

《高等物理化学》

(凝聚相) 化学动力学部分

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- (1) 势能面的概念, 过渡态理论;
- (2) 电子转移反应;
- (3) 激发态能量转移;
- (4) 吸收发射光谱、时间分辨光谱。

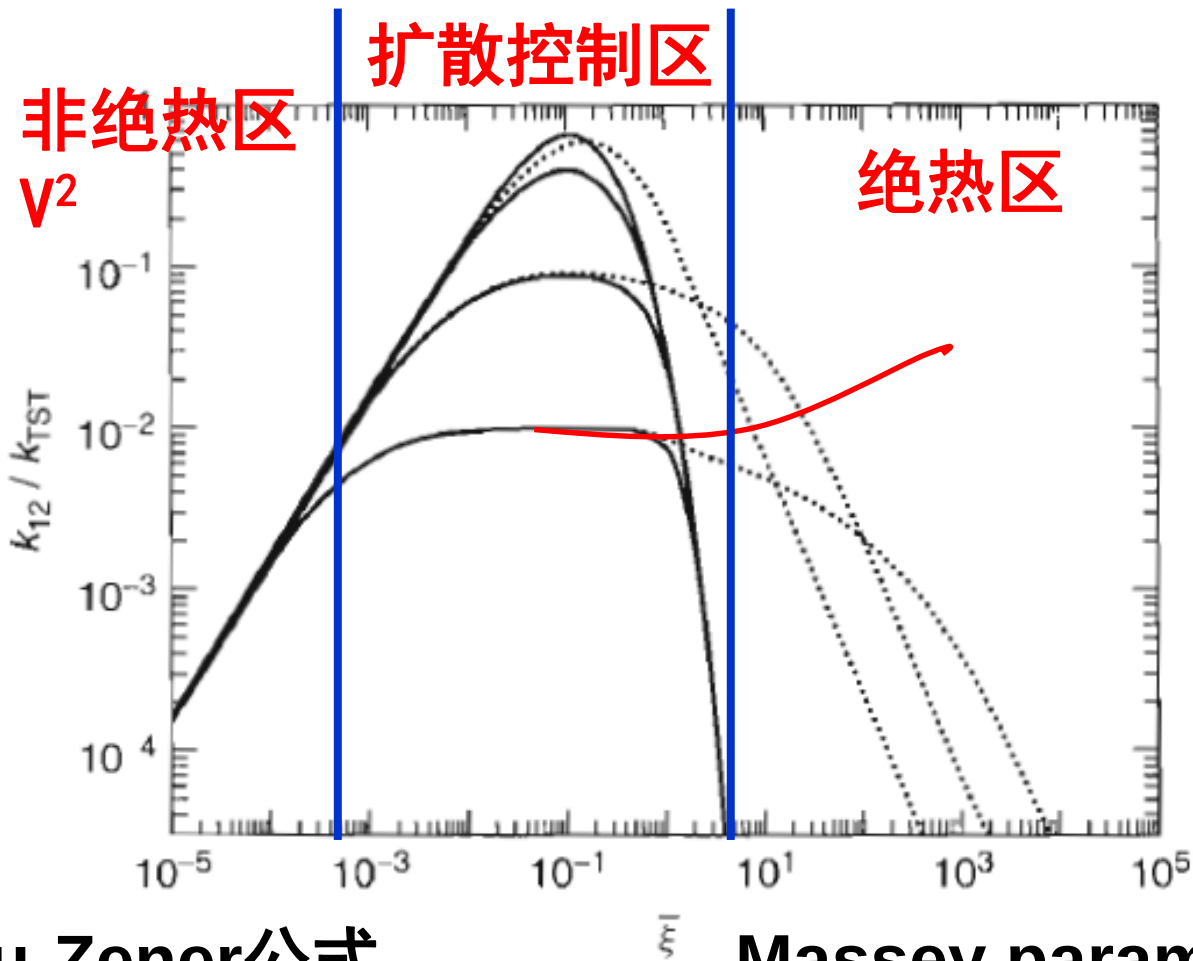
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2018.12.6, Lecture 4

1. 上节内容回顾
2. 含时微扰方法
3. 吸收和发射光谱（单个分子激发态）
4. 激发态能量转移的电子态耦合常数
5. 荧光共振能量转移（FRET），分子间耦合小情况，Förster公式
6. 小结

