \\ &= \frac{1}{2} \langle \underbrace{\alpha(1)}_1 \underbrace{\beta(2)}_2 | \underbrace{\alpha(1)}_1 \underbrace{\beta(2)}_2 \rangle + \frac{1}{2} \langle \underbrace{\beta(1)}_1 \underbrace{\alpha(2)}_2 | \underbrace{\alpha(1)}_1 \underbrace{\beta(2)}_2 \rangle + \\ &\quad + \frac{1}{2} \langle \underbrace{\beta(1)}_1 \underbrace{\alpha(2)}_2 | \underbrace{\beta(1)}_1 \underbrace{\alpha(2)}_2 \rangle + \frac{1}{2} \langle \underbrace{\beta(1)}_1 \underbrace{\alpha(2)}_2 | \underbrace{\alpha(1)}_1 \underbrace{\beta(2)}_2 \rangle \end{aligned}$$

H_2



$$H_2: (1\sigma_g^+)^2 (1\sigma_u^+)^0$$

$$\psi_e = \sigma_g^+(1) \sigma_g^+(2)$$

Ground state : $\psi_{es} = \psi_e \psi_s = \sigma_g^+ \sigma_g^+ \frac{1}{\sqrt{2}} [\alpha\beta - \beta\alpha]$

Excited state $(\sigma_g^+)^1 (\sigma_u^+)^1$:

$$\psi_e(\text{sym}) = \frac{1}{\sqrt{2}} [\sigma_g^+ \sigma_u^+ + \sigma_u^+ \sigma_g^+]$$

$$\psi_e(\text{antisym}) = \frac{1}{\sqrt{2}} [\sigma_g^+ \sigma_u^+ - \sigma_u^+ \sigma_g^+]$$

$$\psi_{es} = \frac{1}{2} [\sigma_g^+ \sigma_u^+ + \sigma_u^+ \sigma_g^+] [\alpha\beta - \beta\alpha] \quad \uparrow \uparrow \text{singlet}$$

$$\left. \begin{aligned} \psi_{es} &= \frac{1}{\sqrt{2}} [\sigma_g^+ \sigma_u^+ - \sigma_u^+ \sigma_g^+] [\alpha\alpha] \\ &\frac{1}{\sqrt{2}} [\sigma_g^+ \sigma_u^+ - \sigma_u^+ \sigma_g^+] [\beta\beta] \\ &\frac{1}{2} [\sigma_g^+ \sigma_u^+ - \sigma_u^+ \sigma_g^+] [\alpha\beta + \beta\alpha] \end{aligned} \right\} \begin{array}{l} \uparrow \\ \uparrow \\ \uparrow \\ \text{triplet} \end{array}$$

Reminder: For a many-electron atom or molecule

$$M_s = \sum_i m_s^i$$

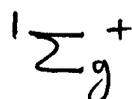
Stationary States

Rules for determining the orbital symmetries and spin multiplicities of the stationary states which arise from particular configurations of molecules:

0: A filled molecular orbital has the full symmetry of the molecule (transforms according to the totally symmetric irreducible representation of the point group)

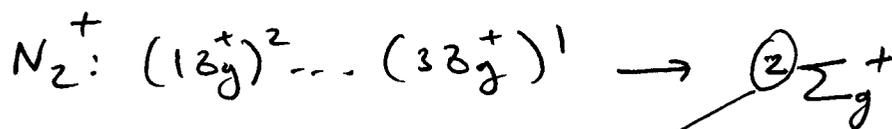
1: All occupied orbitals are fully occupied

H_2 (ground), $D_{\infty h}$ has fully symmetric representation Σ_g^+ . The electronic state becomes:



2: The only unoccupied orbital is singly occupied

The electronic state is $2X$ symmetry of the orbital



spin multiplicity, doublet

3 : Two singly occupied orbitals

The symmetries of possible states are given by the direct product of the symmetries of partially occupied orbitals

$(b_{1u})'(b_{2g})'$ in ethylene (D_{2h})

p. 479, Appendix B

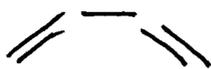
D_{2h}	A	B_1	B_2	B_3
A	A	B_1	B_2	B_3
B_1		A	B_3	B_2
B_2			A	B_1
B_3				A

$b_{1u} \times b_{2g} = B_{3u}$ — $^1B_{3u}$

$u \times g = u$ — $^3B_{3u}$

— a_2

+ b_1



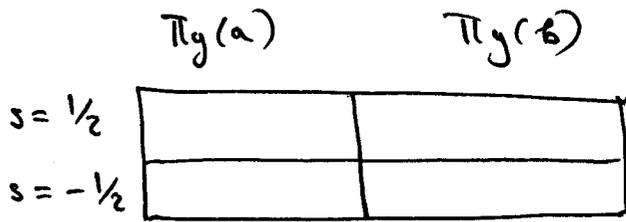
+ a_2

+ b_1

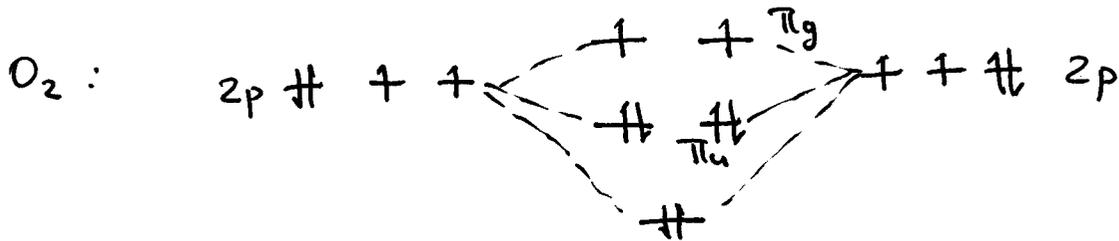
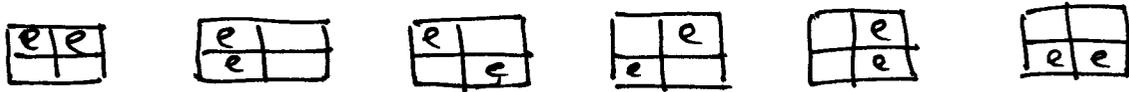
$a_2 \times b_1 (C_{2v}) = B_2$

Electronic states: $^1B_2, ^3B_2$

5: Two electrons in a degenerate orbital



Six orbitals:



$$\pi_g \times \pi_g (\text{Dorb}) : \Sigma_g^+ + \Sigma_g^- + \Delta_g$$

$$\pi_g' \times \pi_g' = \underbrace{{}^1\Sigma_g + {}^1\Sigma_g^- + {}^1\Delta_g + {}^3\Sigma_g + {}^3\Sigma_g^- + {}^3\Delta_g}_{16 \text{ functions}}$$

singlet \rightarrow antisymmetric orbital wave function

triplet \rightarrow symmetric orbital wave function

Appendix B, p. 488 :

D_{orb}	Σ^+	Σ^-	Π	Δ	...
Σ^+	Σ^+	Σ^-	Π	Δ	...
Σ^-		Σ^+	Π	Δ	...
Π			$\Sigma^+ [\Sigma^-] + \Delta$		
Δ					
...					

the term in brackets is antisymmetric component of the direct product

symmetric χ

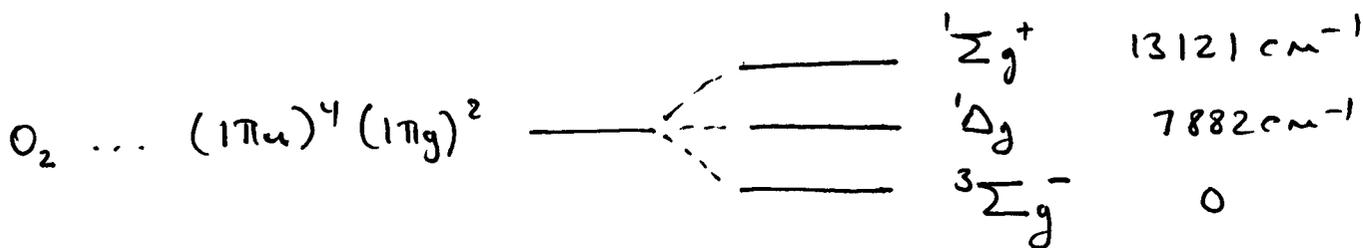
$$\chi^+ = \frac{1}{2} [\chi(R)^2 + \chi(R^e)]$$

$$\chi^- = \frac{1}{2} [\chi(R)^2 - \chi(R^e)]$$

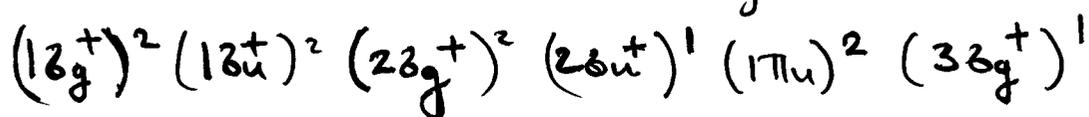
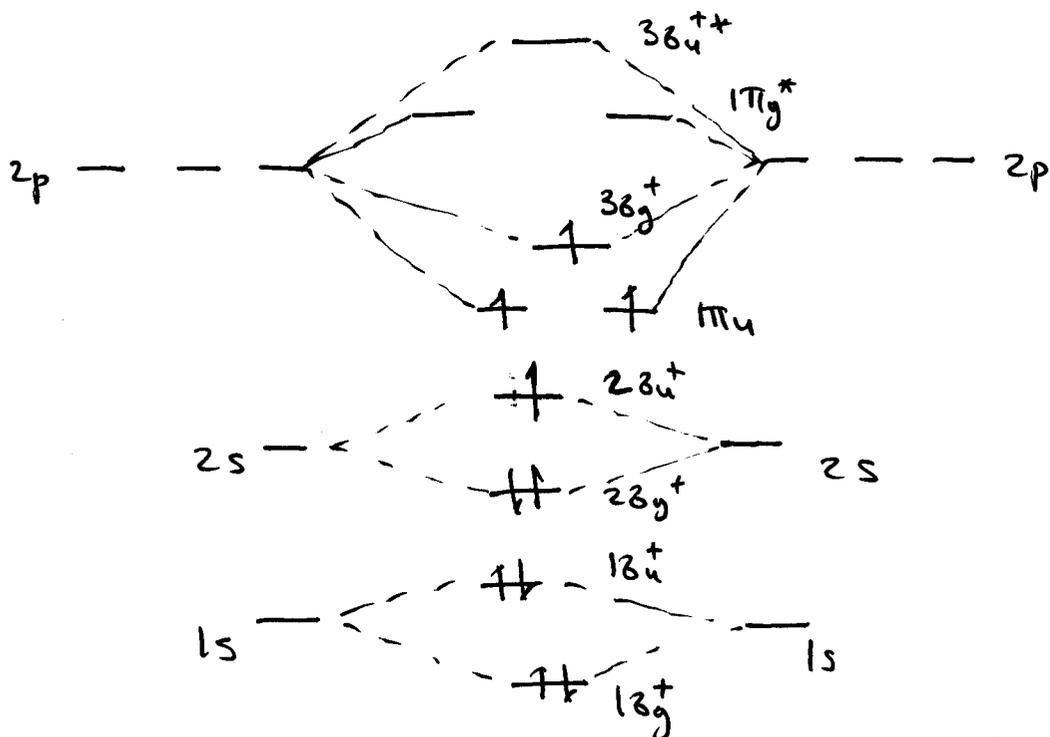
antisymmetric χ

States of $(\pi_g)^2 = \underbrace{{}^1\Sigma_g^+}_{1} + \underbrace{{}^1\Delta_g}_{2} + \underbrace{{}^3\Sigma_g^-}_{3}$

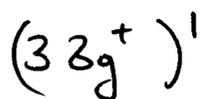
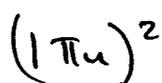
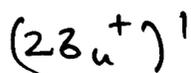
6 wave functions



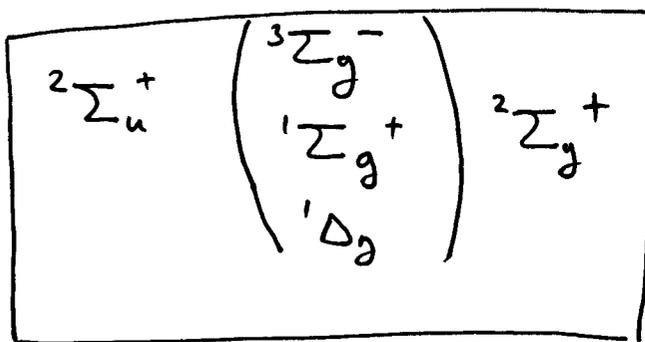
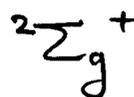
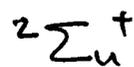
B_2



Configuration



States



all electronic state
of the ground state
electronic configuration

$$\underbrace{{}^2\Sigma_u^+ \quad {}^3\Sigma_g^- \quad {}^2\Sigma_g^+}_{\rightarrow} = ({}^2\Sigma_u^- + {}^4\Sigma_u^-) {}^2\Sigma_g^+ =$$

$$s_1 = \frac{1}{2} \quad s_2 = 1$$

$$s = 3/2, 1/2$$

$$= {}^1\Sigma_u^- + {}^3\Sigma_u^- + {}^5\Sigma_u^- + {}^3\Sigma_u^-$$

$$s_1 = \frac{1}{2} \quad s_2 = \frac{1}{2}$$

$$s = 1, 0$$

$$s_1 = \frac{3}{2} \quad s_2 = \frac{1}{2}$$

$$s = 2, 1$$

$$\underbrace{{}^2\Sigma_u^+ \quad {}^1\Sigma_g^+ \quad {}^2\Sigma_g^+}_{\rightarrow} = {}^2\Sigma_u^+ \quad {}^2\Sigma_g^+ = {}^1\Sigma_u^+ + {}^3\Sigma_u^+$$

$$\underbrace{{}^2\Sigma_u^+ \quad {}^1\Delta_g \quad {}^2\Sigma_g^+}_{\rightarrow} = {}^2\Delta_u \quad {}^2\Sigma_g^+ = {}^1\Delta_u + {}^3\Delta_u$$

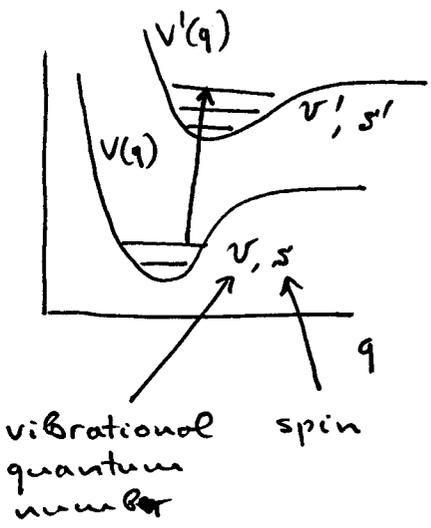
states of $B_2 = {}^1\Sigma_u^- + 2 \times {}^3\Sigma_u^- + {}^5\Sigma_u^- +$

$+ {}^1\Sigma_u^+ + {}^3\Sigma_u^+ + {}^1\Delta_u + {}^3\Delta_u$

↗

8 energy levels and 24 wave functions

Transition moment for electronic transitions



$$M = \langle \psi' | \hat{M} | \psi \rangle = \int \psi'^*(\tau) \hat{M} \psi(\tau) d\tau$$

$\{\vec{r}, \vec{q}, s\}$

$$\hat{M} = \underbrace{-e \sum \vec{r}_i}_{\hat{M}_e} + e \sum Z_j \underbrace{\vec{R}_j}_{\hat{M}_n} = \hat{M}_e + \hat{M}_n$$

electronic dipole moment operator \hat{M}_e
 nuclear dipole moment operator \hat{M}_n

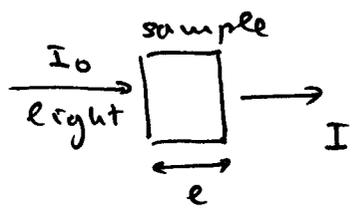
$$M = \langle \psi_{e's'} | \psi_{v'} | (\hat{M}_n + \hat{M}_e) | \psi_{es} \psi_v \rangle = \langle \psi_{e's'} | \psi_{es} \rangle \langle \psi_{v'} | \hat{M}_n | \psi_v \rangle + \langle \psi_{v'} | \psi_v \rangle \langle \psi_{e's'} | \hat{M}_e | \psi_{es} \rangle$$

Wave functions $\psi_{v'}$ and ψ_v belong to different electronic states and therefore $\langle \psi_{v'} | \psi_v \rangle$ may be non-zero for $v \neq v'$.

$$M = \underbrace{\langle \psi_{v'} | \psi_v \rangle}_{\text{Franck-Condon factor}} \underbrace{\langle \psi_{e's'} | \hat{M}_e | \psi_{es} \rangle}_{\text{orbital selection rules}} \underbrace{\langle \psi_{s'} | \psi_s \rangle}_{\text{spin selection rules}}$$

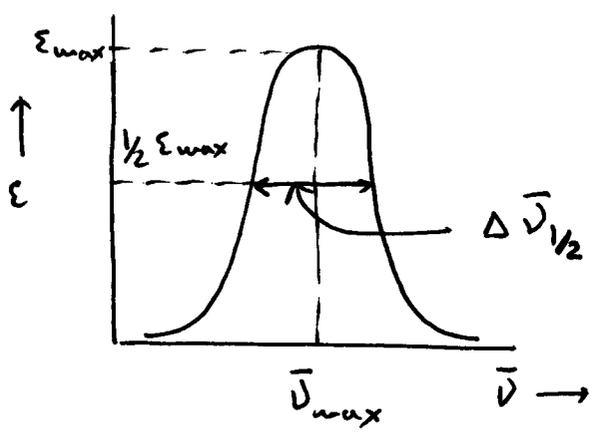
Factoring of the wave function is based on a set of approximations (Born-Oppenheimer + neglect of spin-orbit coupling) \rightarrow selection rules are not rigorous.

Extinction coefficient



extinction coefficient, $M^{-1}cm^{-1}$

$$\frac{I}{I_0} = 10^{-\epsilon[A]e}$$



Gaussian approximation:

$$\epsilon(\bar{\nu}) = \epsilon_{max} e^{-\frac{(\bar{\nu} - \bar{\nu}_{max})^2}{2\sigma^2}}$$

$$\sigma^2 = \langle \bar{\nu}^2 \rangle - \bar{\nu}_{max}^2$$

is the variance

$$\langle \bar{\nu}^2 \rangle = \int \bar{\nu}^2 \epsilon(\bar{\nu}) d\bar{\nu} / \int \epsilon(\bar{\nu}) d\bar{\nu}$$

The width at half height: $\Gamma = \Delta \bar{\nu}_{1/2} / 2$

$$\frac{\frac{1}{2} \epsilon_{max}}{\epsilon_{max}} = e^{-\frac{\Gamma^2}{2\sigma^2}} \rightarrow \Gamma^2 = 2\sigma^2 \ln 2$$

$$(\Delta \bar{\nu}_{1/2})^2 = 8 \ln 2 \sigma^2$$

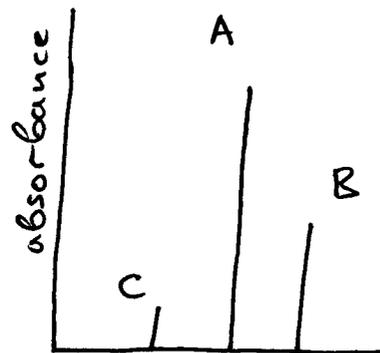
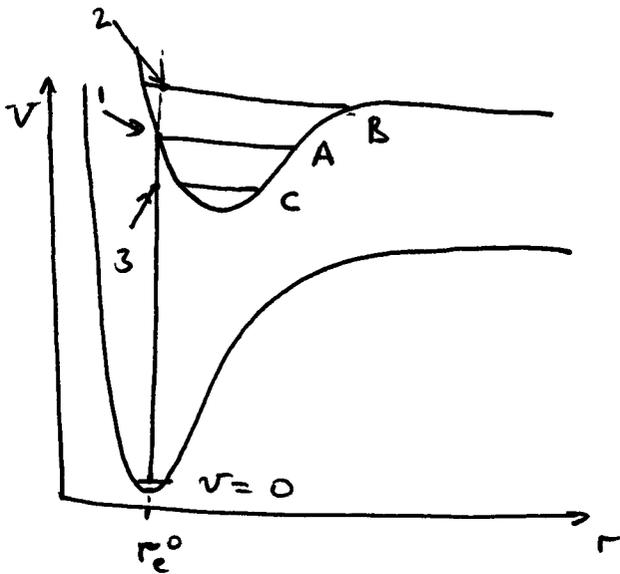
$$\epsilon(\bar{\nu}) = \epsilon_{max} e^{-\frac{4(\ln 2)(\bar{\nu} - \bar{\nu}_{max})^2}{(\Delta \bar{\nu}_{1/2})^2}}$$

Intensities of electronic transitions:

- spin-forbidden $10^{-5} - 10^0 \leftarrow \epsilon_{max} / M^{-1}cm^{-1}$
- spin-allowed, orbitally-forbidden $10^0 - 10^3$
- spin- and orbitally-allowed $10^3 - 10^5$

Franck-Condon principle

An electronic transition is so fast ($\sim 10^{-15}$ s), compared to the nuclear motion ($\sim 10^{-13}$ s), that the nuclei still have nearly the same position and momentum immediately after the transition as before.



- * The momentum is small at the initial state at r_e^0
- * The momentum is still small at the turning point of A (point 1)
- * Transition to B involves a change in momentum (2) and transition to C goes to the state forbidden by classical mechanics

Homework. Evaluate the momentum at point 2 assuming that the electronic terms refer to Cl_2 and the vibrational frequency is $\bar{\omega}_e = 1500 \text{ cm}^{-1}$.

Spin Selection Rules

A transition is spin-allowed if and only if the multiplicities of the two states involved are identical

$$\langle \psi_s | \psi_{s'} \rangle = \delta_{s,s'}$$

Triplet-singlet transition:

$$\begin{aligned} \langle {}^3\psi | {}^1\psi \rangle &= \frac{1}{\sqrt{2}} \langle \alpha(1)\alpha(2) | \alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle = \\ &= \frac{1}{\sqrt{2}} \underbrace{\langle \alpha(1)\alpha(2) | \alpha(1)\beta(2) \rangle}_{=1} - \frac{1}{\sqrt{2}} \underbrace{\langle \alpha(1)\alpha(2) | \beta(1)\alpha(2) \rangle}_{=0} = 0 \end{aligned}$$

Singlet-singlet transition

$$\begin{aligned} \langle {}^1\psi | {}^1\psi \rangle &= \frac{1}{2} \langle \alpha(1)\beta(2) - \beta(1)\alpha(2) | \alpha(1)\beta(2) - \beta(1)\alpha(2) \rangle \\ &= \frac{1}{2} \underbrace{\langle \alpha(1)\beta(2) | \alpha(1)\beta(2) \rangle}_{=1} + \frac{1}{2} \underbrace{\langle \beta(1)\alpha(2) | \beta(1)\alpha(2) \rangle}_{=1} \\ &\quad - \frac{1}{2} \underbrace{\langle \alpha(1)\beta(2) | \beta(1)\alpha(2) \rangle}_{=0} - \frac{1}{2} \underbrace{\langle \beta(1)\alpha(2) | \alpha(1)\beta(2) \rangle}_{=0} \\ &= 1 \end{aligned}$$

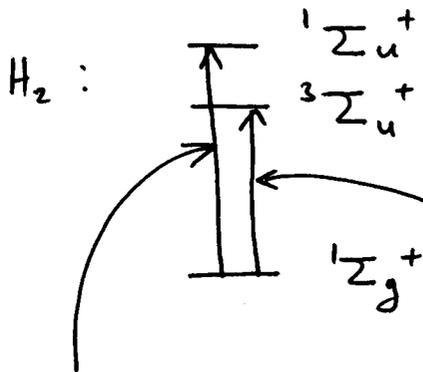
Orbital Selection Rules

An electronic transition is orbitally-allowed if and only if the triple direct product $\Gamma(\psi_e) \times \Gamma(\hat{m}_e) \times \Gamma(\psi_g)$ contains the totally symmetric irreducible representation of the point group of the molecule

$${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$$

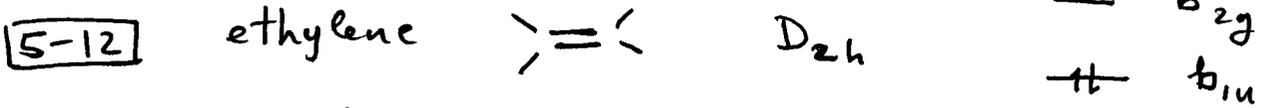
$$\langle \psi_e | \hat{m}_e | \psi_g \rangle \sim \Sigma_u^+ \begin{pmatrix} \sigma_u^+ \\ \pi_u \end{pmatrix} \Sigma_g^+ = \begin{pmatrix} \sigma_g^+ \\ \pi_g \end{pmatrix}$$

allowed



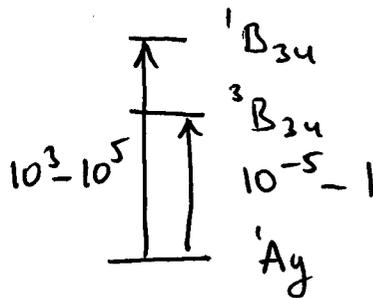
spin forbidden,
orbitally allowed

spin + orbitally
allowed =
fully allowed



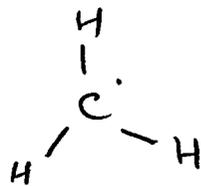
$$(b_u)^2 (b_{2g})^0 = {}^1A_g$$

$$(b_{1u})^1 (b_{2g})^1 = \begin{cases} {}^3B_{3u} \\ {}^1B_{3u} \end{cases}$$



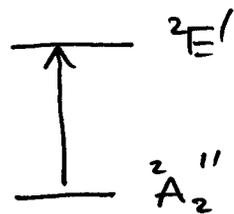
5-13

Planar methyl radical :



$$\dots (a_1')^2 (e')^4 (a_2'')^1 = {}^2A_2''$$

$$e' \rightarrow a_2'' = \dots (a_1')^2 (e')^3 (a_2'')^2 = {}^2E'$$



$$a_2'' \begin{pmatrix} e' \\ a_2'' \end{pmatrix} e' \sim \begin{pmatrix} a_2'' \\ e' \end{pmatrix}$$

\hat{M} (with an arrow pointing to the matrix)

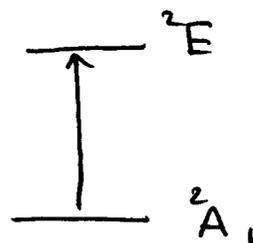
This transition is spin-allowed and orbitally forbidden, $\epsilon_{\max} \approx 1-10^3 \text{ M}^{-1}\text{cm}^{-1}$

Pyramidal CH₃ : $\dots (a_1)^2 (e)^4 (a_1)^1 = {}^2A_1$

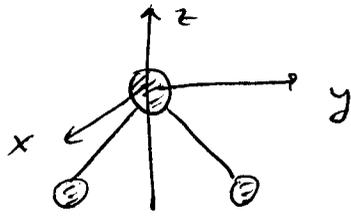
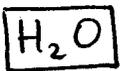
$$e \rightarrow a_1 = \dots (a_1)^2 (e)^3 (a_1)^2 = {}^2E$$

$$a_1 \begin{pmatrix} a_1 \\ e \end{pmatrix} e = \begin{pmatrix} e \\ \boxed{a_1} \end{pmatrix}$$

\hat{M} (with an arrow pointing to the matrix)

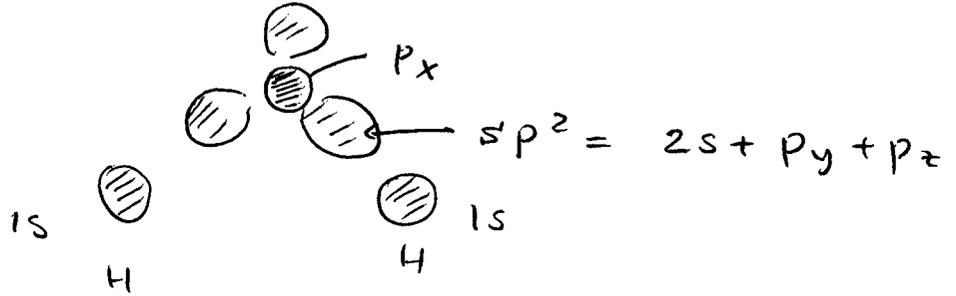


Spin + orbitally allowed, $\epsilon_{\max} \approx 10^3 - 10^5 \text{ M}^{-1}\text{cm}^{-1}$

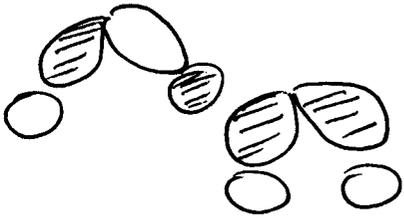


1) MO analysis

Basis set :



C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
$2H(1s)$	2	0	0	2	$= a_1 + b_2$
$3C(sp^2)$	3	1	1	3	$= 2a_1 + b_2$
$1p_x$	1	-1	1	-1	$= b_1$



— $2b_2$
 — $3a_1$ } δ -antibonding

— $1b_1$ p_x lone pair

~~—~~ $2a_1$ sp^2 lone pair



~~—~~ $1b_2$ } δ -bonding



~~—~~ $1a_1$

2) Vibrational analysis :

$$\Gamma_{\text{vib}} = 2a_1 + b_2 = \nu_s(a_1) + \nu_{as}(b_2) + \delta(a_1)$$

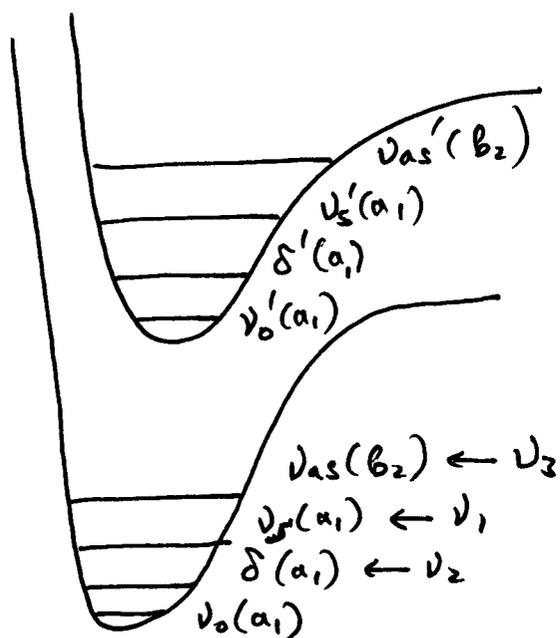
3) Electronic transitions and vibronic selection rules

0-0 transition:

$$b_1 \text{ --- } \uparrow$$

$$a_1 \text{ --- } \uparrow \text{ --- } \uparrow \left\{ \begin{array}{l} {}^1B_1 \\ {}^3B_1 \end{array} \right.$$

${}^1A_1 \rightarrow {}^3B_1 \leftarrow$ spin forbidden



$$B_1 a_1 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} A_1 a_1 =$$

$$\begin{matrix} \uparrow & & \uparrow \\ \psi_{v'} & & \psi_v \end{matrix}$$

$$= \begin{pmatrix} b_1 \\ \boxed{a_1} \\ a_2 \end{pmatrix} \leftarrow \text{allowed}$$

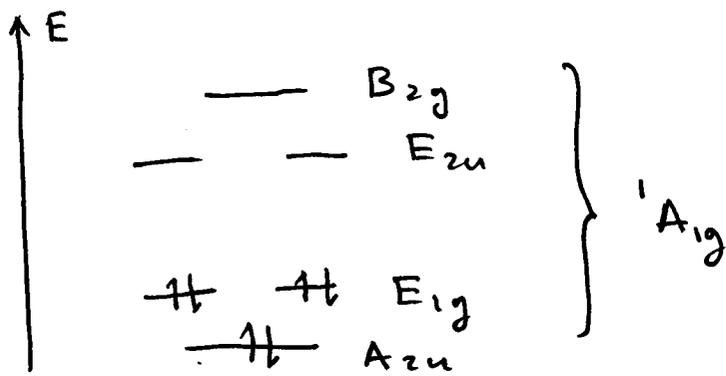
$${}^3_0^1 :$$

$$B_1 b_2 \begin{pmatrix} a_1 \\ b_1 \\ b_2 \end{pmatrix} A_1 a_1 = \begin{pmatrix} a_2 \\ b_2 \\ b_1 \end{pmatrix}$$

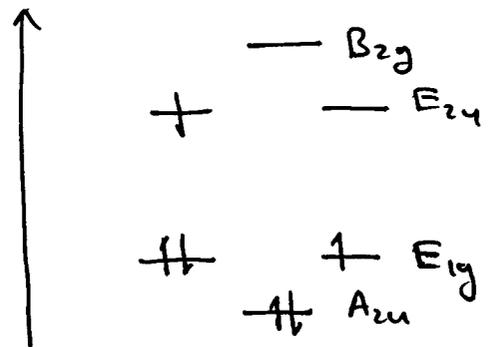
$$\begin{matrix} \uparrow \\ \psi_{v'} \end{matrix}$$

forbidden

Orbitally-forbidden 0-0 transition



benzene (D_{6h})



$$e_{1g} \times e_{2u} = b_{1u} + b_{2u} + e_{1u}$$

Transition ${}^1A_{1g} \rightarrow {}^1B_{2u}$

$$B_{2u} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} A_{1g} = \begin{pmatrix} b_{1g} \\ e_{2g} \end{pmatrix} \leftarrow \text{forbidden}$$

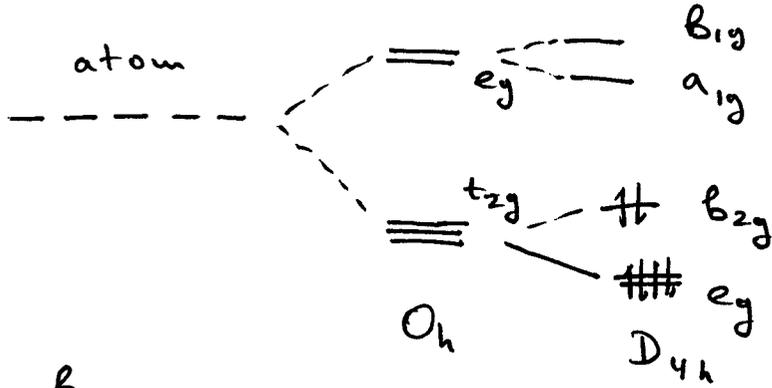
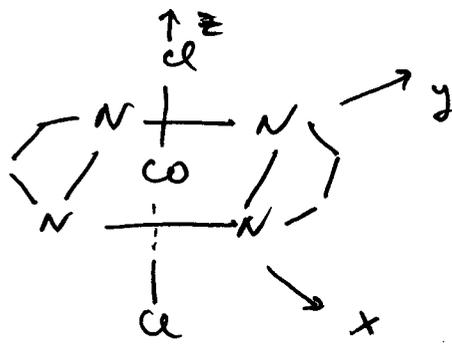
$\swarrow z$
 $\nwarrow (x,y)$

$\begin{pmatrix} b_{1g} \\ e_{2g} \end{pmatrix}$ indicates that transitions i_0' with b_{1g} and e_{2g} vibrations will be allowed

$$B_{2u} e_{2g} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} A_{1g} a_{1g} = e_{1u} \begin{pmatrix} a_{2u} \\ e_{1u} \end{pmatrix} a_{1g} = \begin{pmatrix} e_{1g} \\ a_{1g} + a_{2g} + e_{2g} \end{pmatrix}$$

allowed

This is a vibronically-allowed, orbitally-forbidden transition



- b_{1g}
- a_{1g}
- †† b_{2g}
- †† †† e_g

} ¹A_{1g}

b_{2g} → a_{1g}
 b_{2g} → b_{1g}

¹B_{2g}
 b₂ × b₁ = a₂ ¹A_{2g}

e_g → a_{1g}
 e_g → b_{1g} } ¹E_g

Singlet transitions:

¹A_{1g} → ¹B_{2g}
¹A_{2g}
¹E_g

	¹ A _{1g} → ¹ A _{2g}	¹ A _{1g} → ¹ B _{2g}	¹ A _{1g} → ¹ E _g
$\int \psi'_e(z) \psi_e d\tau$	A _{1u}	B _{1u}	E _u
$\int \psi'_e \begin{pmatrix} x \\ y \end{pmatrix} \psi_e d\tau$	E _u	E _u	A _{1u} + A _{2u} + B _{1u} + B _{2u}

z → a_{2u}

(x, y) → e_u

(b) vibronic analysis:

CoN_4Cl_2 vibrations transform as:

$$2a_{1g} + b_{1g} + b_{2g} + e_g + 2a_{2u} + b_{1u} + 3e_u$$

Will any of the vibronic transitions i_0^1 be allowed, where i is the number of the normal mode?

Transition	Polarization with vibronic coupling	
	x	(x,y)
${}^1A_{1g} \rightarrow {}^1A_{2g}$	F	A
${}^1A_{1g} \rightarrow {}^1B_{2g}$	A	A
${}^1A_{1g} \rightarrow {}^1E_g$	A	A

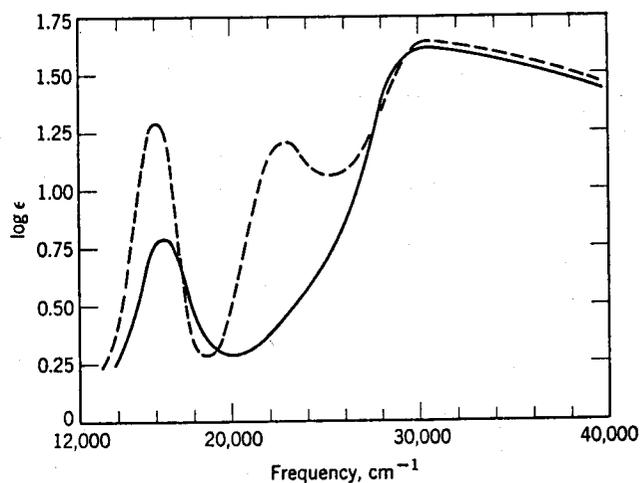


Figure 9.13 Dichroism of $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ after the results of Yamada et al. (*loc. cit*) on $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot 2\text{HCl}\cdot 2\text{H}_2\text{O}$. The full line shows the spectrum with light polarized parallel (or nearly parallel) to the Cl—Co—Cl axis, and the dashed line shows the spectrum with light polarized perpendicular to the Cl—Co—Cl axis.