上节内容回顾

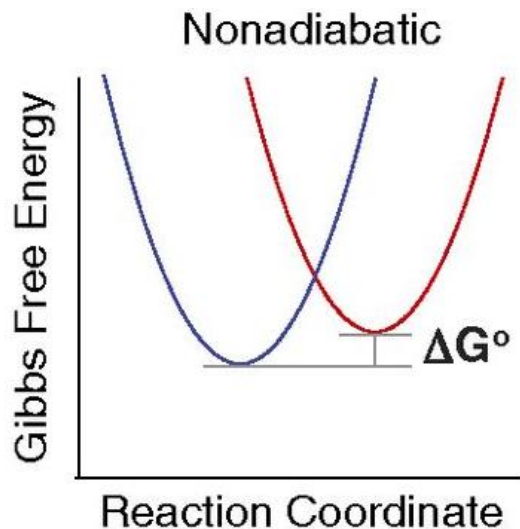
1.1 电子转移速率与耦合大小的关系



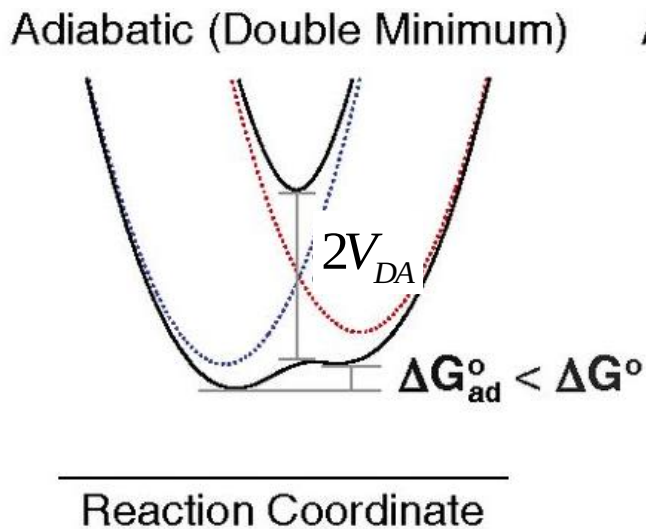
Landau-Zener公式

Massey parameter

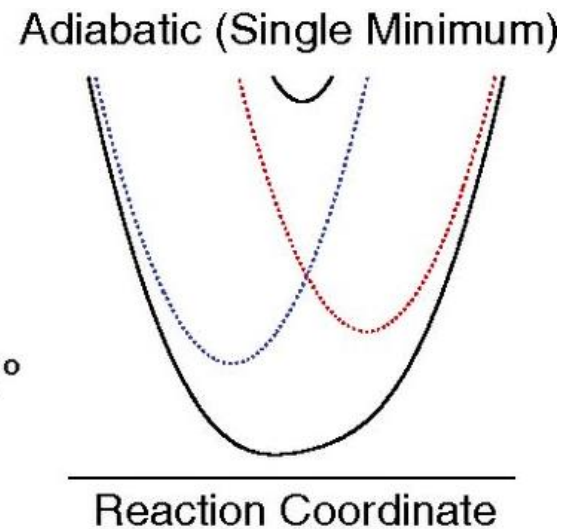
$$2V_{DA} \ll \lambda$$



$$2V_{DA} < \lambda$$



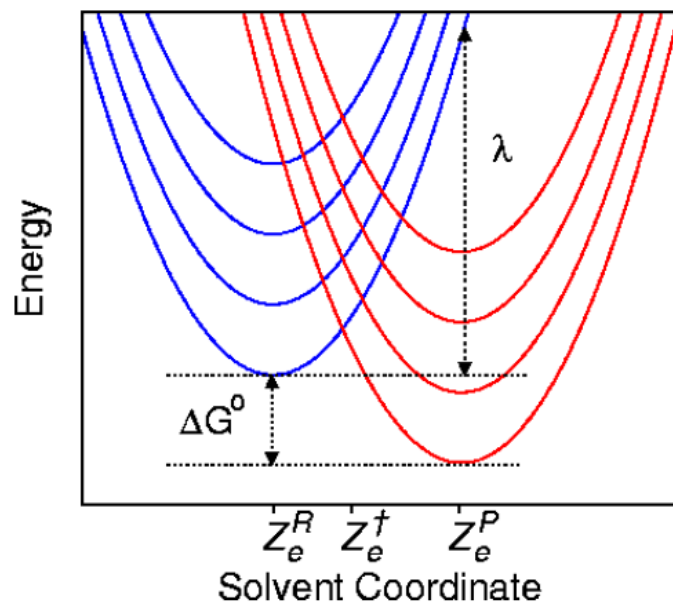
$$2V_{DA} > \lambda$$



混合价态化合物
Mixed-Valence

随着耦合增大，从非绝热到绝热电子转移的转变

1.2 Bixon-Jortner 公式，原子核的量子效应，应用：质子耦合的电子转移



$$k_{\mu\nu}(R) \approx \frac{|V_{\mu\nu}(R)|^2}{\hbar} \sqrt{\frac{\pi}{\lambda_{\mu\nu}(R)k_B T}} \exp\left[-\frac{(\Delta G_{\mu\nu}(R) + \lambda_{\mu\nu}(R))^2}{4\lambda_{\mu\nu}(R)k_B T}\right]$$

将高频模式量子化，化为多对势能面之间的电子转移问题

核隧穿问题、KIE问题等

1.3 电子转移的微观模型：分子内振动模式，溶剂极化效应

位移谐振子模型、自旋-玻色模型（**Spin-Boson**）

两个势能面，振动频率、简正模式都相同，只有平衡位置不同

$$H_A = \sum_{j=1}^N \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right] ,$$

$$H_B = \Delta\epsilon + \sum_{j=1}^N \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(q_j - \frac{c_j}{m_j \omega_j^2} \right)^2 \right] .$$

黄昆因子： $S_j = d_j^2 m_j \omega_j^2 / 2\hbar \omega_j = \frac{c_j^2}{2\hbar m_j \omega_j^3}$ $\lambda = \sum_{j=1}^N S_j \hbar \omega_j$

位移谐振子模型下的速率公式

$$C(t) = \frac{1}{Z_A} \langle e^{-\beta H_A} e^{\frac{i}{\hbar} H_A t} e^{-\frac{i}{\hbar} H_B t} \rangle$$

$$k_{ET} = \frac{K^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left\{ -\frac{i\Delta\epsilon t}{\hbar} + \frac{\pi}{\hbar} \int_0^{\infty} d\omega \frac{4J(\omega)}{\omega^2} \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) [\cos(\omega t) - 1] + i(\sin \omega t) \right] \right\}$$

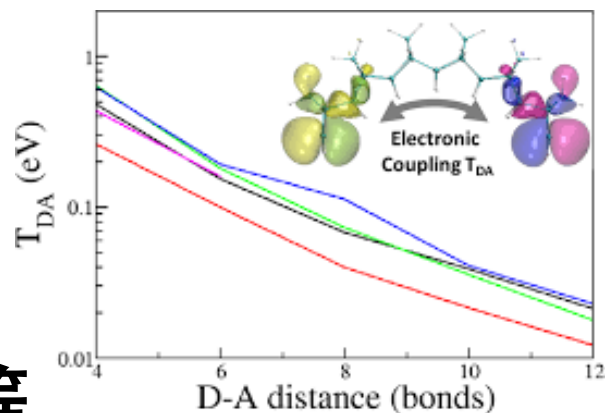
1. 完全包含了核运动的量子力学效应，可以得到Marcus公式、Bixon-Jortner公式。
2. 高估电子转移速率。
3. 在能量转移、光谱计算中都要用到。