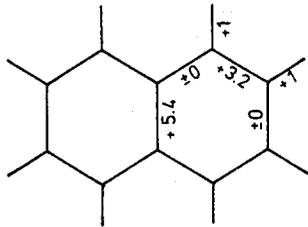
* S. Yamada et al., *Bull. Chem. Soc. Japan*, **25**, 127 (1952); **28**, 222 (1955).

Ground- and excited-state geometry

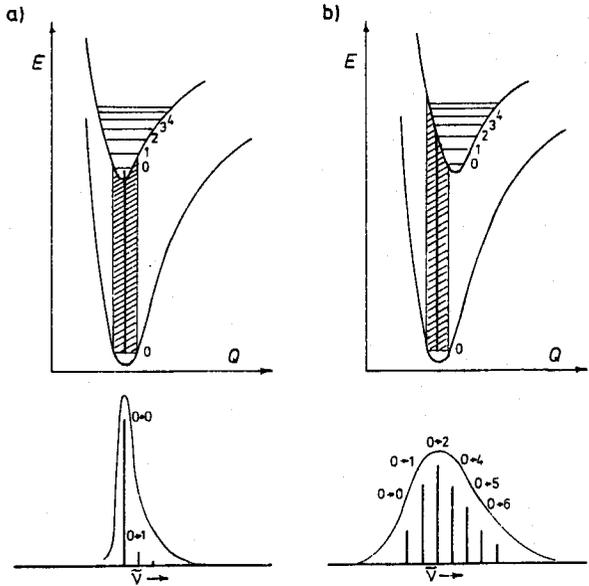
The excitation of an electron from a bonding orbital into a nonbonding (antibonding) orbital changes the bonding situation and thus the equilibrium geometry of the molecule.

Excited-State Geometries, all Distances in pm

	CH ₂ O ^{a,b}				CH≡CH ^c		
	S ₀	S ₁	T ₁		S ₀	S ₁	T ₁
R _{CO}	120.8	132.1	130	R _{C≡C}	120	131.7	135.6
R _{CH}	111.6	109.2	111	∠HCC	180°	130.5°	128.0°
∠HCO	116.5°	121.5°	116°			(trans)	(cis)
φ ^d	0.0	21°	36°				



Bond-length changes of naphthalene (pm) on 310-nm excitation (adapted from Innes, 1975).



Extinction coefficient: Einstein model

Extinction coefficient of absorption:

$$\frac{\epsilon(\nu)}{\nu} = A \frac{f^2(n_D)}{n_D} I(\nu)_{obs}$$

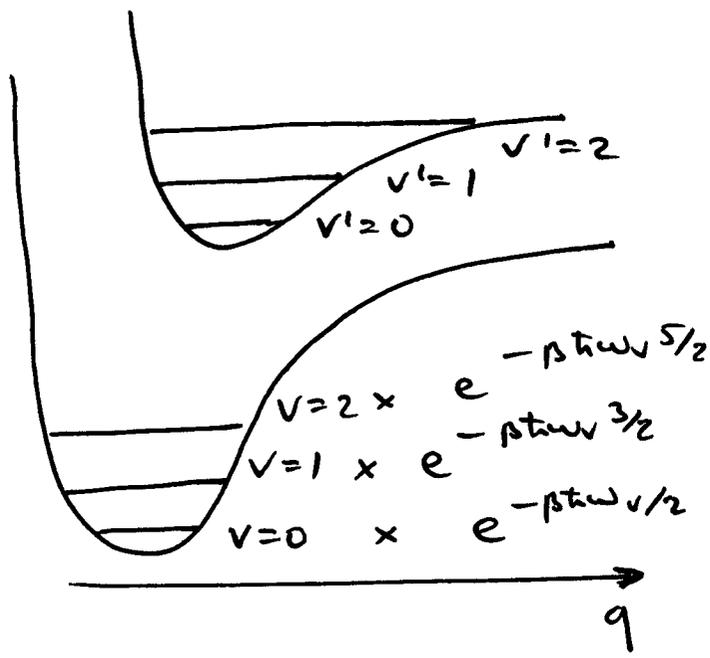
$$A = \frac{8\pi^3 N_A}{3000 \ln(10) c}$$

↓ Avogadro number
 ↑ speed of light

$$f(n_D) = \frac{3n_D^2}{2n_D^2 + 1}$$

The factor n_D accounts for the fact that the light propagating through a medium polarizes electronic shells of the molecules

$$I(\nu)_{obs} = \left\langle \sum_{v'} |\langle \psi_e, \psi_{v'} | \hat{m} | \psi_g, \psi_v \rangle|^2 \delta(\Delta E - h\nu) \right\rangle_v$$



$\sum_{v'}$ summation over the vibrationally excited states

$\langle \dots \rangle_v$ statistical average over the ground-state vibrations

A model with one characteristic vibrational mode is often referred to as Einstein model.

$$\Delta E = \underline{\underline{\Delta E_{00}}} + \hbar\omega_v (v' - v)$$

o-o transition energy

When $\hbar\omega_v \gg kT$, the molecule is in its $v=0$ state, the statistical average over vibrational excitations can be removed. Also,

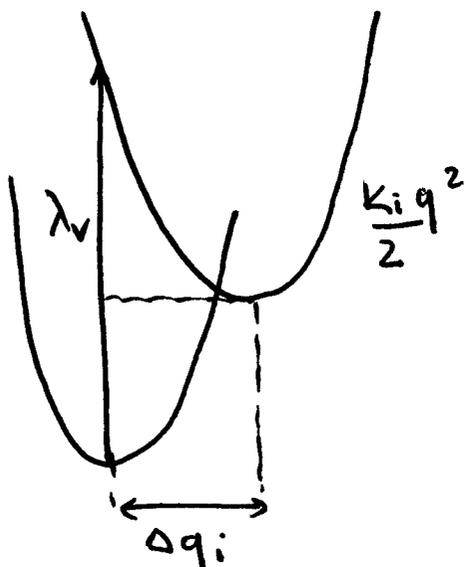
$$\Delta E = \Delta E_{00} + \hbar\omega_v v'$$

The overlap of vibrational wave functions

$$|\langle \Psi_{v'} | \Psi_0 \rangle|^2 = \frac{s^{v'}}{(v')!} e^{-s} \leftarrow \text{Huang \& Rhys, 1950}$$

$$s = \frac{\lambda_v}{\hbar\omega_v} \leftarrow \text{Huang-Rhys factor}$$

$$\lambda_v = \frac{1}{2} \sum_i k_i (\Delta q_i)^2 \leftarrow \text{vibrational reorganization energy}$$



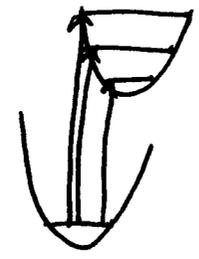
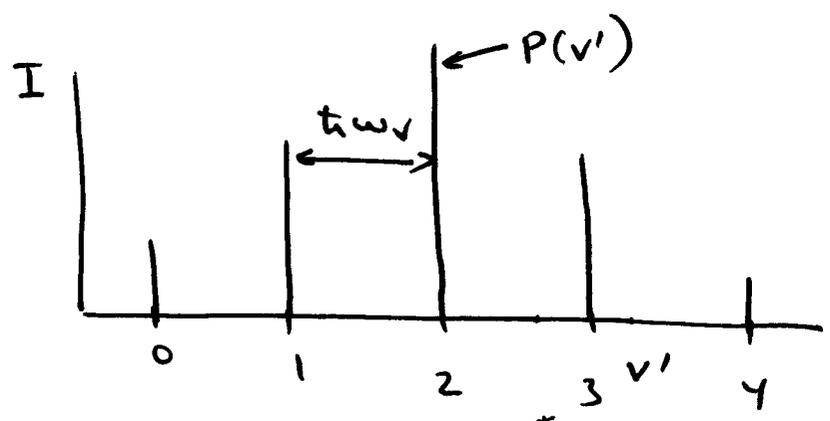
λ_v is the energy invested to stretch the bonds of the molecule in the initial state to the length corresponding to the final state

Vibronic progression

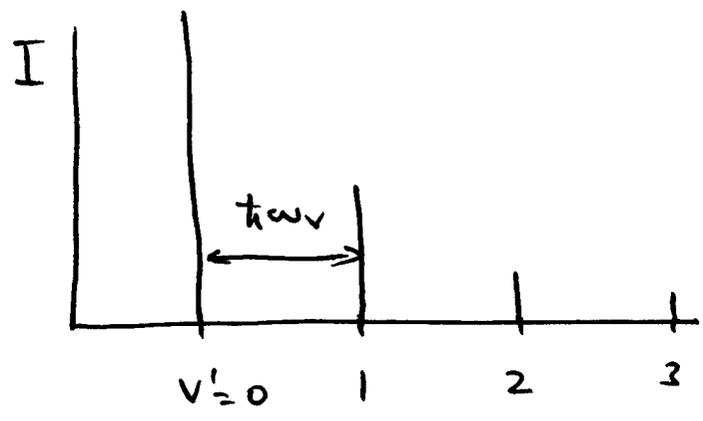
$$I(\nu) = |M_{ec}|^2 e^{-s'} \sum_{v'=0}^{\infty} \frac{(s')^{v'}}{(v')!} \delta(\Delta E_{00} + v' \hbar \omega_v - h\nu)$$

$$P(n) = \frac{a^n}{n!} e^{-a} \leftarrow \text{Poisson distribution}$$

resonance of external radiation energy with vibrational excitations of the excited state



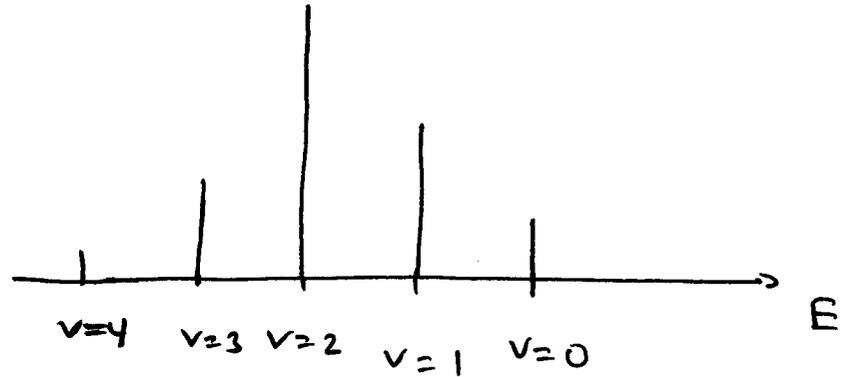
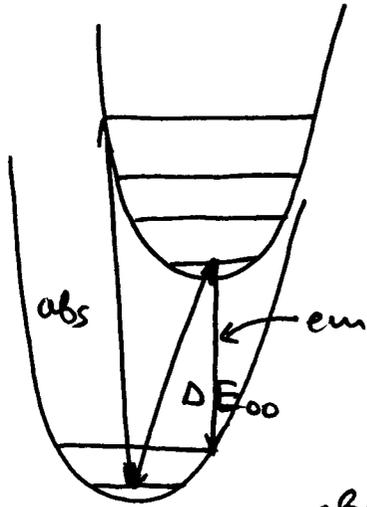
large vibrational reorganization energy



small vibrational reorganization energy

Emission progression

$$I_{em}(\nu) = |M_{ee}|^2 e^{-s} \sum_{v=0}^{\infty} \frac{(s)^v}{v!} \delta(\Delta E_{00} - \nu h\nu - h\nu)$$



absorption: $h\nu_{abs} > \Delta E_{00}$

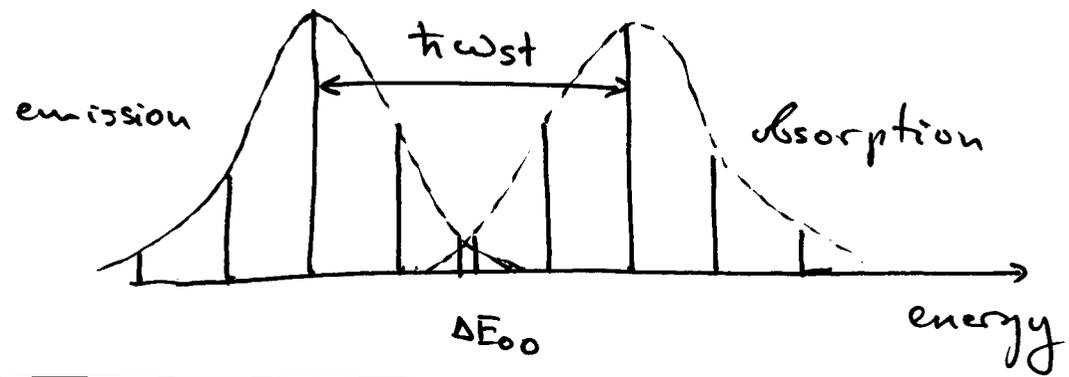
emission: $h\nu_{em} < \Delta E_{00}$

↖ most probable transition energy

The most probable transition frequencies for absorption and emission appear to be shifted relative to each other. The difference of maximum intensity energies of absorption and emission is called the

Stokes shift:

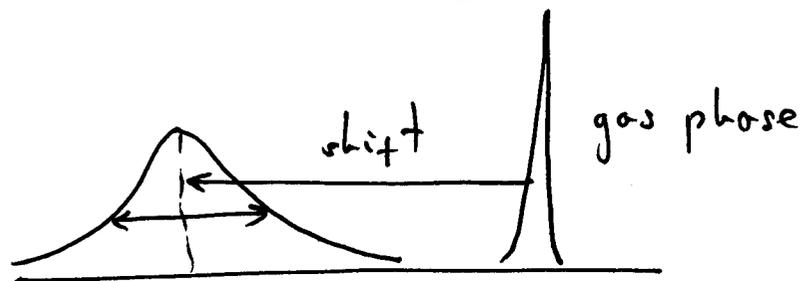
$$h\nu_{abs} - h\nu_{em} = h\nu_{st}$$



The absorption and emission vibronic envelopes are related by mirror symmetry relative to the 00 transition

Spectra in condensed phase

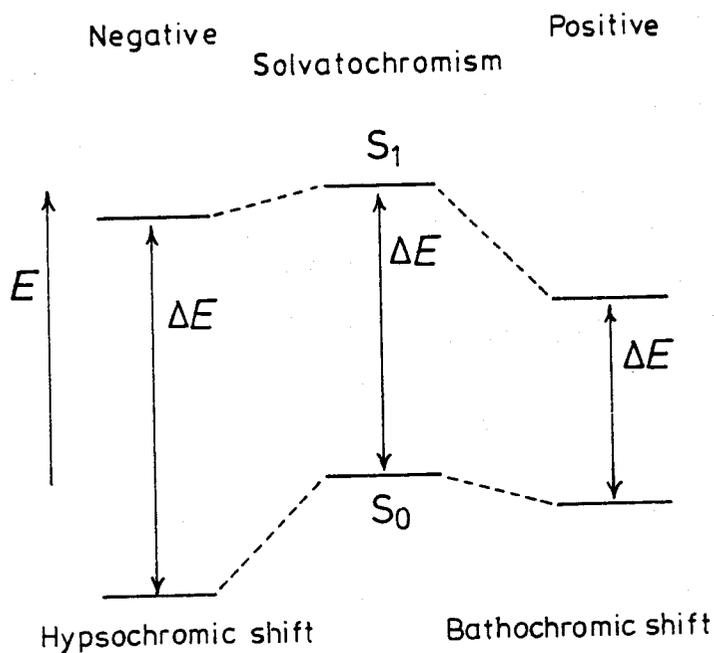
Line shift + Broadening :



width = 100s to 1000s cm^{-1}

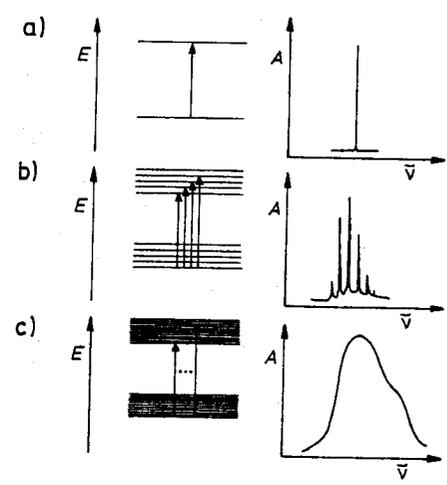
Bathochromic shift = red shift \leftarrow to lower energies
 hyperchromic shift = blue shift \leftarrow to higher energies

Intensity up = hyperchromic effect
 Intensity down = hypochromic effect

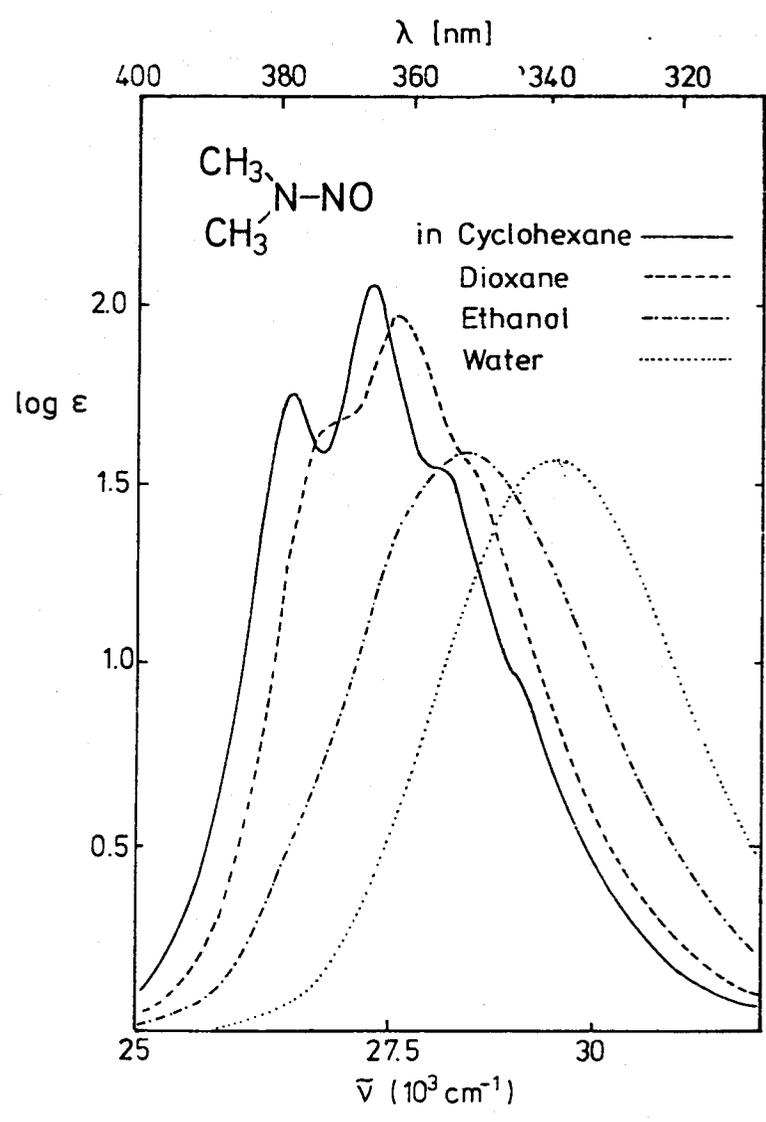


Spectral width

Spectral width goes up with increasing solvent polarity for chromophores possessing the dipole moment.



Atomic and molecular spectra: a) sharp-line absorption typical for isolated atoms in the gas phase, b) absorption band with vibrational structure typical for small or rigid molecules, and c) structureless broad absorption typical for large molecules in solution (adapted from Turro, 1978).



Absorption spectrum of N-nitrosodimethylaniline in different solvents (by permission from Jaffé and Orchin, 1962).

Vibronic progression in condensed-phase solvents

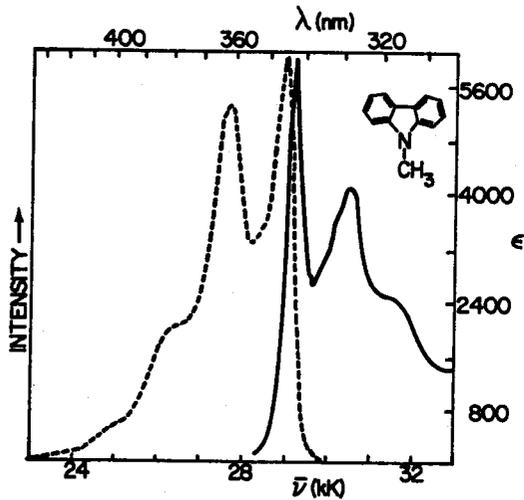


Fig. 5-22. Absorption (solid line) and emission (broken line) spectra of N-methylcarbazole in cyclohexane solution illustrating the approximate mirror image relationship between absorption and emission. From I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, N.Y., 1971.

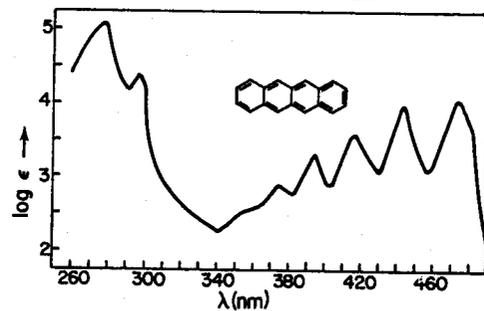


Fig. 5-41. Spectrum of tetracene in benzene solution. From R.A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, N.Y., 1951.

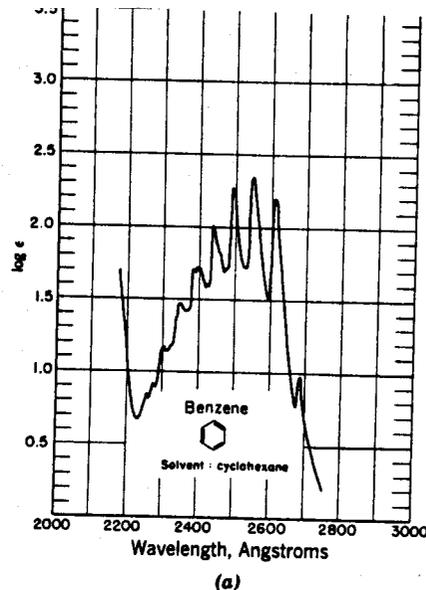


Fig. 12.3 The 1L_b band of benzene, (a) in cyclohexane; (b) as vapor. (Reprinted by permission from R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951.)

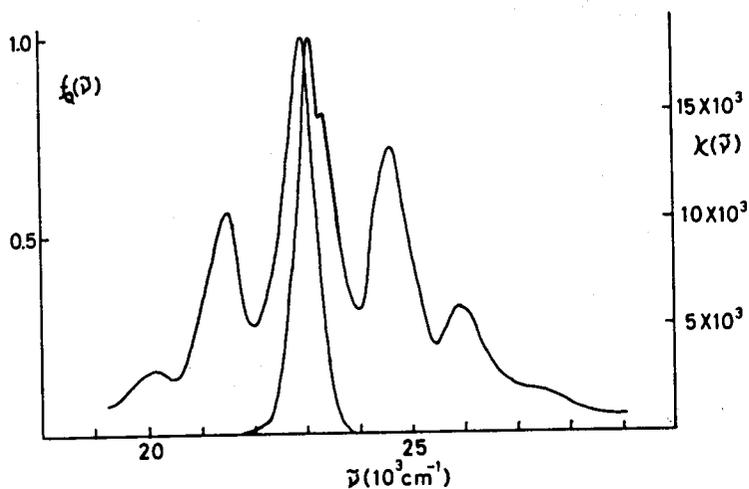
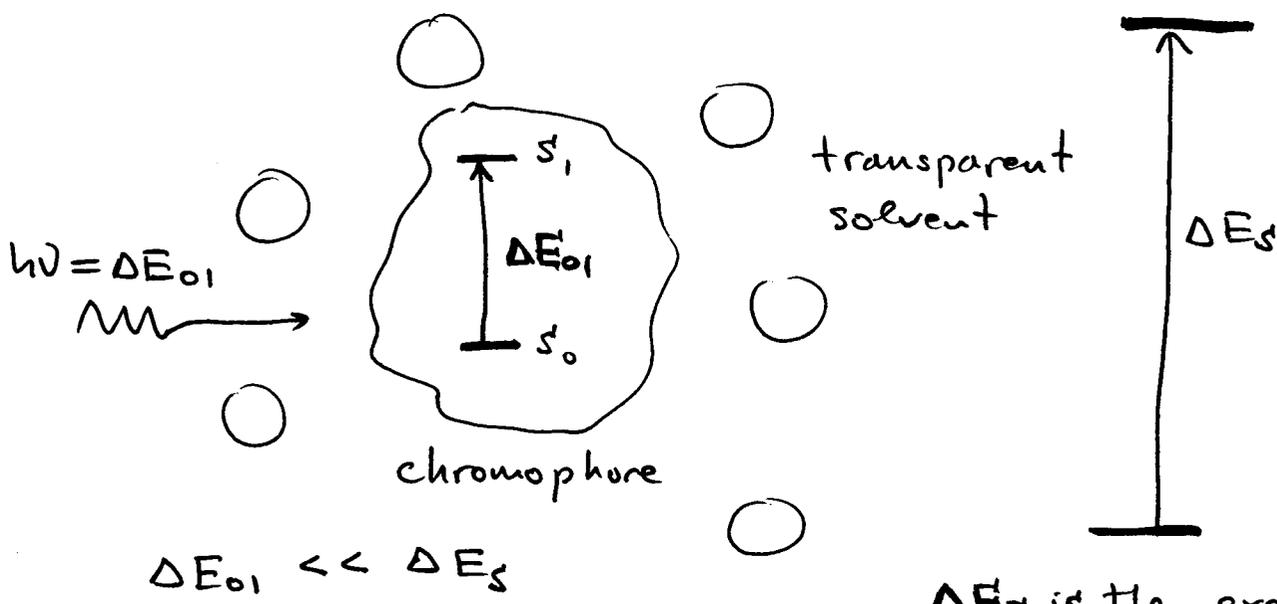


Fig. 3-5. Absorption and fluorescence spectra of perylene in n-hexane solution at room temperature [unpublished measurement by Y. Torihashi and the author (n.m.)].

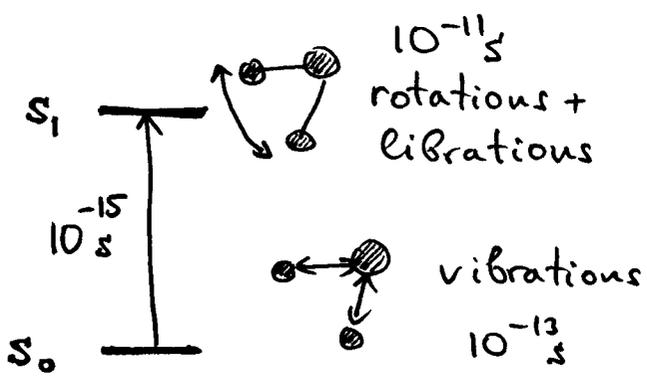
"Fast" and "slow" solvation



ΔE_s is the excitation energy of the solvent molecules

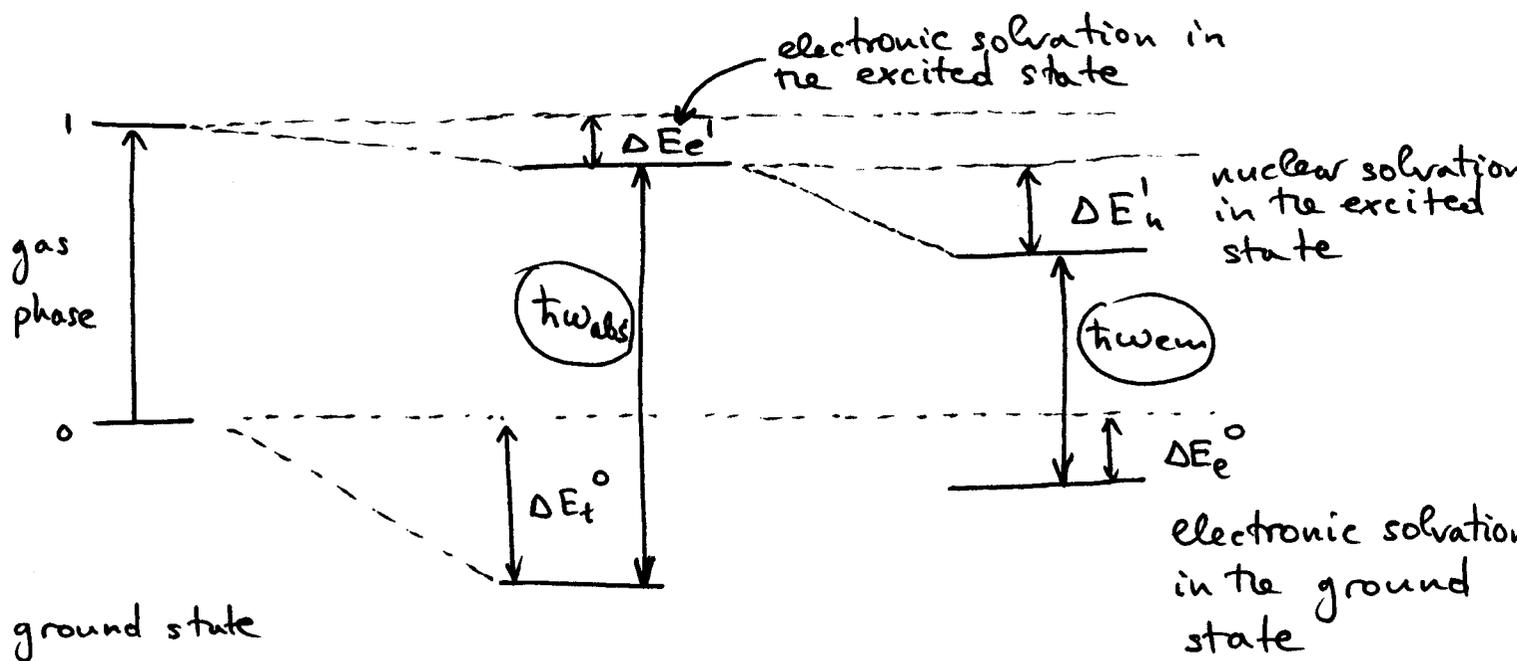
$$\tau_{01} = \frac{\hbar}{\Delta E_{01}} \gg \frac{\hbar}{\Delta E_s}$$

electrons of the chromophore are slower than electrons in the solvent



Nuclear motions are much slower than the transferred electron — they make the slow modes and slow solvation

Transition energies in condensed solvents



$$\Delta E_t^0 = \Delta E_n^0 + \Delta E_e^0$$

interaction with the nuclei of the solvent

interaction with the electrons of the solvent

Absorption energy: $hw_{abs} = \Delta E_{00} + \Delta E_t^0 + \Delta E_e^1$

Emission energy: $hw_{em} = \Delta E_{00} + \Delta E_t^1 + \Delta E_e^0$

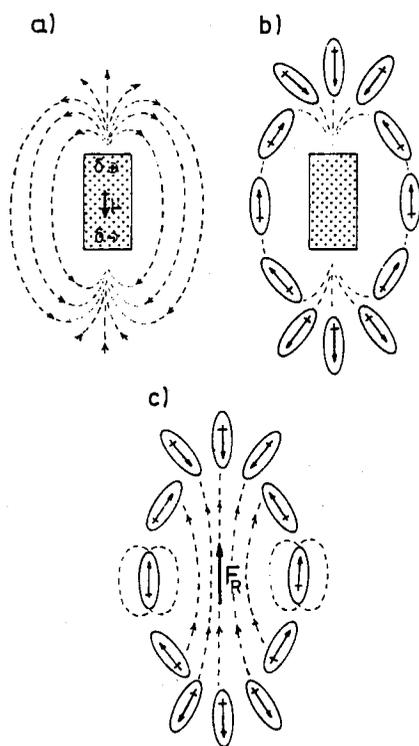
Stokes shift:

$$hw_{st} = \Delta E_t^0 - \Delta E_t^1 + \Delta E_e^1 - \Delta E_e^0 = \underline{\underline{\Delta E_n^0 - \Delta E_n^1}}$$

Stokes shift is a measure of nuclear solvation only.

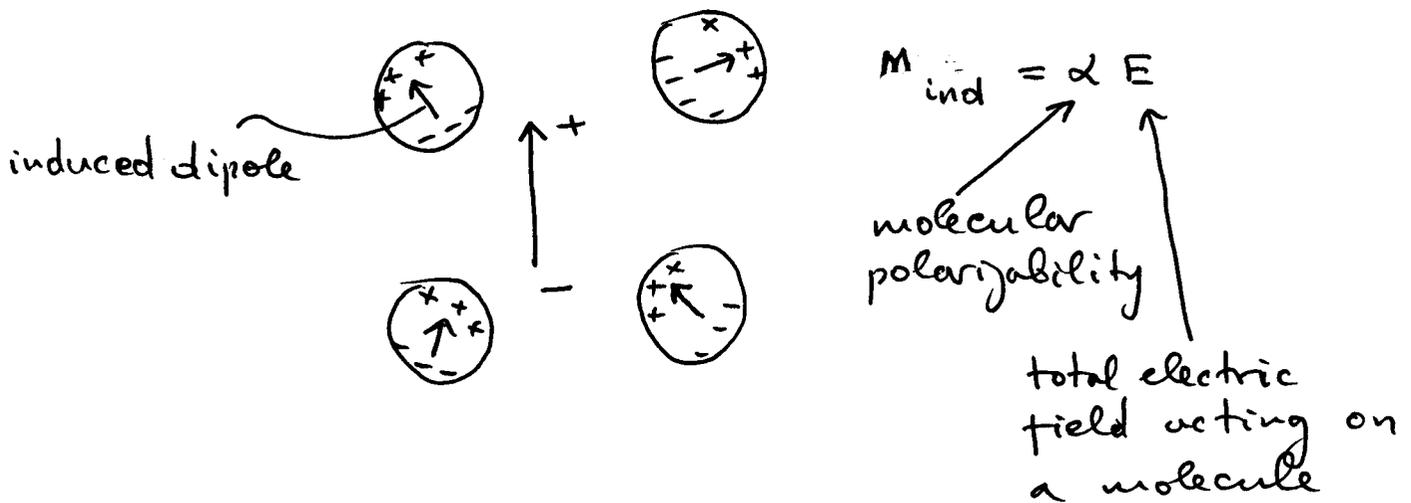
Reaction field of a dipole

Reaction field is the field of the solvent in equilibrium with the solute at the location of the solute point dipole.



Reaction field of a polar solute. a) Dipole field of the isolated molecule, b) orientation of polar solvent molecules parallel to the dipole field, and c) reaction field from the solvent molecules in the cavity if the solute molecule has been removed after freezing all electronic and nuclear coordinates (adapted from Liptay, 1969).

Electronic reaction field



$$\vec{R}_{ind} = \sum_j \vec{E}_{ind,j} (\vec{\mu}_{ind,j})$$

reaction field of the induced dipoles

electric field of the induced dipole

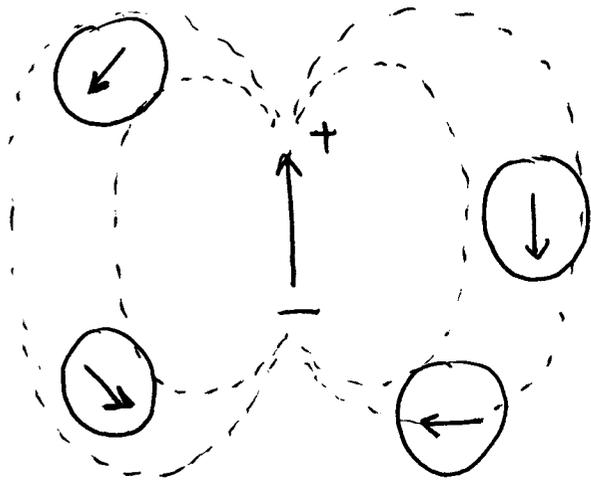
Homework. Estimate the induced dipole of water in the first coordination sphere of Na^+ . Radius of Na^+ is 0.95 \AA , the radius of water molecule is 1.43 \AA , polarizability of water $\alpha = 1.46 \text{ \AA}^3$.