1.4 电子转移反应举例

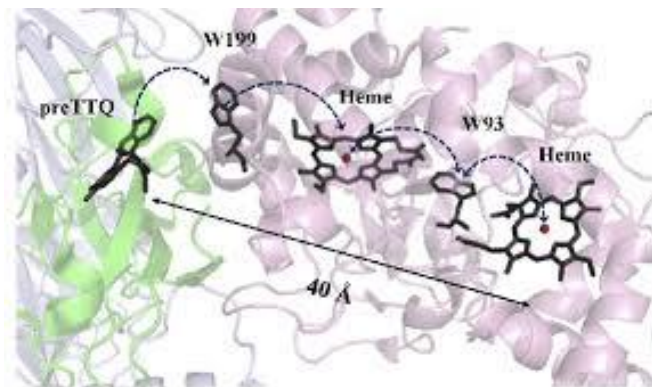
Through Space:
有效转移距离3-6Å

$$V_{DA} \propto e^{-\alpha R_{DA}}$$

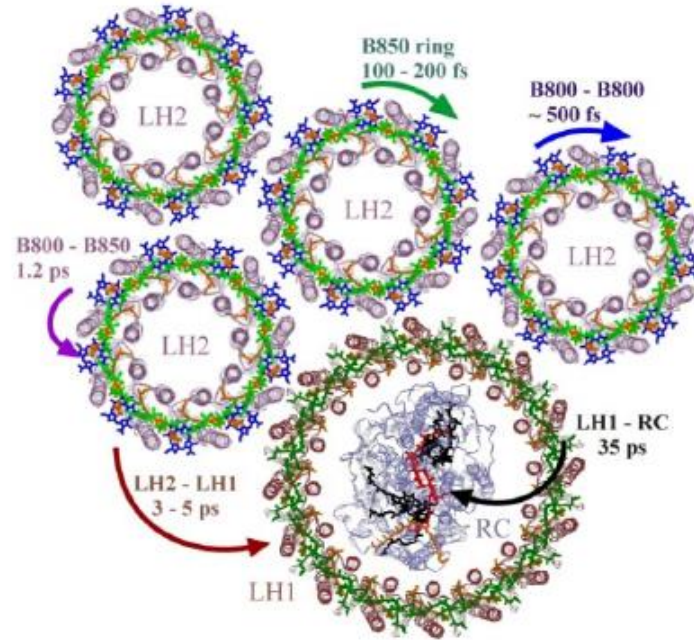
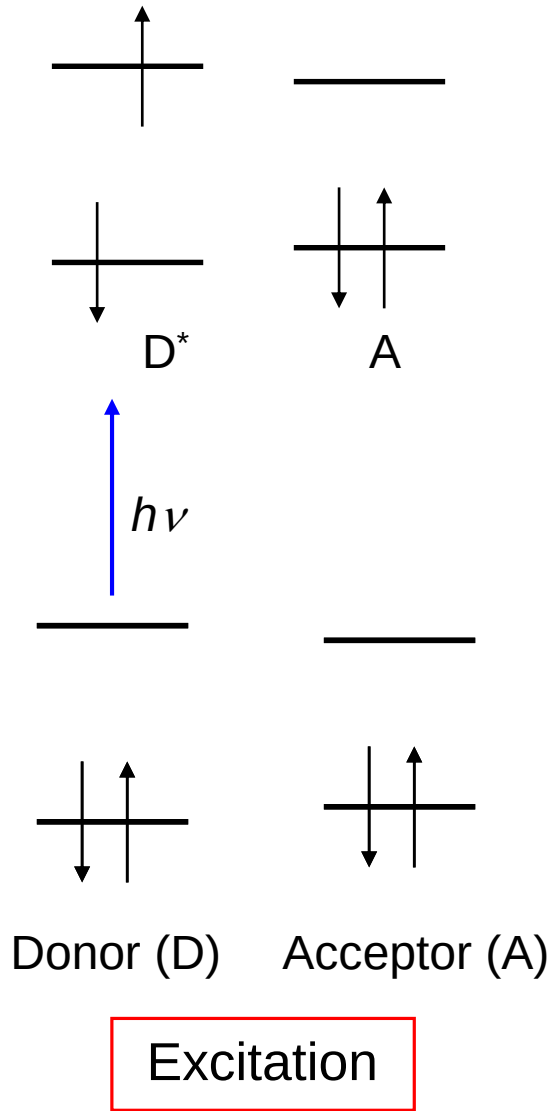
Through Bond: 10Å



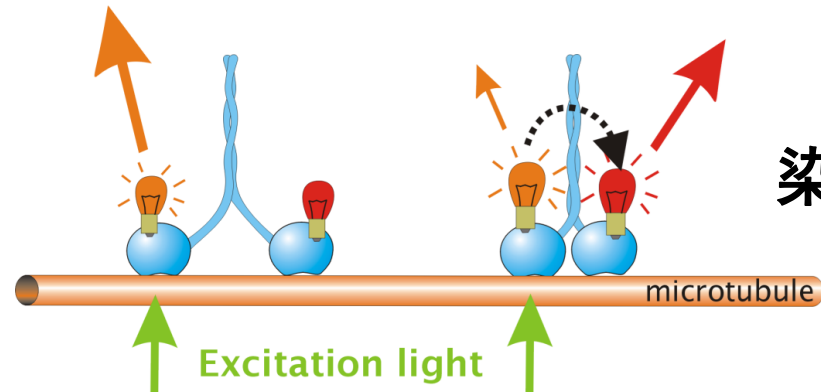
Super-Exchange, 中间态等
, 20-50Å, 长程电子转移



1.5 激发态能量转移简介



光合作用体系



染料分子

FÖRSTER传能公式

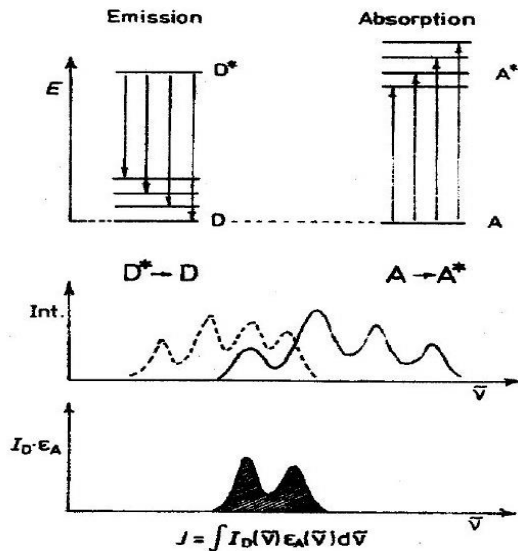
分子间耦合常数

Donor发射光谱

$$k_{D \rightarrow A} = \frac{9c^4 \kappa_{DA}^2}{8\pi n_{\text{agg}} |X_{DA}^{(0)}|^6} \int_0^\infty \frac{d\omega}{\omega^4} I_D(\omega) \alpha_A(\omega)$$