Interaction energy:

$$V_{ind} = - \vec{\mu} \cdot \vec{R}_{ind} = - \mu R_{ind}$$

dipole moment of the chromophore

Nuclear reaction field



$$\vec{R}_n = \sum_j E_j (\vec{m}_j)$$

solvent dipole moment

electric field created
by the j th dipole of
the solvent at the location
of the solute

Interaction energy :

$$V_n = - \vec{m} \cdot \vec{R}_n = - m R_n$$

dipole moment of
the chromophore

Electronic and nuclear solvation

The reaction field is created by polarization of the solvent by the solute. The magnitudes of R_e and R_n are proportional to m (linear response approximation). The direction of $\vec{R}_{e,n}$ coincides with the direction of \vec{m} :

$$\vec{R}_e = a_e \vec{m}$$

↑
electronic response coefficient

$$\vec{R}_n = a_n \vec{m}$$

↑
nuclear response coefficient

Equilibrium solvation of a dipole:

$$E_t = -R_n(m)m - \left(\frac{1}{2}\right) R_e(m)m$$

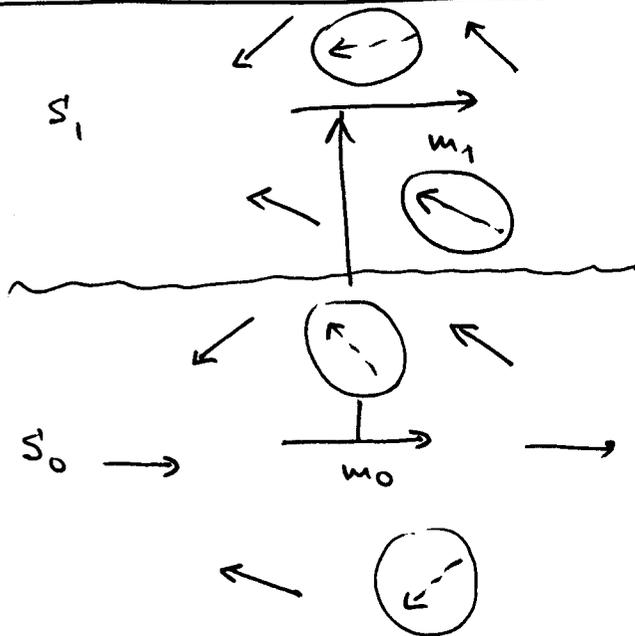
(half of the energy goes into polarizing the solvent)

Energy gap for absorption:

$$\Delta E_{abs} = h\nu_{abs} = \Delta E_{00} - R_n(m_0)\Delta m - \frac{1}{2} R_e(m_1)m_1 + \frac{1}{2} R_e(m_0)m_0$$

$m_1 - m_0$

Absorption shift, emission shift, Stokes shift



Only "fast" induced dipoles change their orientations on the time-scale of electronic transition

$$h\nu_{abs} = \Delta E_{00} - a_n m_0 \Delta m - \frac{1}{2} a_e (m_1^2 - m_0^2)$$

$$h\nu_{em} = \Delta E_{00} - a_n m_1 \Delta m - \frac{1}{2} a_e (m_1^2 - m_0^2)$$

Stokes shift:

$$h\nu_{st} = a_n \Delta m^2$$

Onsager model for dipole solvation:

$$a_n = \frac{2}{R_0^3} \left(\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1} \right)$$

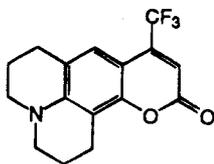
$$a_e = \frac{2}{R_0^3} \frac{n_D^2 - 1}{2n_D^2 + 1}$$

$\epsilon = n_D^2 = \epsilon_\infty$ ← electronic response

$\epsilon = \epsilon_s$ ← total, nuclear + electronic response



Example: Coumarin-153 spectroscopy



Coumarin 153

change in the dipole moment

$$\hbar \omega_{st} = \hbar(\omega_{abs} - \omega_{em}) = \frac{2\overline{\Delta\mu}^2}{R_0^3} \left(\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1} \right)$$

radius of the molecule

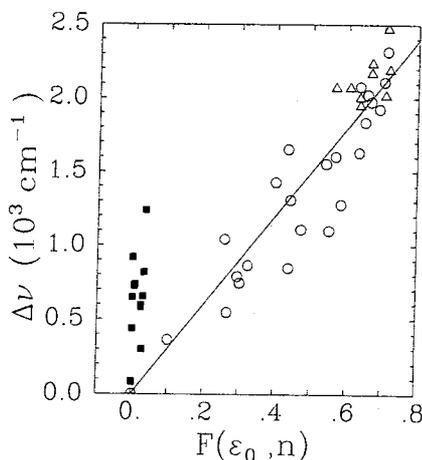


Figure 2. Stokes shift magnitudes $\Delta\nu$ plotted as a function of the reaction field factor $F(\epsilon_0, n)$ defined by eq 1. Simple dipolar solvents are shown as circles, hydrogen-bond-donating solvents as triangles, and nondipolar solvents as filled squares. The line represents the least-squares fit of the open symbols to the proportionality $\Delta\nu = (3.0 \times 10^3 \text{ cm}^{-1})F(\epsilon_0, n)$ [correlation coefficient $R = 0.94$, for $n = 34$ solvents].

$$\leftarrow \frac{\epsilon_s - 1}{\epsilon_s + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}$$

Homework: Using the Stokes shift in acetone, acetonitrile, and chloroform (Table on the next page) determine the radius of coumarin-153 based on the dipole moment change

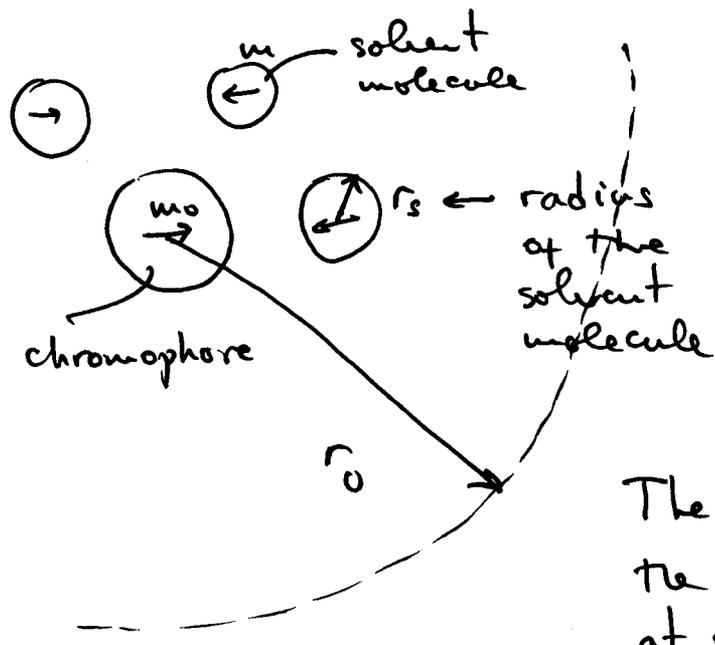
$$\Delta\mu = 7.5D.$$

TABLE 1: Summary of Solvent Properties and Steady-State Spectral Data

solvent	no.	solvent properties ^b						characteristics of steady-state and "time-zero" spectra ^c						Stokes shift ^d
		μ	ϵ_0	n_D	$F(\epsilon_0, n)$	π^*	E_N^T	$\bar{\nu}_{\text{abs}}$	Γ_{abs}	$\bar{\nu}_{\text{em}}$	Γ_{em}	δ_0	Γ_{inh}	
acetonitrile	1	3.53	35.9	1.342	0.71	0.66	0.460	24.38	3.89	18.35	3.27	1.74	1.70	2.32 (10)
propylene carbonate	2	4.94	64.9	1.420	0.70	0.83	0.472	24.05	3.90	18.26	3.27	1.99	1.71	2.11 (10)
propionaldehyde	3	2.54	18.5	1.359	0.63	0.71		24.31	3.87	18.48	3.36	1.69	1.67	2.08 (10)
dimethyl sulfoxide	4	4.06	46.5	1.478	0.66	1.00	0.444	23.74	3.91	18.03	3.32	2.21	1.71	2.02 (12)
dimethylformamide	5	3.24	36.7	1.428	0.67	0.88	0.386	23.95	3.89	18.24	3.26	2.03	1.67	1.98 (13)
nitromethane	6	3.56	35.9	1.380	0.69	0.75	0.481	24.10	3.83	18.37	3.18	1.99	1.61	1.92 (10)
acetone	7	2.69	20.6	1.356	0.65	0.62	0.355	24.41	3.87	18.69	3.30	1.65	1.64	1.84 (11)
methyl acetate	8	1.72	6.7	1.359	0.43	0.49	0.253	24.73	3.83	19.18	3.37	1.32	1.50	1.65 (10)
HMPA	9	4.31	29.3	1.457	0.63	0.87	0.315	23.82	3.84	18.41	3.28	2.25	1.54	1.63 (10)
cyclohexanone	10	3.08	16.1	1.450	0.57	0.68	0.281	24.22	3.79	18.78	3.29	1.76	1.49	1.60 (12)
fluoroform ($\rho = 0.84$)	11	1.65	6.2	1.145	0.54			25.55	3.82	19.87	3.37	0.66	1.47	1.55 (20)
ethyl acetate	12	1.82	6.0	1.370	0.40	0.45	0.228	24.75	3.81	19.36	3.47	1.27	1.43	1.43 (10)
tetrahydrofuran	13	1.75	7.6	1.405	0.44	0.55	0.207	24.69	3.79	19.35	3.36	1.39	1.40	1.31 (12)
benzointrile	14	4.01	25.2	1.526	0.58	0.88	0.333	23.96	3.68	18.75	3.16	2.06	1.24	1.28 (14)
dichloromethane	15	1.14	8.9	1.421	0.47	0.73	0.309	24.21	3.68	19.15	3.20	1.77	1.21	1.11 (13)
1,2-difluorobenzene	16	2.40	14.3	1.443	0.55	0.72	0.265	24.40	3.71	19.40	3.28	1.59	1.25	1.10 (10)
diethylamine	17	1.19	3.9	1.383	0.26	0.35	0.145	25.01	3.73	19.89	3.43	1.02	1.16	1.04 (10)
1,3-difluorobenzene	18	1.58	5.2	1.437	0.32	0.50	0.204	24.72	3.71	19.89	3.31	1.26	1.12	0.86 (10)
1-chlorobutane	19	1.90	7.4	1.400	0.44	0.40		24.57	3.69	19.91	3.35	1.22	1.13	0.85 (10)
chloroform	20	1.15	4.8	1.443	0.29	0.69	0.259	24.37	3.83	19.52	3.20	1.67	1.07	0.79 (12)
diethyl ether	21	1.15	4.2	1.350	0.30	0.24	0.117	25.18	3.72	20.32	3.47	0.84	1.06	0.75 (10)
diisopropyl ether	22	1.38	3.9	1.366	0.27	0.19	0.105	25.26	3.69	20.60	3.41	0.75	0.92	0.55 (10)
1,1,2-TCTF ethane	23	< 4	2.4	1.356	0.10	0.01	0.077	25.61	3.66	21.02	3.46	0.44	0.78	0.36 (10)
2-methylbutane	24	0.00	1.8	1.351	0.00	-0.15	0.006	26.13	3.66	21.74	3.38	0.00	0.00	0.00 (10)
cyclohexane	25	0.00	2.0	1.424	-0.00	0.00	0.006	25.98	3.57	21.75	3.48	0.09	0.00	-0.04 (10)
1,4-dioxane	31	0.45	2.2	1.420	0.03	0.49	0.164	24.96	3.82	19.74	3.35	1.02	1.36	1.24 (10)
1,2,4,5-TFbenzene	32			1.407	0.00			24.90	3.73	20.01	3.34	1.07	1.15	0.92 (10)
1,4-difluorobenzene	33	0.00	2.3	1.441	0.03	0.49	0.176	24.80	3.72	20.00	3.31	1.18	1.10	0.82 (10)
1,4-xylene	34	0.02	2.3	1.493	0.01	0.45	0.074	24.87	3.67	20.07	3.48	1.09	0.99	0.74 (10)
benzene	35	0.00	2.3	1.498	0.01	0.55	0.111	24.77	3.65	20.00	3.31	1.24	1.00	0.72 (10)
hexafluorobenzene	36	0.33	2.1	1.375	0.03	0.27	0.108	25.20	3.71	20.46	3.36	0.83	1.07	0.65 (10)
carbon dioxide ($\rho = 0.80$)	37	0.00	~1.4	1.193	0.00	-0.06	0.030	26.29	4.13	21.24	3.65	-0.06	1.18	0.65 (10)
toluene	38	0.31	2.4	1.494	0.02	0.49	0.099	24.82	3.67	20.20	3.35	1.14	0.97	0.59 (10)
<i>n</i> -butylbenzene	39	0.36	2.4	1.487	0.02			24.92	3.66	20.28	3.41	1.03	0.88	0.58 (10)
1,3,5-trifluorobenzene	40	~0	~2	1.414	0.00	0.18	0.077	25.40	3.72	20.90	3.32	0.54	0.84	0.44 (10)
carbon tetrachloride	41	0.00	2.3	1.460	0.03	0.21	0.052	25.77	3.89	21.61	3.39	0.67	0.65	0.30 (20)
carbon disulfide	42	0.06	2.6	1.627	0.00	0.51	0.065	24.75	3.30	20.43	3.17	1.37	0.52	0.09 (10)
perfluorohexane	43	~0	1.6	1.252	0.00	-0.48		26.45	3.54	22.18	3.54	-0.51	0.19	0.08 (13)
methanol	51	1.7	32.7	1.327	0.71	0.60	0.762	24.02	3.97	17.99	3.07	2.04	1.85	2.47 (10)
ethanol	52	1.66	24.6	1.359	0.67	0.54	0.654	24.08	3.88	18.10	3.18	1.95	1.72	2.23 (17)
1-propanol	53	1.7	20.5	1.384	0.63	0.52	0.617	24.13	3.84	18.30	3.17	1.92	1.53	2.00 (18)
2-propanol	54	1.66	19.9	1.375	0.63	0.48	0.546	24.16	3.81	18.41	3.37	1.89	1.56	1.95 (10)
1-butanol	55	1.75	17.5	1.397	0.61	0.47	0.586	24.12	3.84	18.32	3.18	1.90	1.63	2.07 (11)
1-pentanol	56	1.70	13.9	1.407	0.57		0.586	24.13	3.83	18.35	3.15	1.80	1.60	2.07 (13)
<i>N</i> -methylformamide	57	3.86	182.4	1.447	0.72		0.722	23.99	3.89	17.99	3.24	2.10	1.69	2.19 (15)
ethylene glycol	58	2.31	37.7	1.431	0.67	0.92	0.790	23.54	3.93	17.62	3.12	2.50	1.80	2.17 (30)
formamide	59	3.37	111.0	1.447	0.71	0.97	0.775	23.49	3.93	17.72	3.16	2.60	1.71	2.02 (17)

^a Solvents are sorted into three categories: "simple" dipolar solvents (nos. 1–25), nondipolar solvents (nos. 31–44), and hydrogen-bond-donating solvents (nos. 51–59). "HMPA" and "1,1,2-TCTF ethane" denote hexamethylphosphoramide and 1,1,2-trichlorotrifluoroethane, respectively. Except for fluoroform and carbon dioxide, all solvents are liquids at room temperature. For the former solvents, pressures and temperatures (~35 °C) were chosen to provide near-liquid densities (shown in parentheses in units of g/cm³). ^b Dipole moments (μ [D]), taken mainly from measurements in benzene solution), static dielectric constants (ϵ_0), and refractive indices (n_D) are for 25 °C and were taken from the compilations in: Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986). $F(\epsilon_0, n)$ are the reaction field factors defined by eq 1. The values of the solvatochromic polarity π^* are from ref 9, and E_N^T values are from ref 10. ^c $\bar{\nu}_{\text{abs}}$ and $\bar{\nu}_{\text{em}}$ are the average (first moment) frequencies of the (lowest frequency) absorption and emission bands of C153. Γ_{abs} and Γ_{em} are the full widths at half-maximum of these bands. δ_0 and Γ_{inh} are the parameters that characterize the inhomogeneous line broadening function used to relate the spectrum in a given solvent to that in the reference noninteracting solvent, 2-methylbutane. δ_0 and Γ_{inh} are respectively the shift and full width of the Gaussian function used to represent this line-broadening function. (See refs 5 and 6 for details.) All frequencies are in units of 10³ cm⁻¹. ^d Estimates of the magnitude [10³ cm⁻¹] of the time-dependent Stokes shift $\Delta\nu = \nu(0) - \nu(\infty)$ determined from the difference between the frequencies of "time-zero" spectra and steady-state spectra. In determining these frequencies, we used an average of the first-moment frequencies and the frequencies of the upper frequency half-height points of the spectra. For nondipolar solvents this procedure is more accurate than using the first-moment frequencies alone, as was done in ref 5. The numbers in parentheses indicate the estimated uncertainties in the final digits of these Stokes shifts. Because C153 undergoes an excited-state reaction in carbon tetrachloride, the value of $\Delta\nu$ listed for this solvent was estimated from the correlation between $\Delta\nu$ and Γ_{inh} .⁷

Onsager radius



Onsager radius:

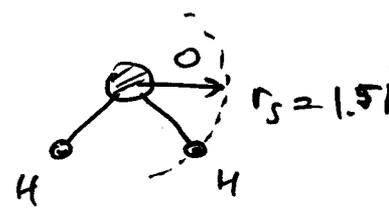
$$\frac{m_0 m}{\epsilon_s r_0^3} = k_B T$$

$$r_0 = \left(\frac{m_0 m}{\epsilon_s k_B T} \right)^{1/3}$$

The Onsager radius defines the characteristic distance at which the solute-solvent interaction is equal to $k_B T$

$m_0 = 10 D, \quad m = 3 D, \quad \epsilon_s = 20 :$

$r_0 = 9 \text{ \AA}$



$N_0 = \rho \cdot V_0 = \frac{4\pi r_0^3}{3} \rho = \eta \left(\frac{r_0}{r_s} \right)^3$
 number of solvent molecules within r_0

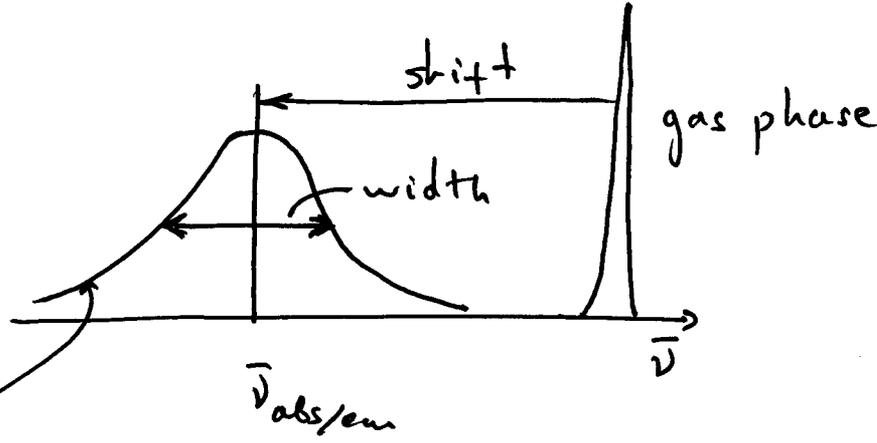
$\eta = \frac{4\pi r_s^3}{3} \rho$ is the packing fraction of liquids or solids,
 $\eta = 0.4 - 0.45$ at room temperature

For the aqueous solution,

$$N_0 = 0.4 \times \left(\frac{9}{1.5} \right)^3 = \underline{\underline{86}}$$

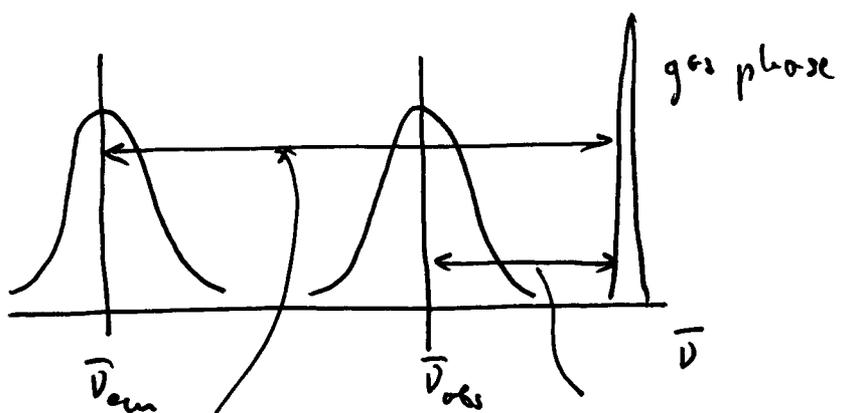
Gaussian Band-shape

Many solvent molecules interact with the solute → the statistics of solvent fluctuations is Gaussian (central limit theorem).



$$G_{obs/em}(\bar{\nu}) = [2\pi\bar{\sigma}^2]^{-1/2} \exp\left[-\frac{(\bar{\nu} - \bar{\nu}_{obs/em})^2}{2\bar{\sigma}^2}\right]$$

$$(\Delta\bar{\nu}_{1/2})^2 = 8 \ln(2) \bar{\sigma}^2$$



$\Delta m > 0$ ← red shift

$\Delta m < 0$ ← blue shift

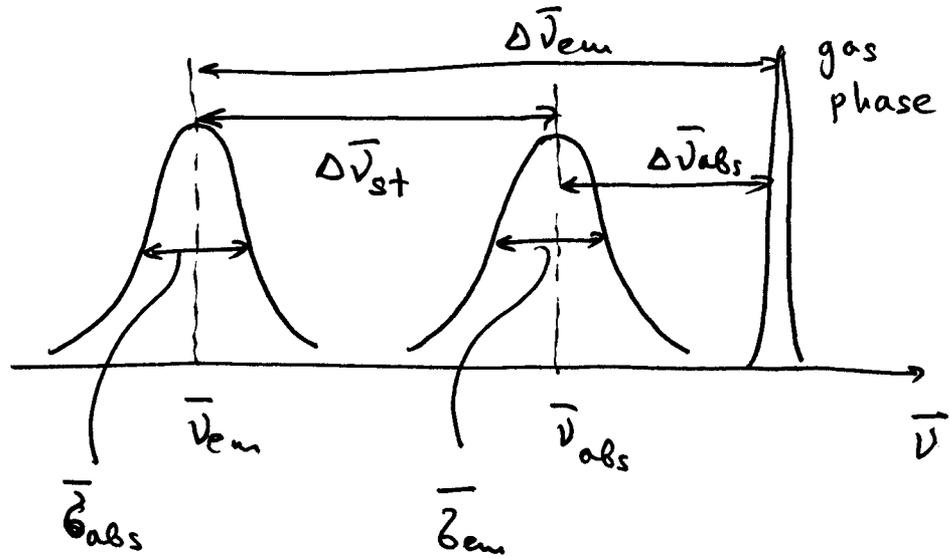
$$\Delta\bar{\nu}_{obs} \approx -a_n m_0 \Delta m$$

$m_1 > m_0$

$$\Delta\bar{\nu}_{em} \approx -a_n m_1 \Delta m$$

Properties of solvent-induced band-shapes

$\Delta u > 0$



$\bar{\nu}_{abs/em}$ refer to the Gaussian line-width

$$\Delta \bar{\nu}_{st} = \frac{a_n \Delta u^2}{hc} = \frac{\bar{\nu}_{abs}^2}{kT} = \frac{\bar{\nu}_{em}^2}{kT}$$

- * Width of absorption = width of emission
- * Stokes shift is directly related to the absorption and emission line-width

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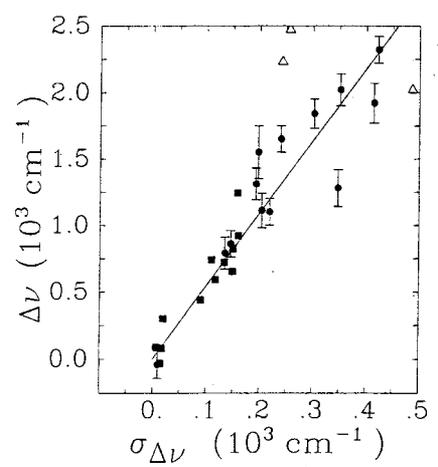
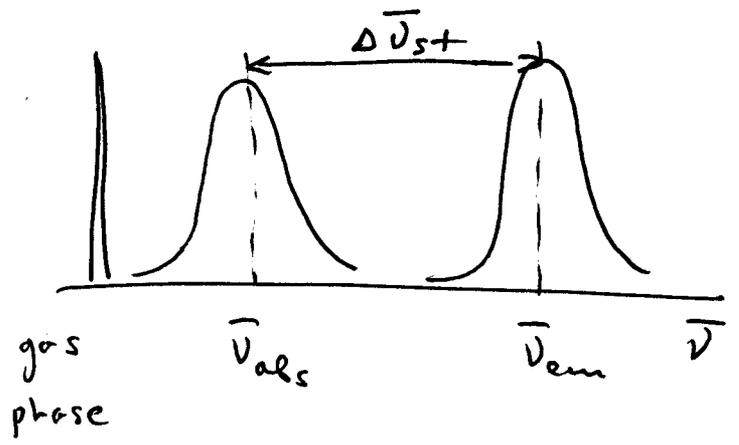
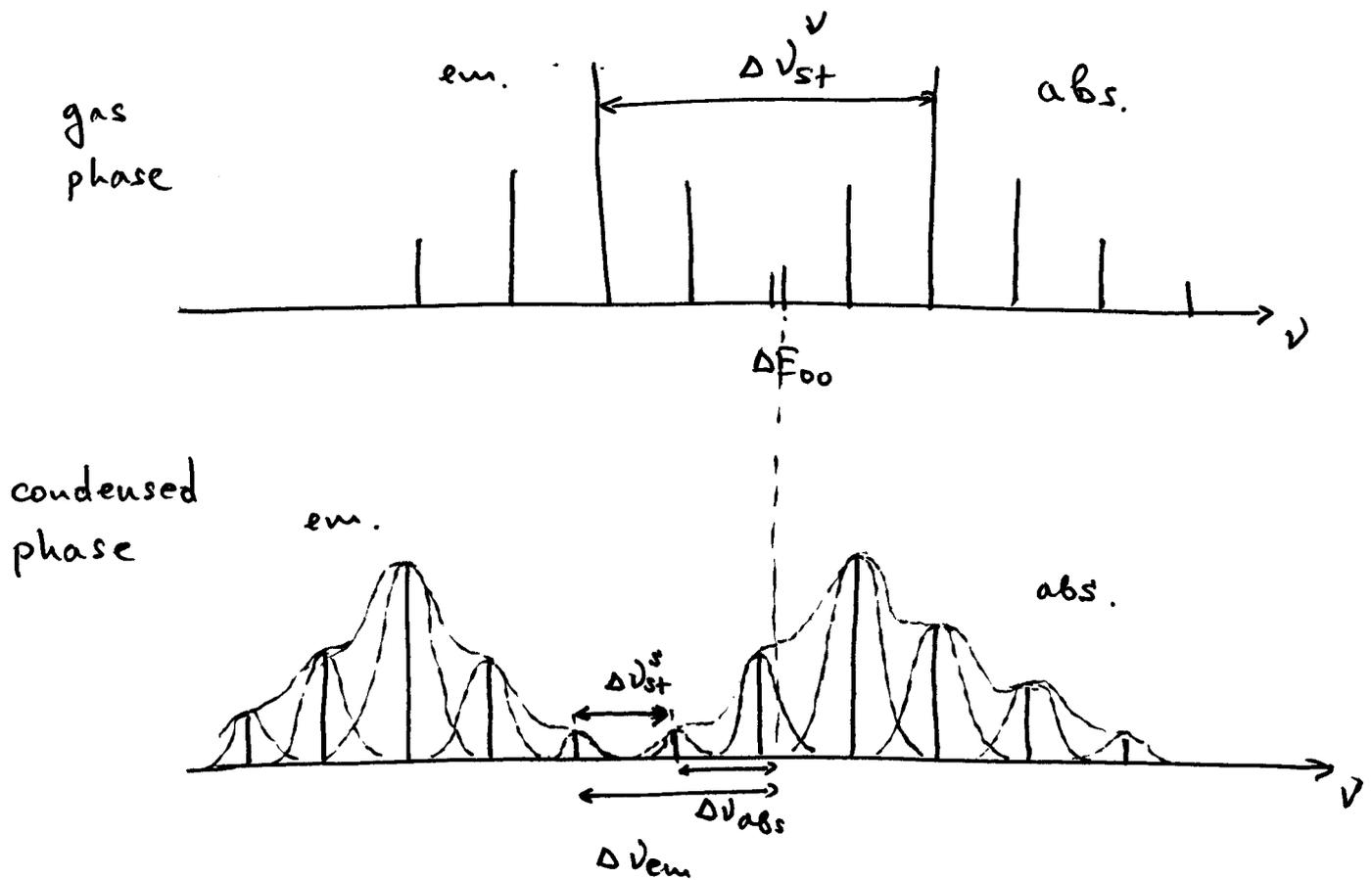


Figure 10. Stokes shift magnitudes $\Delta\nu$ plotted as a function of the width (standard deviation) of the frequency shift distribution, $\sigma_{\Delta\nu}$, calculated from randomly sampled solute-solvent distributions of the sort illustrated in Figure 9. The line drawn here is the best fit of the data shown as filled symbols (i.e., the data excluding the hydrogen-bonding solvents) to the proportionality $\Delta\nu = 0.54\sigma_{\Delta\nu}$ ($R = 0.94$, $n = 26$).

$\Delta u < 0$:



Vibronic bandshape



- * Each vibronic transition is shifted
- * Each vibronic transition is broadened to $\bar{\nu}_{abs/em}$
- * The 0-0 transition splits into the absorption and emission lines separated by the solvent induced Stokes shift $\Delta \nu_{st}^s$
- * The total Stokes shift is the sum of the vibronic and solvent induced component

$$\Delta \nu_{st} = \Delta \nu_{st}^s + \Delta \nu_{st}^v$$

Band-shape function

Gas phase:

$$I_{\text{obs}}(\nu) = |\mu_{ee'}|^2 e^{-s} \sum_{v=0}^{\infty} \frac{s^v}{v!} \delta(\Delta E_{00} + v h\nu_v - h\nu)$$

$$I_{\text{em}}(\nu) = |\mu_{ee'}|^2 e^{-s} \sum_{v=0}^{\infty} \frac{s^v}{v!} \delta(\Delta E_{00} - v h\nu_v - h\nu)$$

Condensed phase: Each sharp vibronic line is replaced by a broad Gaussian function reflecting thermal fluctuations of the surroundings.

$$I_{\text{obs}}(\nu) = |\mu_{ee'}|^2 e^{-s} \sum_{v=0}^{\infty} \frac{s^v}{v!} G(\Delta E_{00} + h\Delta\nu_{\text{obs}} + v h\nu_v - h\nu)$$

$$I_{\text{em}}(\nu) = |\mu_{ee'}|^2 e^{-s} \sum_{v=0}^{\infty} \frac{s^v}{v!} G(\Delta E_{00} + h\Delta\nu_{\text{em}} - v h\nu_v - h\nu)$$

Gaussian function:

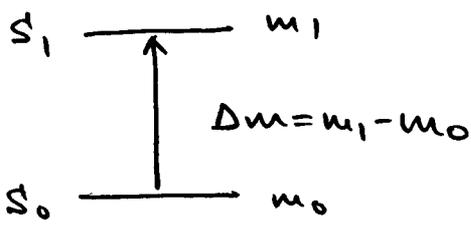
$$G(x) = [2\pi\sigma^2]^{-1/2} \exp\left[-\frac{x^2}{2\sigma^2}\right]$$

Parameters explained

$$G_{abs}^{\nu}(\nu) = [2\pi\beta_{abs}^2]^{-1/2} \exp \left[- \frac{(\Delta E_{00} + h\Delta\nu_{abs} + \nu h\nu_{\nu} - h\nu)^2}{2\beta_{abs}^2} \right]$$

$$G_{em}^{\nu}(\nu) = [2\pi\beta_{em}^2]^{-1/2} \exp \left[- \frac{(\Delta E_{00} + h\Delta\nu_{em} - \nu h\nu_{\nu} - h\nu)^2}{2\beta_{em}^2} \right]$$

Absorption:

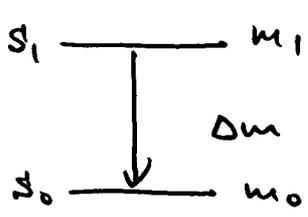


$$h\Delta\nu_{abs} = -a_n \Delta m m_0 - \frac{a_e}{2} (m_1^2 - m_0^2)$$

$$a_n = \frac{2}{R_0^3} \left[\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1} \right]$$

$$a_e = \frac{2}{R_0^3} \frac{n_D^2 - 1}{2n_D^2 + 1}$$

Emission:



$$h\Delta\nu_{em} = -a_n \Delta m m_1 - \frac{a_e}{2} (m_1^2 - m_0^2)$$

$$h\Delta\nu_{st}^s = a_n \Delta m^2$$

Spectral width:

$$\beta_{abs}^2 = \beta_{em}^2 = k_B T h \Delta\nu_{st}^s$$

$$= k_B T a_n \Delta m^2$$

Integrated Intensity

$$\int_{-\infty}^{\infty} G(x) dx = 1$$

$$\int_{-\infty}^{\infty} I_{\text{obs/em}}(\nu) d\nu = |m_{ee'}|^2 e^{-s} \sum_{n=0}^{\infty} \frac{s^n}{n!} \times$$

$$\times \int_{-\infty}^{\infty} G(\Delta E_{00} + h \Delta \nu_{\text{obs/em}} \pm n h \nu - h \nu) \frac{h d\nu}{h}$$

$$= \frac{|m_{ee'}|^2}{h} e^{-s} \underbrace{\sum_{n=0}^{\infty} \frac{s^n}{n!}}_{e^s} = \frac{|m_{ee'}|^2}{h}$$

$$\frac{\epsilon(\nu)}{\nu} = A \frac{f^2(\nu_D)}{n_D} I_{\text{obs}}(\nu)$$

$$\int_0^{\infty} \frac{\epsilon(\nu)}{\nu} d\nu = A \frac{f^2(\nu_D)}{n_D} \frac{|m_{ee'}|^2}{h}$$

$$|m_{ee'}|^2 = \frac{3000 \ln(10) h c}{8 \pi^3 N_A} \frac{n_D}{f^2(\nu_D)} \int_0^{\infty} \frac{\epsilon(\nu)}{\nu} d\nu$$

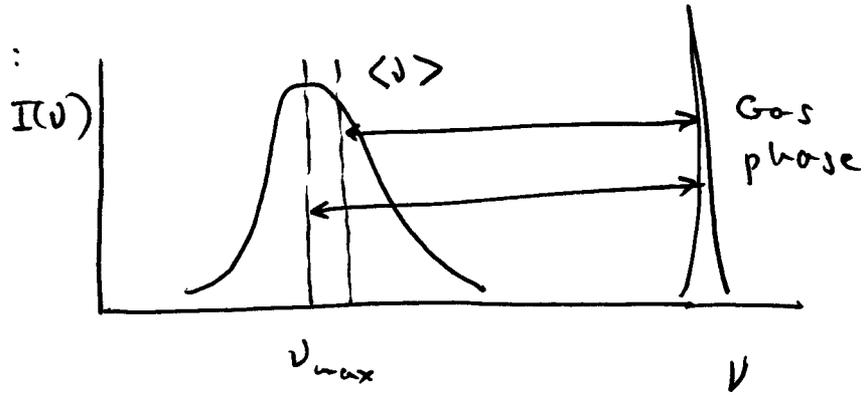


→ / ν

→ Integrate → |m_{ee'}|
 transition dipole moment

Solvent dependence of the spectral shift

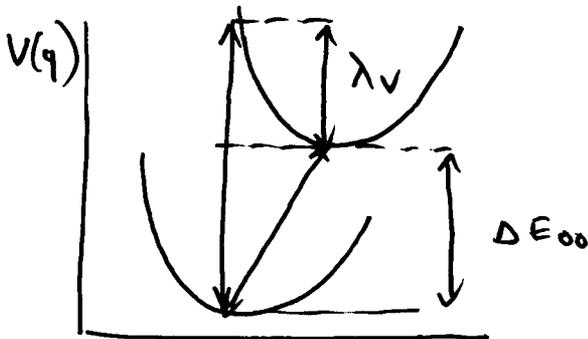
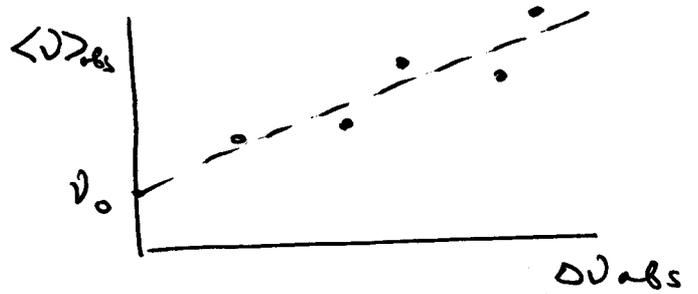
Spectral shift:



ν_{max} is the frequency at the maximum, not a well-defined parameter.

$$\langle \nu \rangle = \frac{\int I(\nu) \nu d\nu}{\int I(\nu) d\nu} \quad \leftarrow \text{first spectral moment}$$

$$\langle \nu \rangle_{obs} = \nu_0 + \Delta \nu_{abs}$$



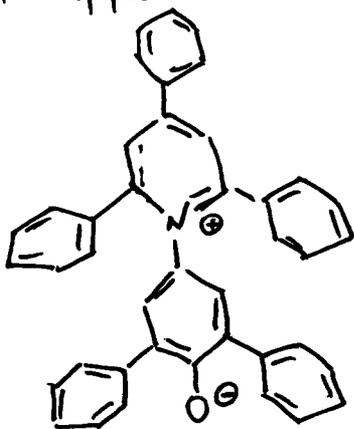
$$h\nu_0 = \Delta E_{00} + \lambda_\nu$$

$$\langle \nu \rangle = \frac{\int \nu e^{-s} \sum_n \frac{s^n}{n!} \delta(\Delta E_{00} + n h \nu_\nu - h\nu) d\nu}{\int e^{-s} \sum_n \frac{s^n}{n!} \delta(\Delta E_{00} + n h \nu_\nu - h\nu) d\nu}$$

$$= e^s \sum_{n=0}^{\infty} \frac{s^n}{n!} \left(\frac{\Delta E_{00}}{h} + n \nu_\nu \right) = \frac{\Delta E_{00}}{h} + \nu_\nu s = \frac{\Delta E_{00} + \lambda_\nu}{h}$$

Example: Steady-state spectroscopy of Betaine-30

Spectroscopy of Betaine-30 is used to calibrate a solvent polarity scale to describe the solvent effect on chemical reactivity



$$m_0 = 14.8 \text{ D}$$

$$m_1 = 6.2 \text{ D}$$

$$R_0 = 6 \text{ \AA}$$

$$\chi_V = 0.4 \text{ eV}$$

$$\bar{\omega}_V = 1500 \text{ cm}^{-1}$$



Solvent dependence:

Solvent	ϵ	n_D	$h\nu_{abs}$, kcal/mol
Ph Me	2.4	1.494	33.90
CHCl_3	4.8	1.443	39.10
Me_2CO	20.6	1.356	42.20
DMSO	46.5	1.478	46.0

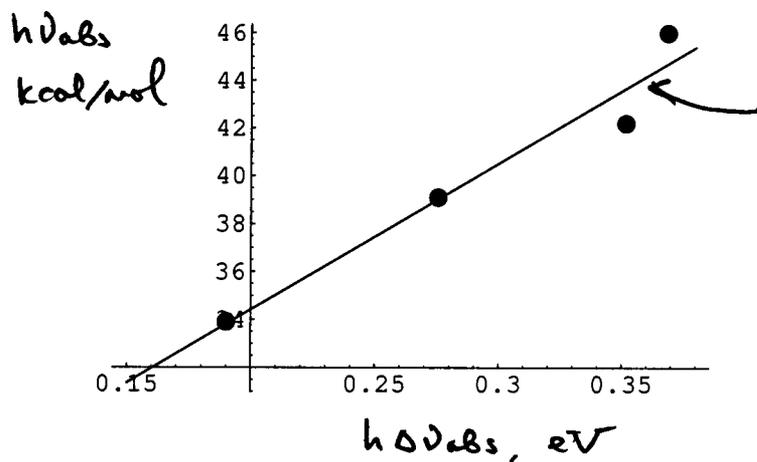
Vacuum energy gap

$$h\nu_{abs} = \Delta E_{00} + h \frac{\Delta \bar{\nu}_{st}^v}{2} + h \Delta \nu_{abs}$$

$$h \Delta \nu_{st}^v = 2 \lambda \nu$$

$$h\nu_{abs} = \Delta E_{00} + \lambda \nu + h \Delta \nu_{abs}$$

solvent-induced shift



regression
 $22.2 + 61.1x$
 ↑
 $\Delta E_{00} + \lambda \nu$

$$\Delta E_{00} + \lambda \nu = \frac{22.2}{23.06} \text{ eV} = 0.963 \text{ eV}$$