Acceptor吸收光谱

分子间距离



本次课主要内容

1. 上节内容回顾
2. 含时微扰方法
3. 吸收和发射光谱（单个分子激发态）
4. 激发态能量转移的电子态耦合常数
5. 荧光共振能量转移（FRET），分子间耦合小情况，Förster公式

激发态能量转移也是两个势能面上运动的问题，
电子转移的很多东西也适用(势能面概念、费米黄金规则)

2. 含时微扰论， 吸收/发射光谱

总的哈密顿量 $H = H_0 + H'(t)$

零级哈密顿量 $H_0\phi_n = E_n\phi_n$

初始状态 $\phi(0) = \phi_k$

t时刻波函数用基函数展开 $\phi(t) = \sum_n c_{nk} e^{-\frac{iE_n t}{\hbar}} \phi_n$

$$P_{nk}(t) = |c_{nk}(t)|^2$$

$$w_{nk} = \frac{d}{dt}P_{nk}(t) = \frac{d}{dt}|c_{nk}(t)|^2$$

问题：求从k态到n态的跃迁速率

$$i\hbar \frac{\partial}{\partial t} \phi(t) = [H_0 + H'(t)] \phi(t)$$

$$i\hbar \sum_n (\dot{c}_{nk} - iE_n/\hbar) \phi_n = \sum_n (E_n + H'(t)) e^{-\frac{i}{\hbar} E_n t} \phi_n$$

微分方程

$$i\hbar\dot{c}_{k'k} = \sum_n e^{i\omega_{k'n}t} \langle k'|H'|n\rangle c_{nk}$$

零级近似，初始态在能级k上

$$c_{k'k}^0 = \delta_{k'k}$$

一级近似

$$i\hbar\dot{c}_{k'k} = e^{i\omega_{k'k}t} H'_{k'k} c_{k'k} = e^{i\omega_{k'k}t} H'_{k'k}$$

将一级近似方程积分

$$c_{k'k}^1(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{k'k}t} H'_{k'k} dt, \quad k' \neq k$$

（我们只感兴趣 $k' \neq k$ 的态）

k' 态的几率

$$P_{k'k}(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{k'k}t} H'_{k'k} dt \right|^2$$

分子与电磁场相互作用

$$H' = \mu E \cos \omega_L t = \frac{\mu E}{2} (e^{-i\omega_L t} + e^{i\omega_L t})$$

(偶极近似)

$$c_{k'k}(t) = -\frac{i\mu_{k'k}E}{2\hbar} \int_0^t [e^{i(\omega_{k'k}-\omega_L)t} + e^{i(\omega_{k'k}+\omega_L)t}] dt,$$

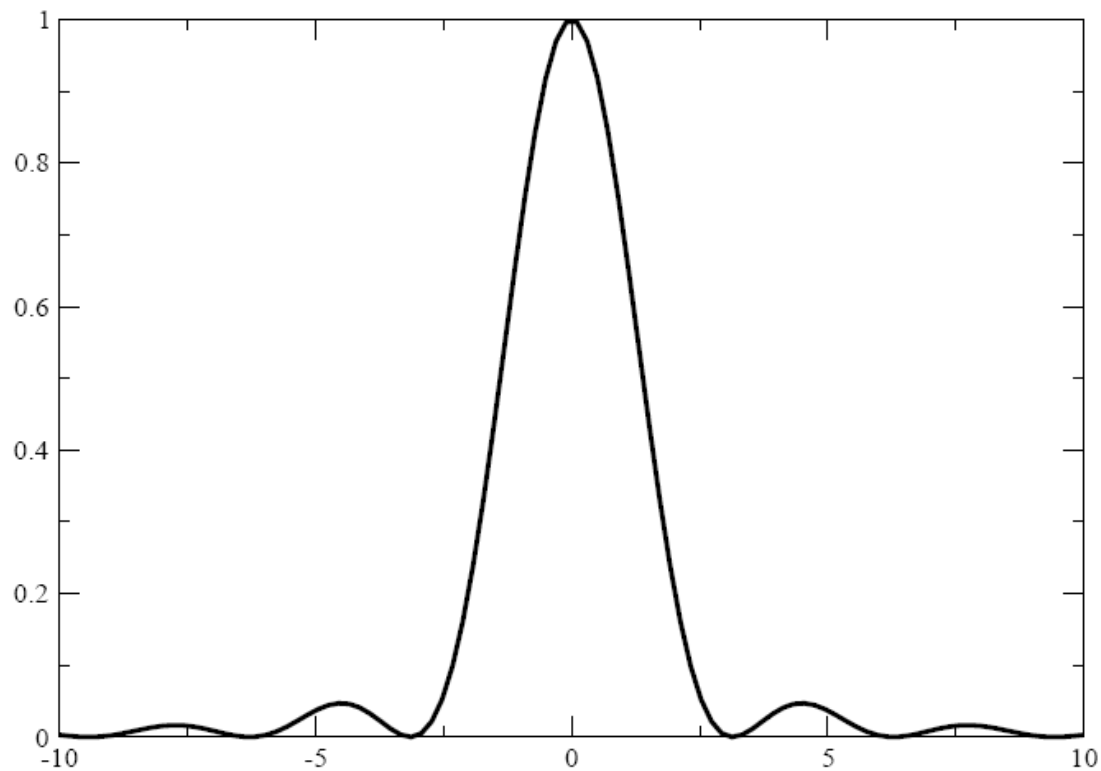
$$c_{k'k}(t) = -\frac{\mu_{k'k}E}{2\hbar} \left[\frac{e^{i(\omega_{k'k}-\omega_L)t} - 1}{\omega_{k'k} - \omega_L} + \frac{e^{i(\omega_{k'k}+\omega_L)t} - 1}{\omega_{k'k} + \omega_L} \right]$$

旋转波近似

$$c_{k'k}(t) = -\frac{\mu_{k'k}E}{2\hbar} \frac{e^{i(\omega_{k'k}-\omega_L)t} - 1}{\omega_{k'k} - \omega_L}$$

$$\begin{aligned} P_{k'k}(t) &= \left(\frac{\mu_{k'k}E}{2\hbar} \right)^2 \frac{(e^{i(\omega_{k'k}-\omega_L)t} - 1)(e^{-i(\omega_{k'k}-\omega_L)t} - 1)}{(\omega_{k'k} - \omega_L)^2} \\ &= \left(\frac{\mu_{k'k}E}{2\hbar} \right)^2 \left[\frac{\sin(\omega_{k'k} - \omega_L)t/2}{(\omega_{k'k} - \omega_L)/2} \right]^2 \end{aligned}$$

$$\lim_{t \rightarrow \infty} \left[\frac{\sin(\omega_{k'k} - \omega_L)t/2}{(\omega_{k'k} - \omega_L)/2} \right]^2 = 2\pi \delta(\omega_{k'k} - \omega_L)$$



$$\int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

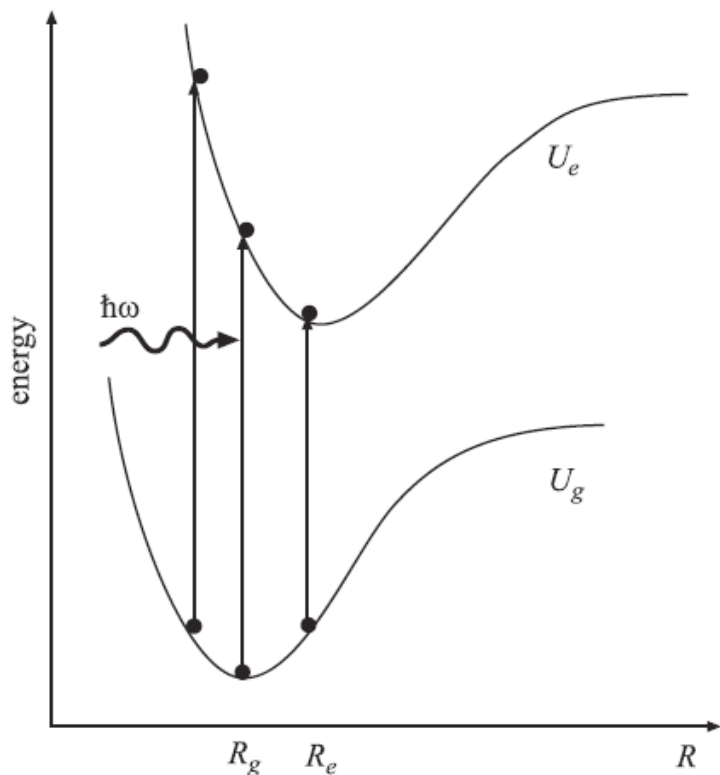
$$\lim_{a \rightarrow \infty} \frac{\sin^2 ax}{\pi ax^2} = \delta(x)$$

跃迁速率

$$P_{k'k}(t) \approx 2\pi \left(\frac{\mu_{k'k} E}{2\hbar} \right)^2 \delta(\omega_{k'k} - \omega_L) t$$

$$w_{k'k}(t) = \frac{d}{dt} P_{k'k}(t) = 2\pi \left(\frac{\mu_{k'k} E}{2\hbar} \right)^2 \delta(\omega_{k'k} - \omega_L)$$

吸收光谱



$$P_k \propto e^{-\beta E_k}$$

$$P_k = \frac{e^{-\beta E_k}}{\sum_n e^{-\beta E_n}} = \frac{1}{Z_g} e^{-\beta E_k}$$

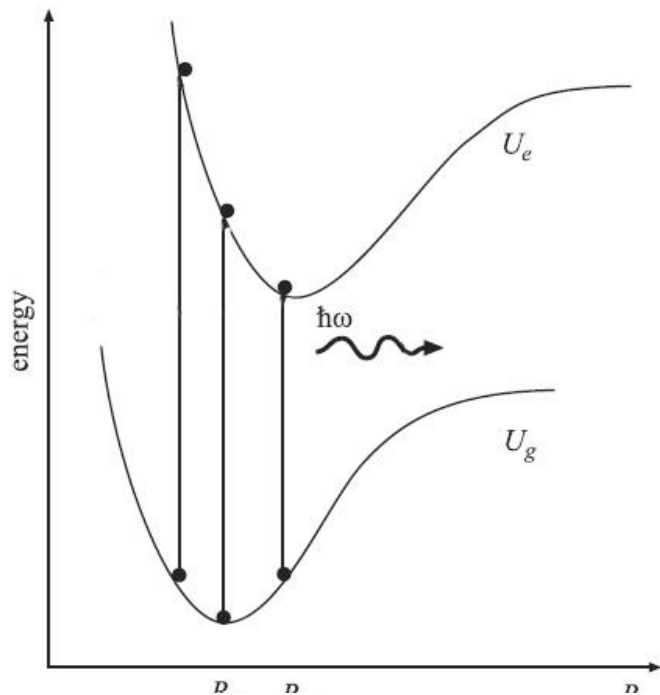
费米黄金规则（分立能级形式）

$$\alpha_{abs}(\omega_L) \propto \frac{\pi}{2\hbar^2 Z_g} \sum_{k',k} e^{-\beta E_k} \mu_{k'k}^2 \delta(\omega_{k'k} - \omega_L) \quad (\text{E}^2 \text{ 正比于光强})$$

$$\alpha_{abs}(\omega_L) = \frac{4\pi^2\omega}{3\hbar c} \sum_{k',k} e^{-\beta E_k} \mu_{k'k}^2 \delta(\omega_{k'k} - \omega_L)$$