Assumption: $\lambda \nu = 0.4 \text{ eV}$
 $\bar{\nu}_v = 1500 \text{ cm}^{-1}$

$$\Delta E_{00} = 0.56 \text{ eV}$$

Band-shape in DMSO

DMSO = dimethyl sulfoxide

$$I_{\text{abs/em}}(\nu) = e^{-s} \sum_{n=0}^{\infty} \frac{s^n}{n!} \frac{1}{[2\pi k_B T \hbar \Delta\nu_{st}^s]^{1/2}} \times$$

$$\times \exp \left[- \frac{(\Delta E_{00} \pm n h \nu_{st} + \hbar \Delta\nu_{\text{abs/em}} - h \nu)^2}{2 k_B T \hbar \Delta\nu_{st}^s} \right]$$

$I_{\text{abs/em}}(\nu)$ is normalized to the energy integration:

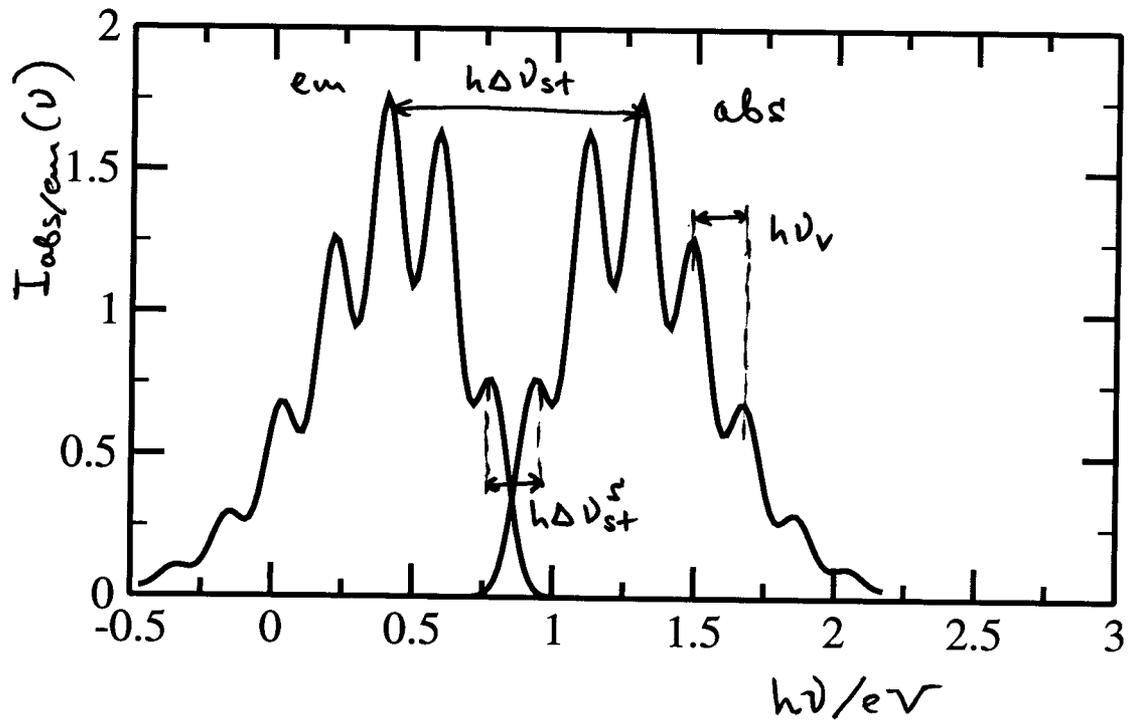
$$\int_{-\infty}^{\infty} I_{\text{abs/em}}(\nu) h d\nu = 1, \quad [I_{\text{abs/em}}] = \frac{1}{\text{energy}}$$

Parameters:

$$s = \frac{\lambda_{\nu}}{h \nu_{st}} = \frac{0.4 \text{ eV}}{1500 \text{ cm}^{-1}} \times 8065 \frac{\text{cm}^{-1}}{\text{eV}} = 2.15$$

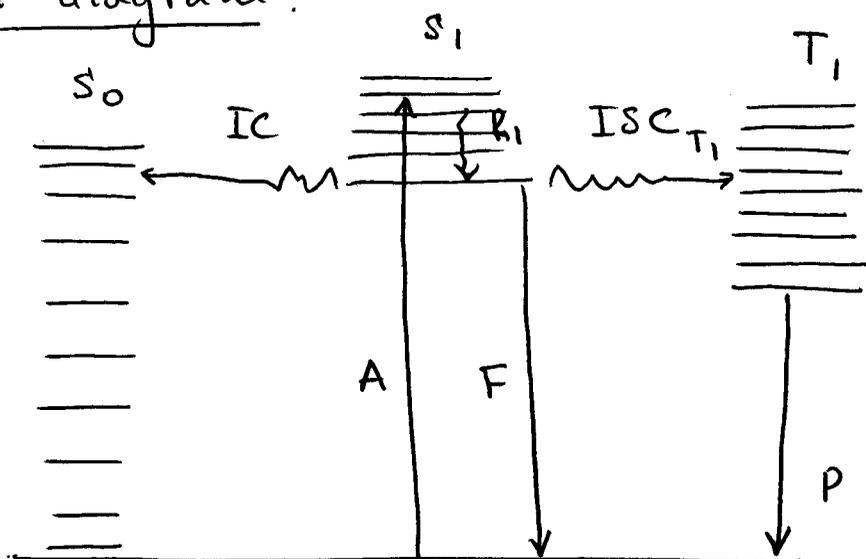
$$\hbar \Delta\nu_{st}^s = \frac{2}{R_0^3} \left[\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1} \right] \Delta\omega^2 = 0.16 \text{ eV}$$

Absorption/Emission Profiles



The Fate of Absorbed Energy

Jablonski diagram:



A = absorption P = phosphorescence ($10^{-4} - 10^2$ s)

F = fluorescence (10^{-8} s) ISC = intersystem crossing

IC = internal conversion

R = vibrational relaxation ($10^{-11} - 10^{-9}$ s)

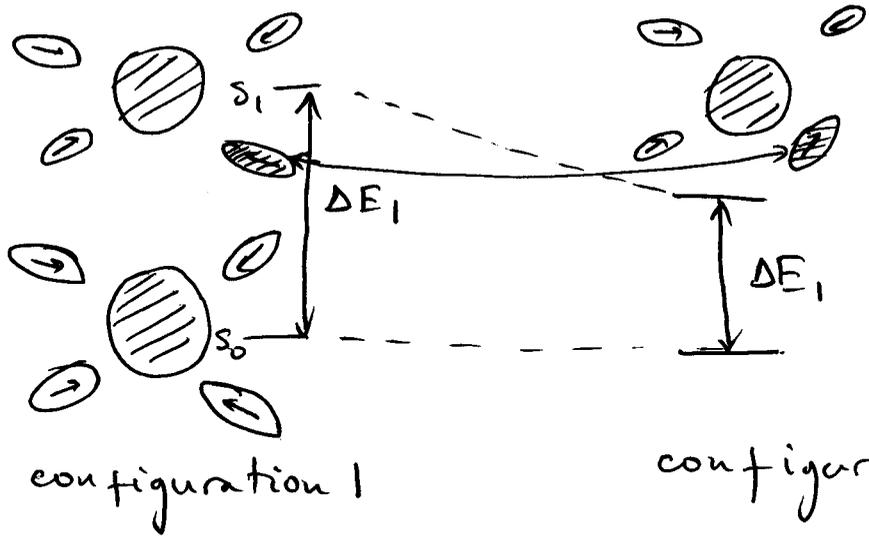
A, F, P ← radiative processes

IC, ISC, R ← non-radiative processes

F = radiative emission involving no change in spin multiplicity

P = radiative emission accompanied by a change of spin multiplicity

Spectroscopic "reaction coordinate"



* Thermal fluctuations of the solvent and classical motions of the solute alter the energy gap between the ground and excited electronic states

ΔE (nuclear configuration) ← spectroscopic "reaction coordinate"

Marcus-Hush picture: Gaussian noise of the energy gap

$\Delta E(q) = \Delta E_{00} - \alpha q$

$F = \frac{kq^2}{2}$

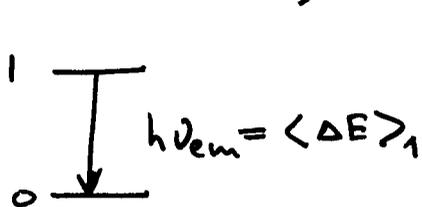
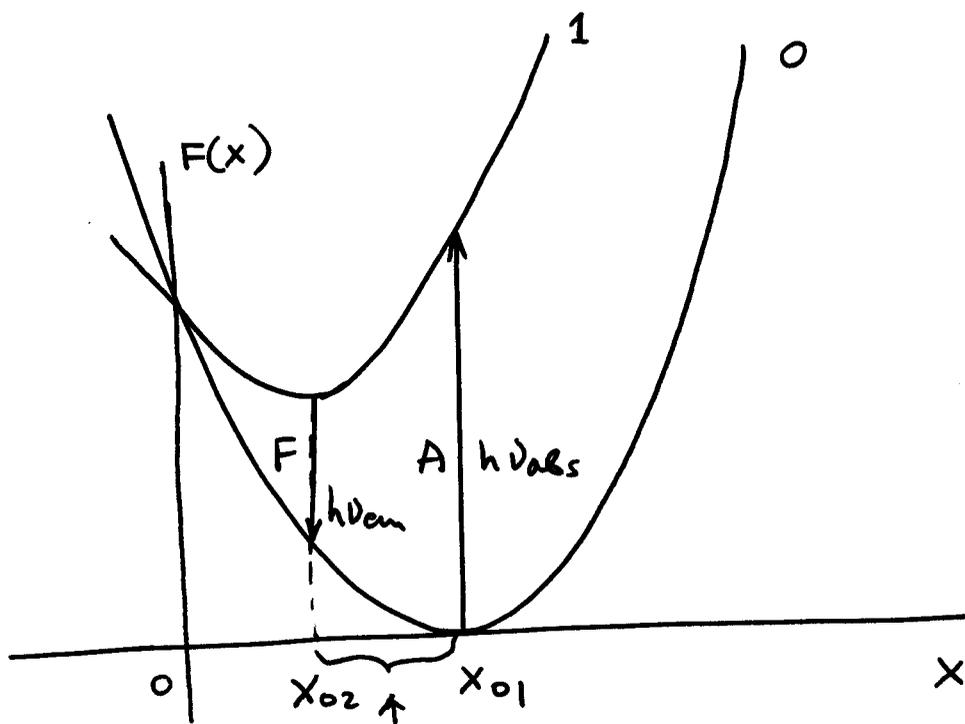
free energy invested to create a fluctuation of the nuclear coordinates

Picture of parabolic surfaces

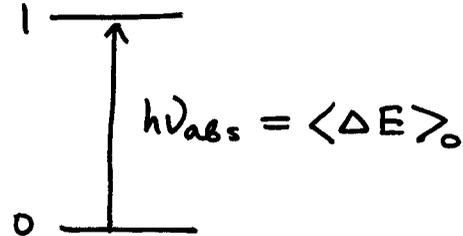
$\Delta E = X \leftarrow$ energy gap

$F(x) \leftarrow$ free energy of the system (chromophore + solvent) with the energy gap X

$P(x) = \frac{e^{-F(x)/k_B T}}{\int e^{-F(x)/k_B T} dx} \leftarrow$ Boltzmann probability to have the energy gap X



$h\nu_{st}^s$

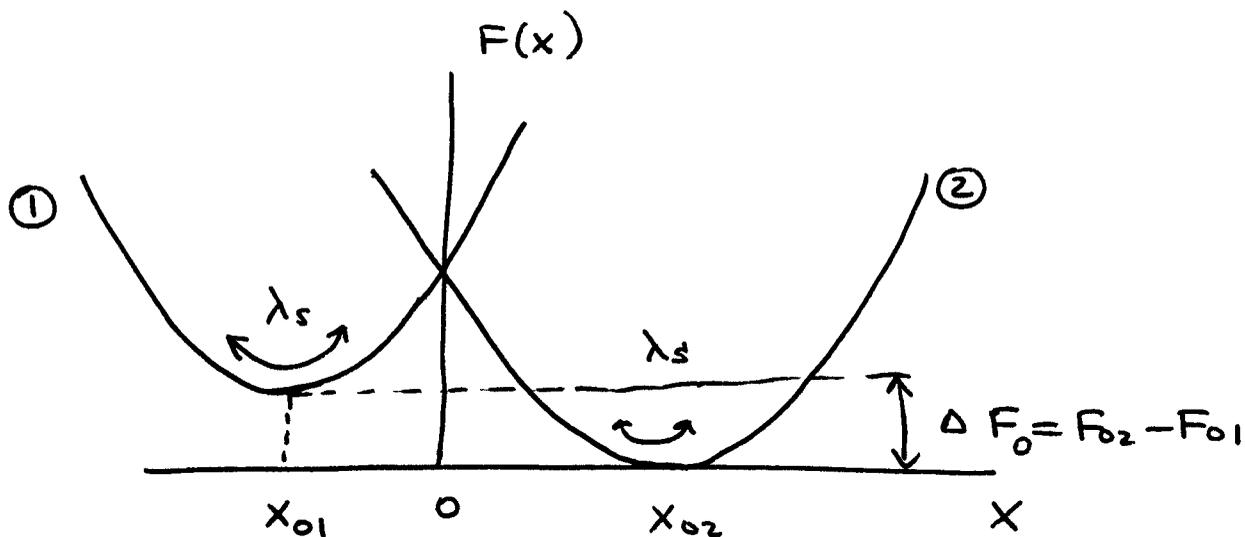


Solvent (classical) Stokes shift

Marcus - Hush parabolas

$$F_1(x) = \frac{(x - x_{01})^2}{4\lambda_s} + F_{10}$$

$$F_2(x) = \frac{(x - x_{02})^2}{4\lambda_s} + F_{02}$$



λ_s defines the curvature of each parabola:

$$\frac{1}{2\lambda_s} = \frac{d^2 F_{1,2}}{dx^2}$$

ΔF_0 is the difference in equilibrium free energies in the excited and ground states (driving force)

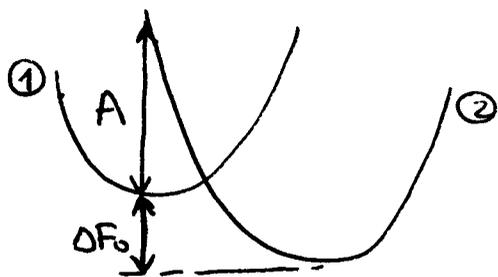
$$x_{02} - x_{01} = 2\lambda_s = h \Delta \nu_{st}^s$$

$$\lambda_s = \frac{h \Delta \nu_{st}^s}{2}$$

λ_s is called the classical (solvent) reorganization energy

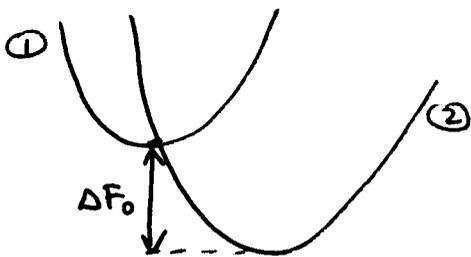
Classification

Charge transfer = electronic transition in which the electronic density is re-distributed within a molecule



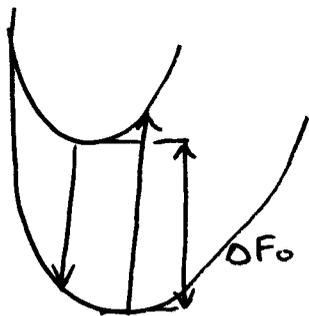
$$\underline{\underline{-\Delta F_0 < \lambda}}$$

Normal region of charge transfer
Only absorption transition is observed



$$\underline{\underline{-\Delta F_0 = \lambda}}$$

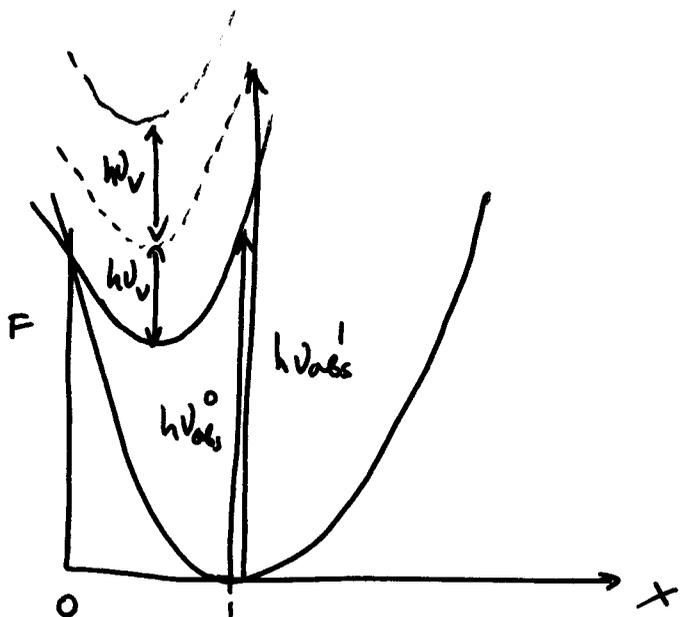
Activationless charge transfer
(absorption is possible only in the final state)



$$\underline{\underline{-\Delta F_0 > \lambda}}$$

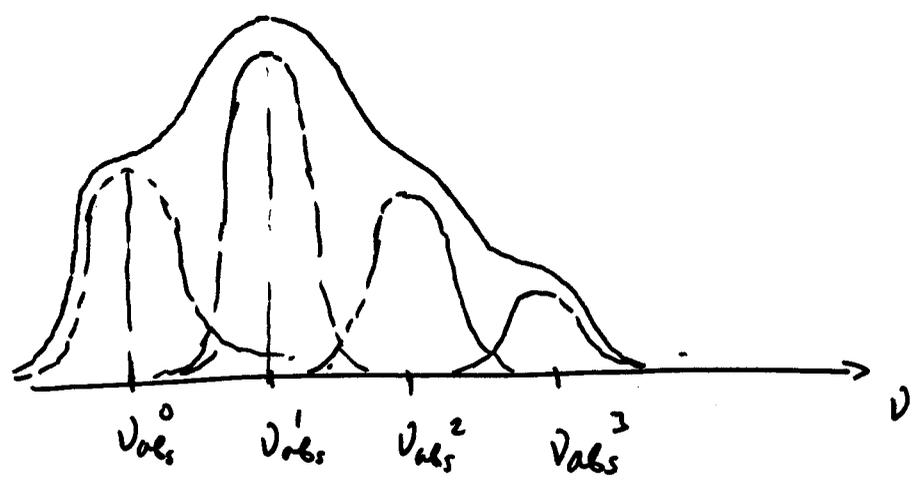
Inverted region of charge transfer
Both absorption and emission transitions are possible