(Lin Review,
May/Kuhn Book)

发射光谱



基本假设：分子激发后很快达到激发态上的平衡态

$$P_{k'} \propto e^{-\beta E_{k'}}$$

$$P_{k'} = \frac{e^{-\beta E_{k'}}}{\sum_{n'} e^{-\beta E_{n'}}} = \frac{1}{Z_e} e^{-\beta E_{k'}}$$

$$I_{ems}(\omega_L) \propto \frac{\pi}{2\hbar^2 Z_e} \sum_{k',k} e^{-\beta E_{k'}} \mu_{k'k}^2 \delta(\omega_{k'k} - \omega_L)$$

$$I_{ems}(\omega_L) = \frac{4\hbar\omega^3}{3c^3 Z_e} \sum_{k',k} e^{-\beta E_{k'}} \mu_{k'k}^2 \delta(\omega_{k'k} - \omega_L)$$

(May/Kuhn book)

例子：位移谐振子

$$\alpha_{abs}(\omega_L) = \frac{4\pi^2\omega}{3\hbar c} \sum_{k',k} e^{-\beta E_k} \mu_{k'k}^2 \delta(\omega_{k'k} - \omega_L)$$

1. 能级位置

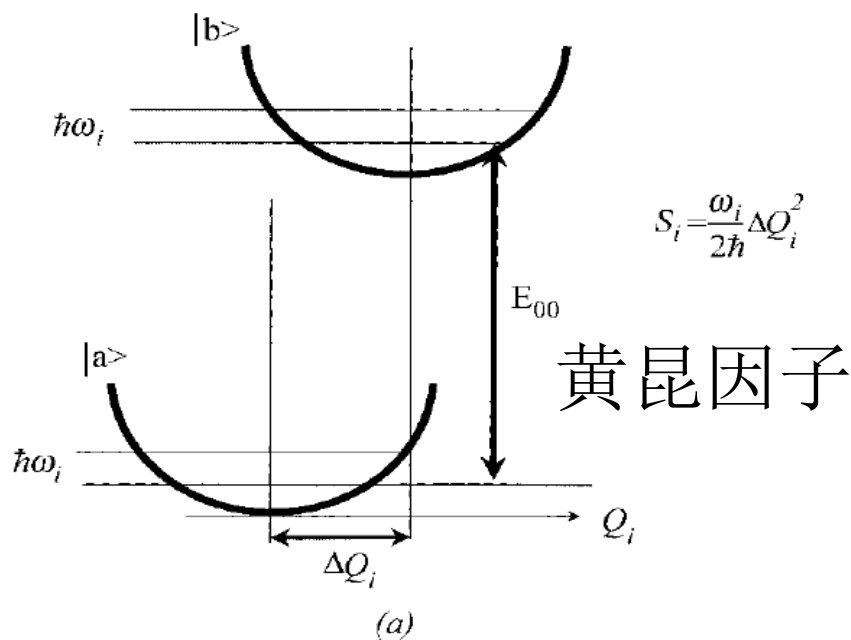
2. 跃迁偶极矩 $\mu_{k'k}$

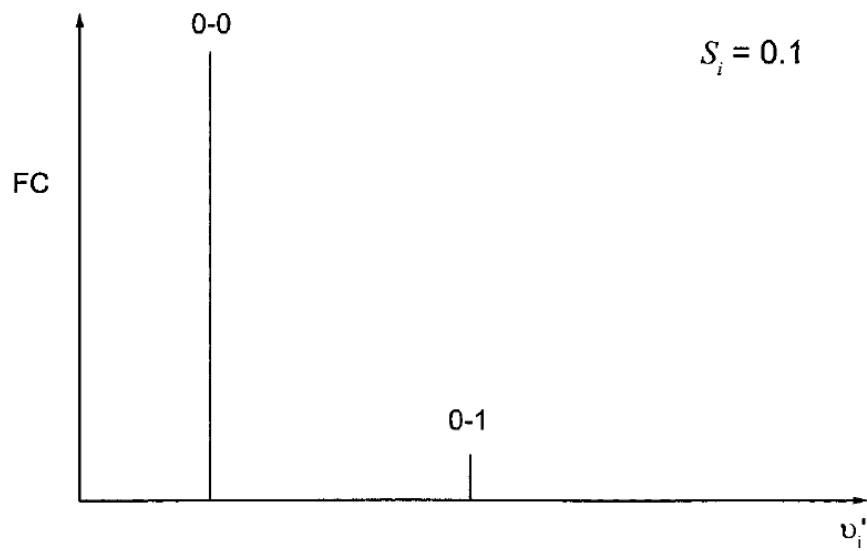
Franck-Condon近似

偶极矩与核构型无关

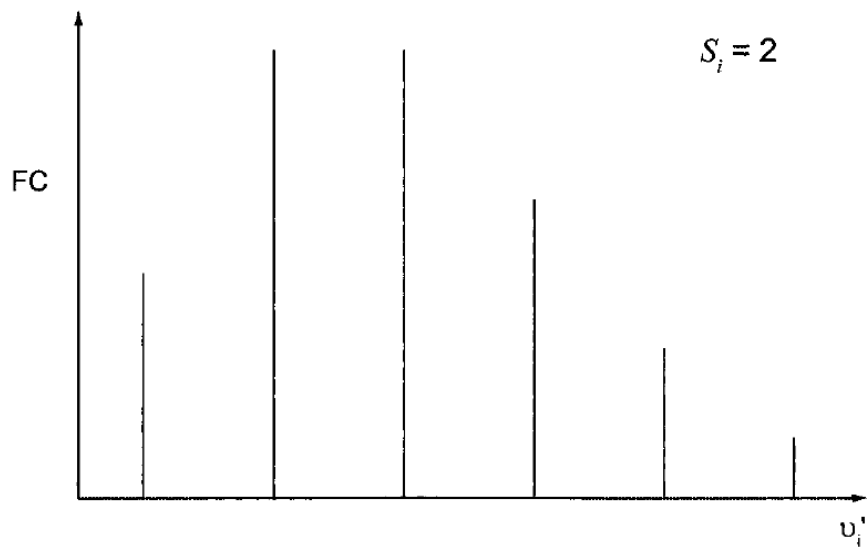
光谱强度正比于波函数重叠的平方

$$|\langle \chi_{bv'_i} | \chi_{a0_i} \rangle|^2 = \frac{S_i^{v'_i}}{v'_i!} e^{-S_i}$$





(b)



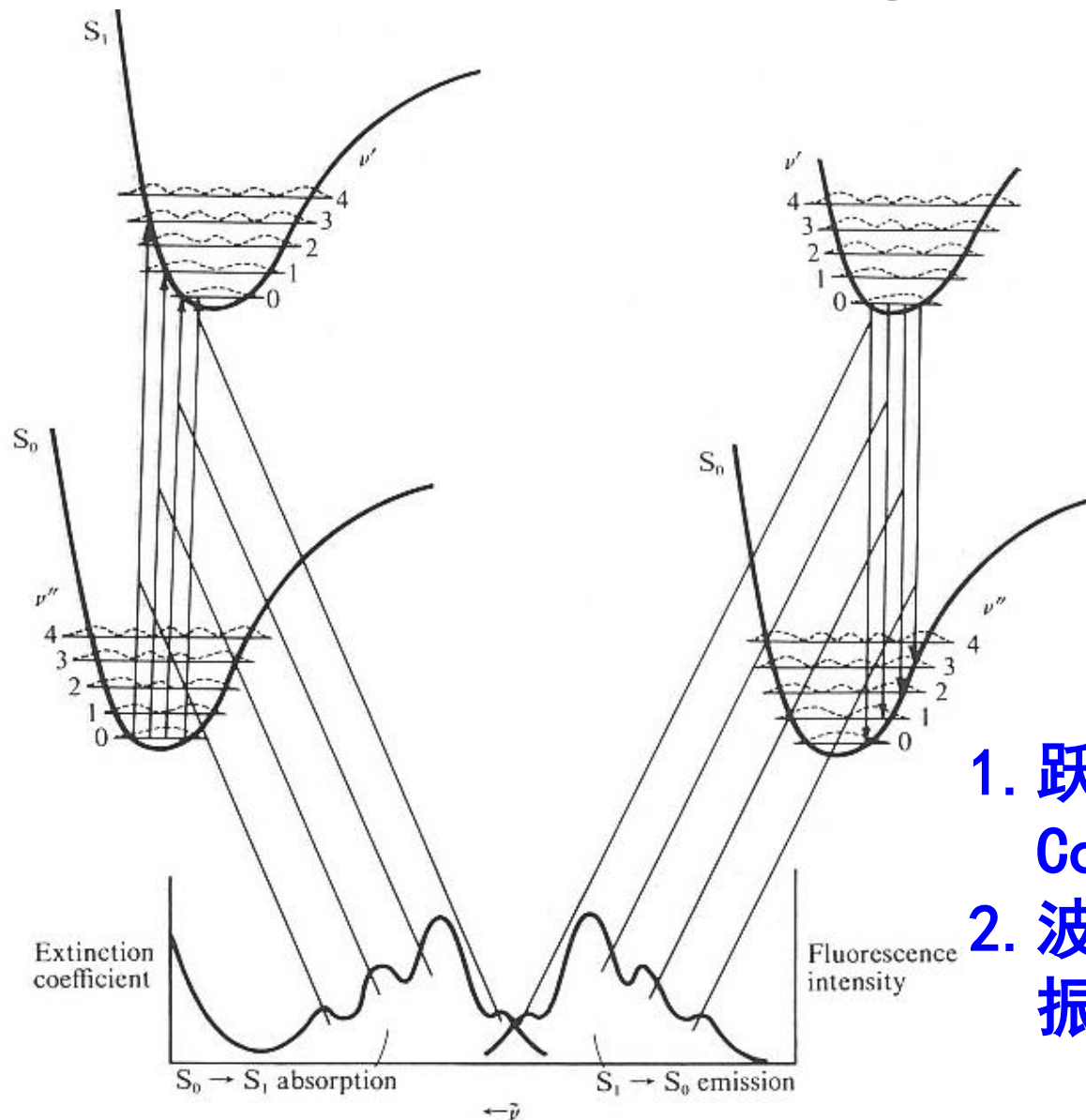
(c)

Franck-Condon因子

位移小，从0-0单调下降

位移大，先上升后下降

Mirror image rule



1. 跃迁偶极矩 (Frank-Condon近似)
2. 波函数重叠 (位移谐振子近似)