Connection to spectroscopic Band-shape



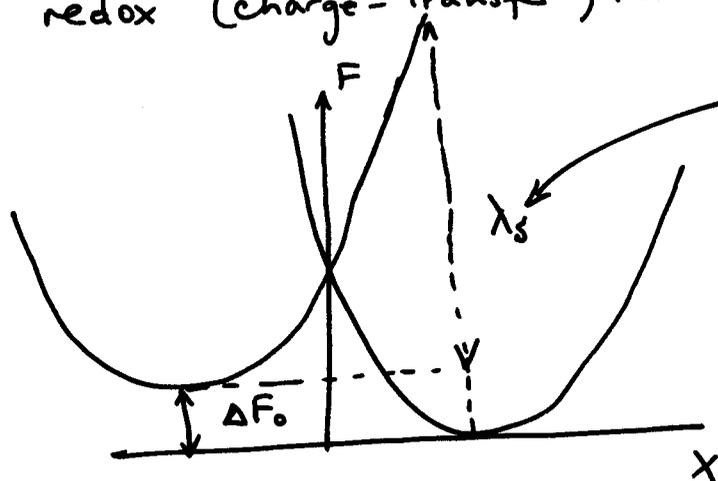
$$P(x) \propto e^{-F(x)} = e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

The band-shape is a sum of all vibronic transitions:



Spectroscopy and rates of radiationless transitions

Spectroscopy can be directly used to predict rates of redox (charge-transfer) reactions



The reorganization energy is equal to the energy supplied to produce the equilibrium energy gap of the final state when the molecule is in its initial state

When A and F are available:

$$\Delta F_0 = \frac{h\nu_{abs} + h\nu_{em}}{2}$$

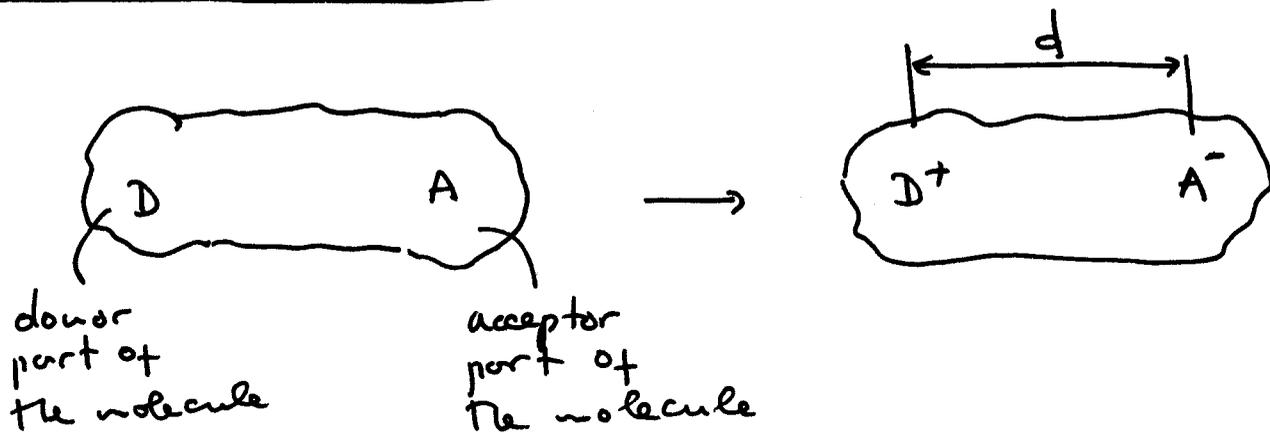
$$\Delta F_0 = \Delta G_{ro} + \text{Coulomb energy}$$

difference of redox potentials of the donor and acceptor of the electron

Reorganization energy:

$$\lambda_s = \frac{h\Delta\nu_{st}^2}{2} = \frac{\beta_{abs}^2}{2k_B T} = \frac{\beta_{em}^2}{2k_B T}$$

Rates of redox reactions



Rate of charge transfer in the Marcus-Hush formulation:

$$k_{ET} = \frac{2\pi}{\hbar} |H_{12}|^2 \frac{1}{(4\pi\lambda_s k_B T)^{1/2}} \exp \left[-\frac{\Delta F^2}{4\lambda_s k_B T} \right]$$

Mulliken-Hush relation

$$H_{12} = \frac{m_{12} \hbar v_{abs}}{ed}$$

$\hbar v_{abs}$

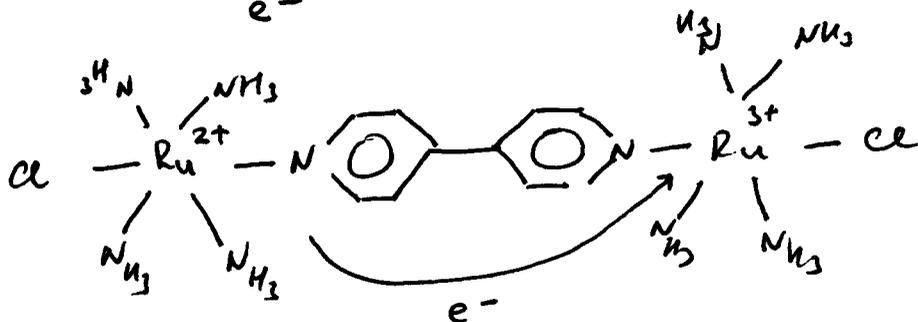
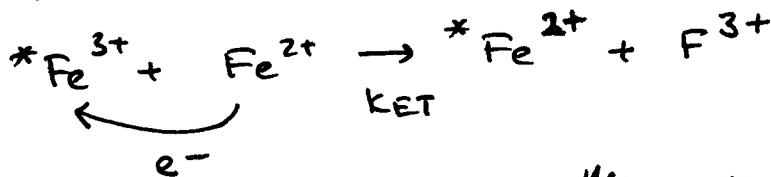
$2\lambda_{abs}^2$

Rate in terms of spectroscopic observables:

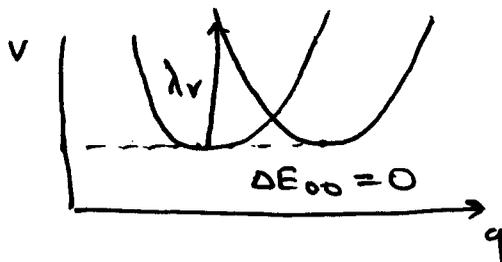
$$k_{ET} = \frac{2\pi}{\hbar} \left(\frac{m_{12} \hbar v_{abs}}{ed} \right)^{1/2} \frac{1}{(2\pi \lambda_{abs}^2)^{1/2}} e^{-\frac{(\hbar v_{abs})^2}{2\lambda_{abs}^2}}$$

Rate of electron self-exchange and absorption profile

Self-exchange is electronic transition (redox reaction) between equal donor and acceptor sites:



Gas phase:



Condensed phase:

$$I_{abs}(0) = e^{-s} \sum_{n=0}^{\infty} \frac{s^n}{n!} \frac{1}{(4\pi\lambda_s k_B T)^{1/2}} \exp\left[-\frac{(\lambda_s + n h\nu_r - h\nu)^2}{4\lambda_s k_B T}\right]$$

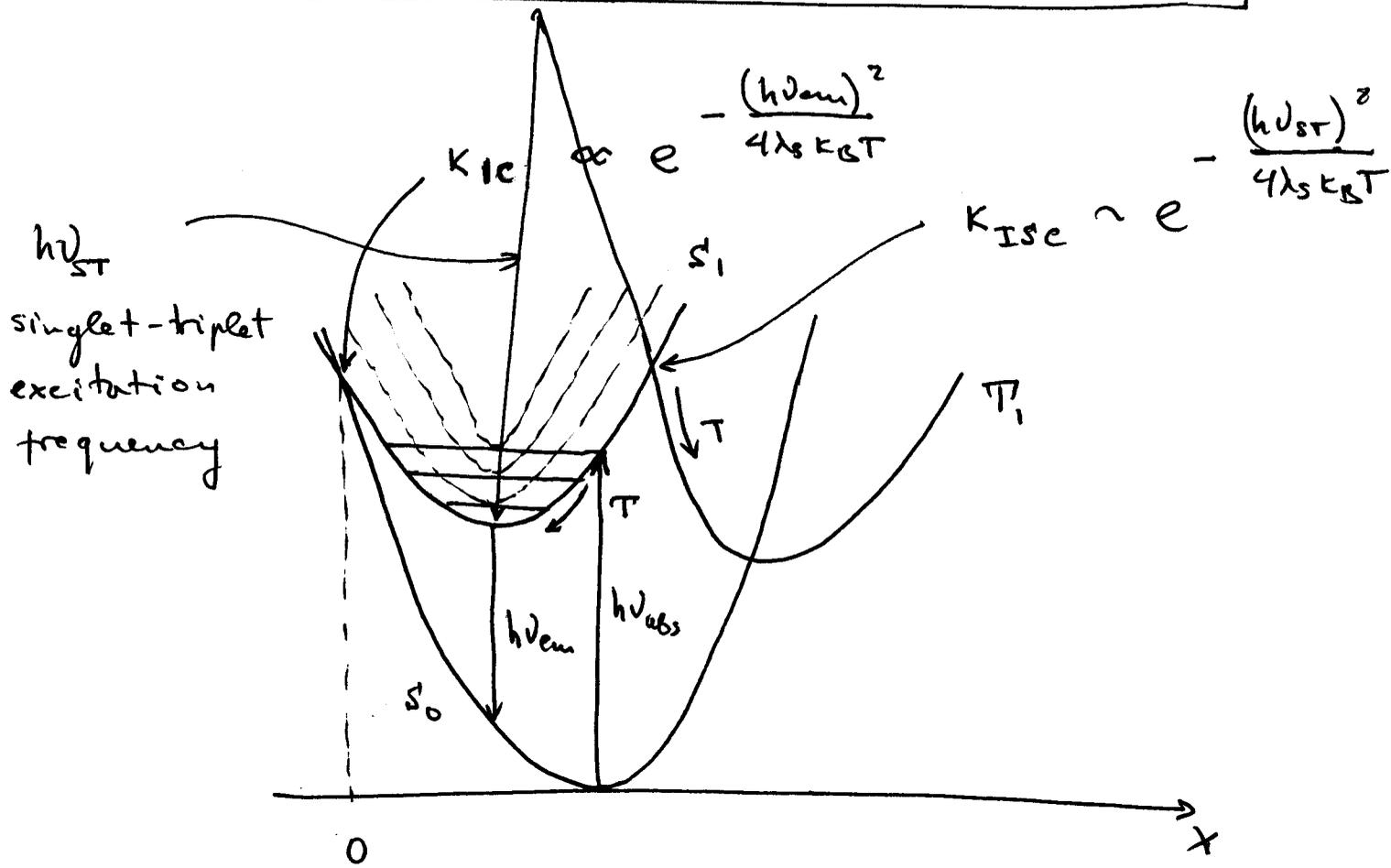
\uparrow
 $v=0$

Probability of finding a system with zero energy gap. This value is significant for radiationless transitions

$$k_{ET} = \frac{2\pi}{\hbar} |H_{12}|^2 I_{abs}(0)$$

$$k_{ET} = \frac{|H_{12}|^2}{\hbar} \left(\frac{\pi}{\lambda_s k_B T}\right)^{1/2} \sum_{n=0}^{\infty} e^{-s} \frac{s^n}{n!} \exp\left[-\frac{(\lambda_s + n h\nu_r)^2}{4\lambda_s k_B T}\right]$$

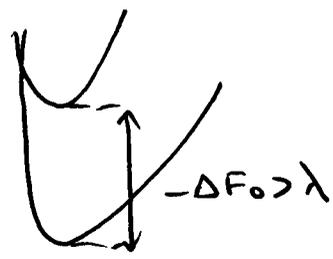
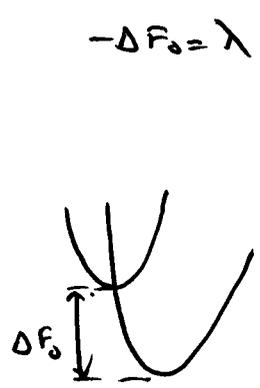
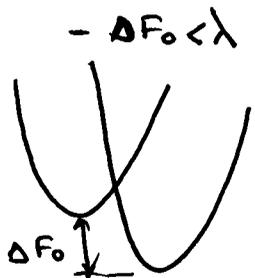
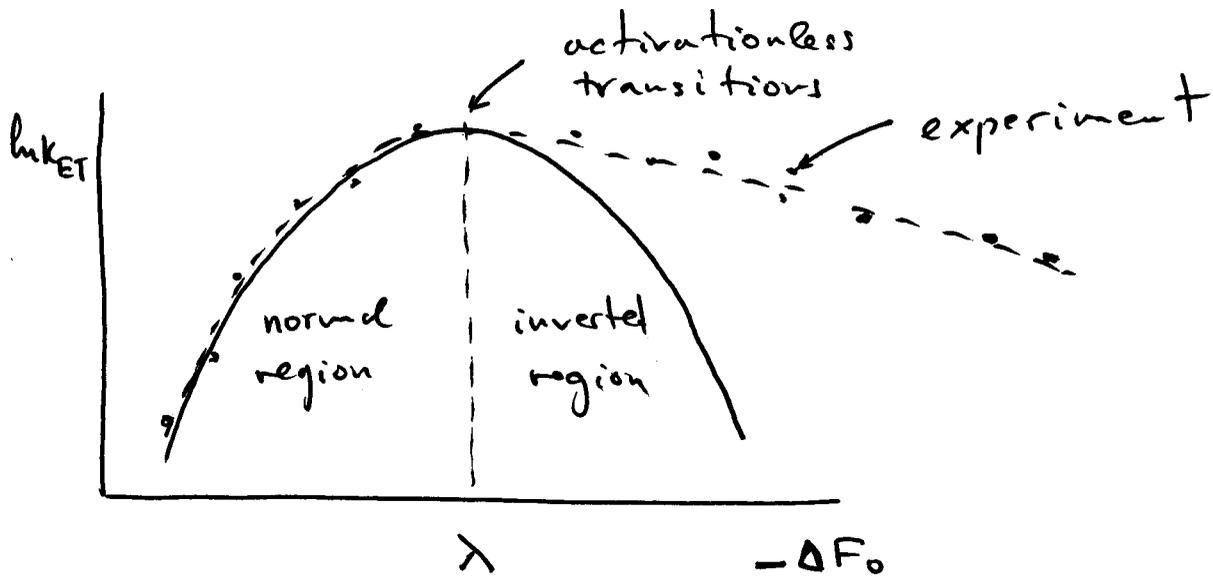
Fate of absorbed energy: Crossing of parabolas



T is the thermalization process, energy is lost to the environment in the form of heat

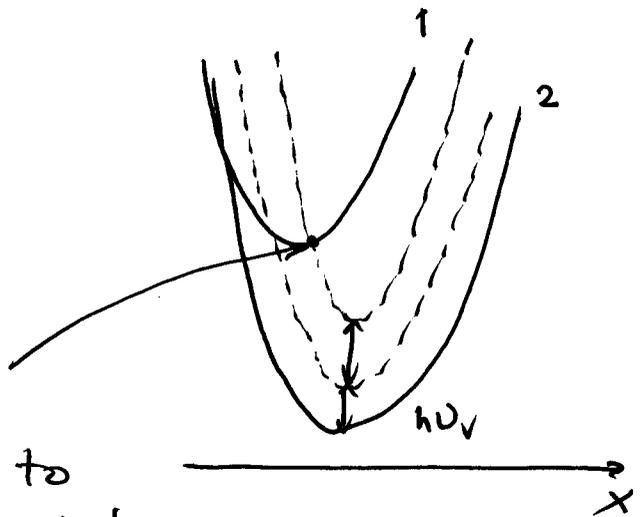
Energy gap law

The energy gap law is the dependence of the rate of radiationless transitions on the free energy gap (driving force) of the reaction



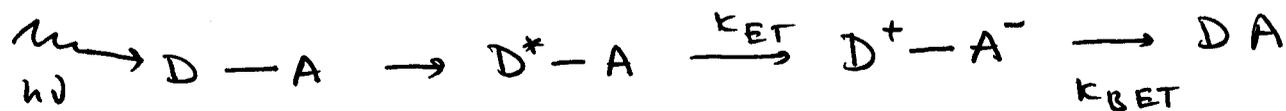
Inverted region:

There is always a possibility of almost activationless transition to



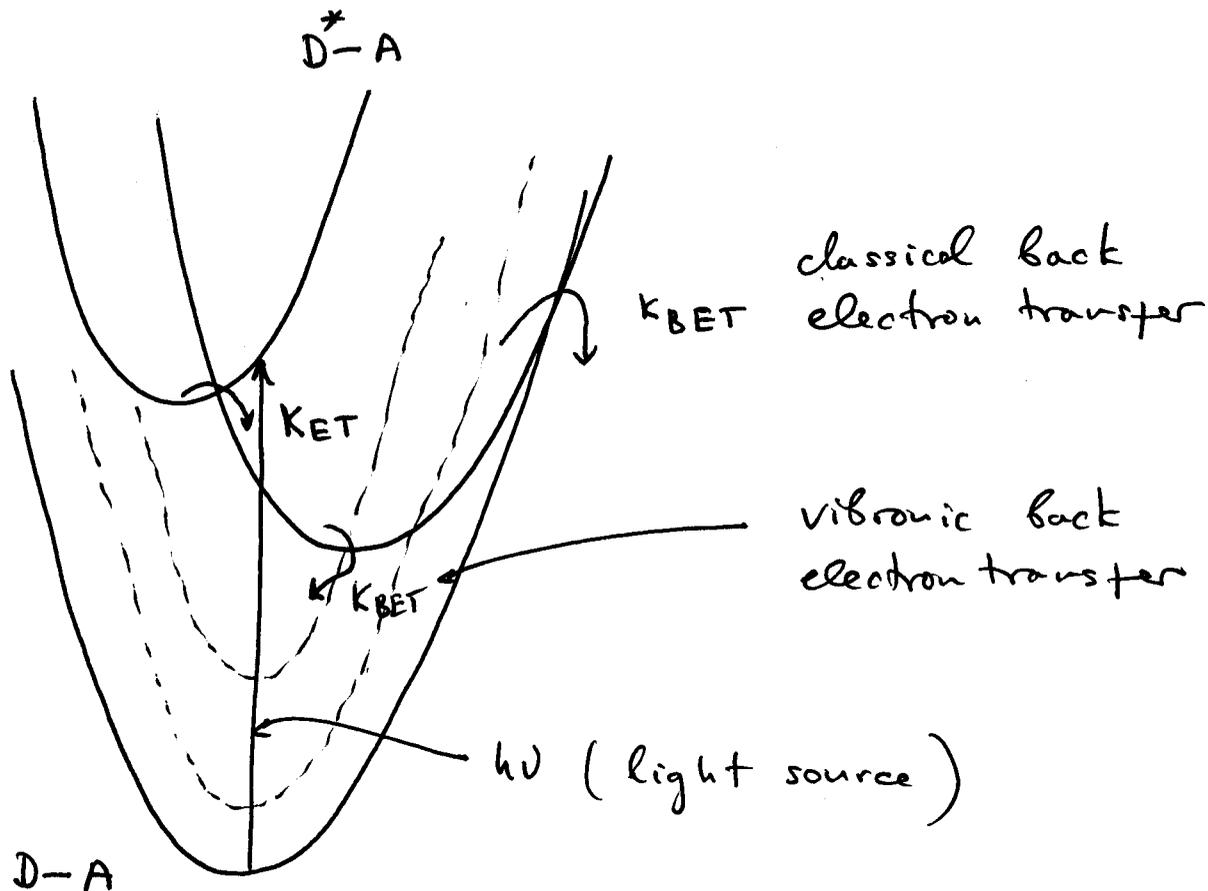
Energy gap law and photovoltaics

Conversion of the energy of light into electricity involves the basic step of charge separation



For high efficiency of photovoltaic devices one wants

$$K_{ET} \gg K_{BET}$$



The existence of transitions with vibrational excitations increases the rate of back electron transfer and lowers the efficiency of charge separation