Stokes 位移

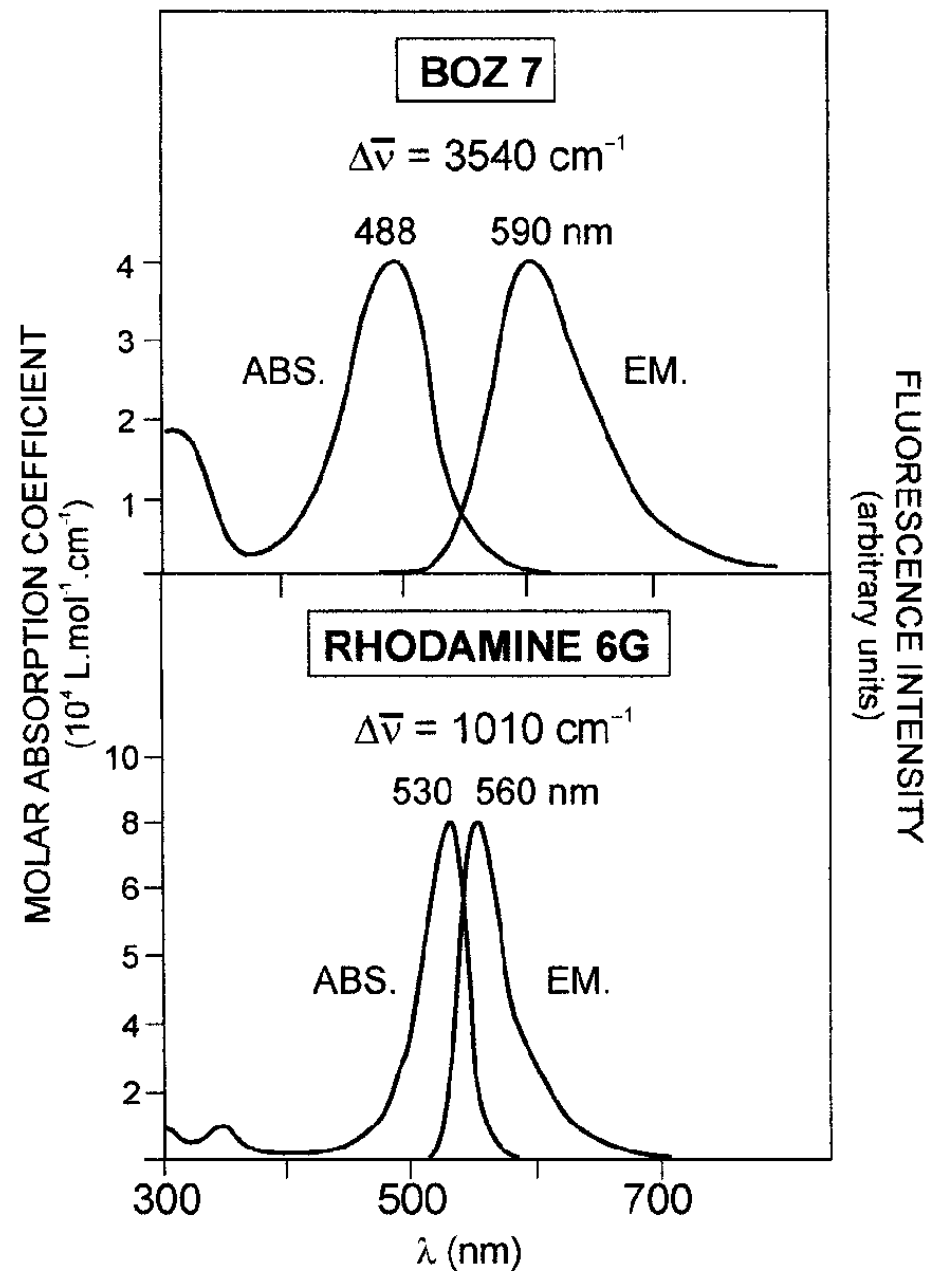
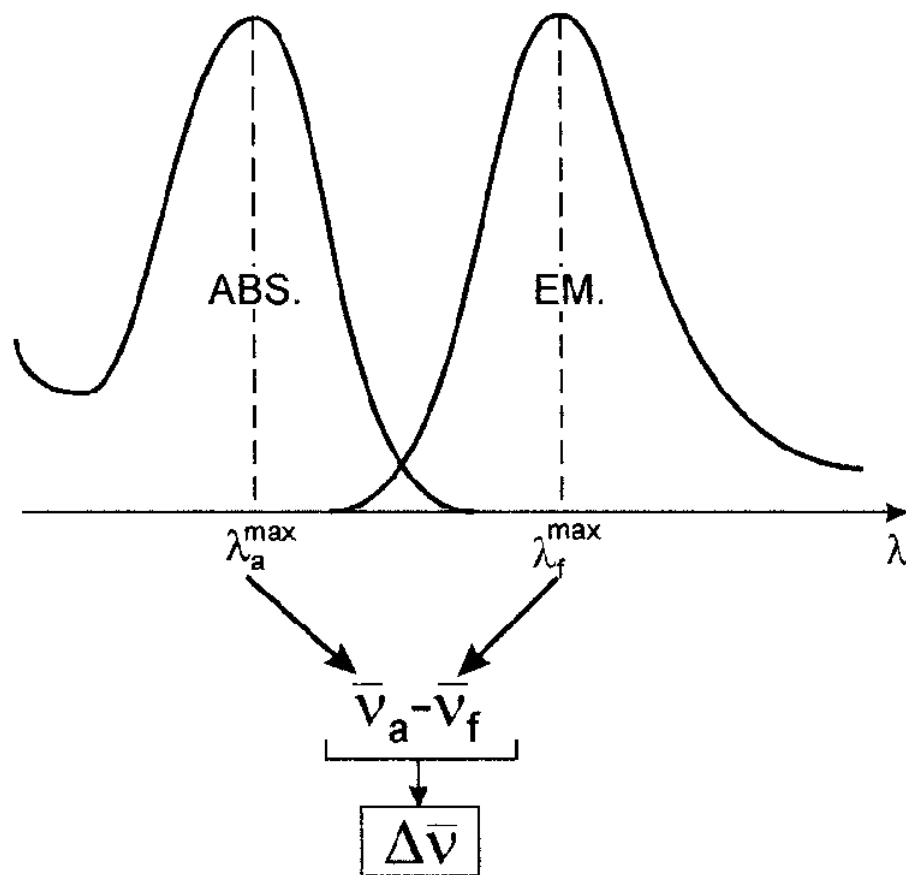


Fig. 3.3. Definition of the Stokes shift. Examples of Stokes shift: benzoxazinone derivative (BOZ 7) and rhodamine 6G.

吸收/发射光谱的关联函数形式

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

$$\tilde{\alpha}_{abs}(\omega_L) = \frac{1}{Z_g} \int_{-\infty}^{\infty} dt \sum_{k',k} e^{-\beta E_k} \mu_{k'k}^2 e^{\frac{E_{k'k} - \hbar\omega_L}{\hbar} t}$$

$$= \frac{1}{Z_g} \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \sum_{k',k} e^{-\beta E_k} \langle k | \hat{\mu} | k' \rangle \langle k' | e^{\frac{iH_e t}{\hbar}} \hat{\mu} e^{\frac{-iH_g t}{\hbar}} | k \rangle$$

$$= \frac{1}{Z_g} \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \text{Tr}[e^{-\beta H_g} \hat{\mu} \hat{\mu}(t)] = \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \langle \hat{\mu} \hat{\mu}(t) \rangle_g$$

关联函数形式

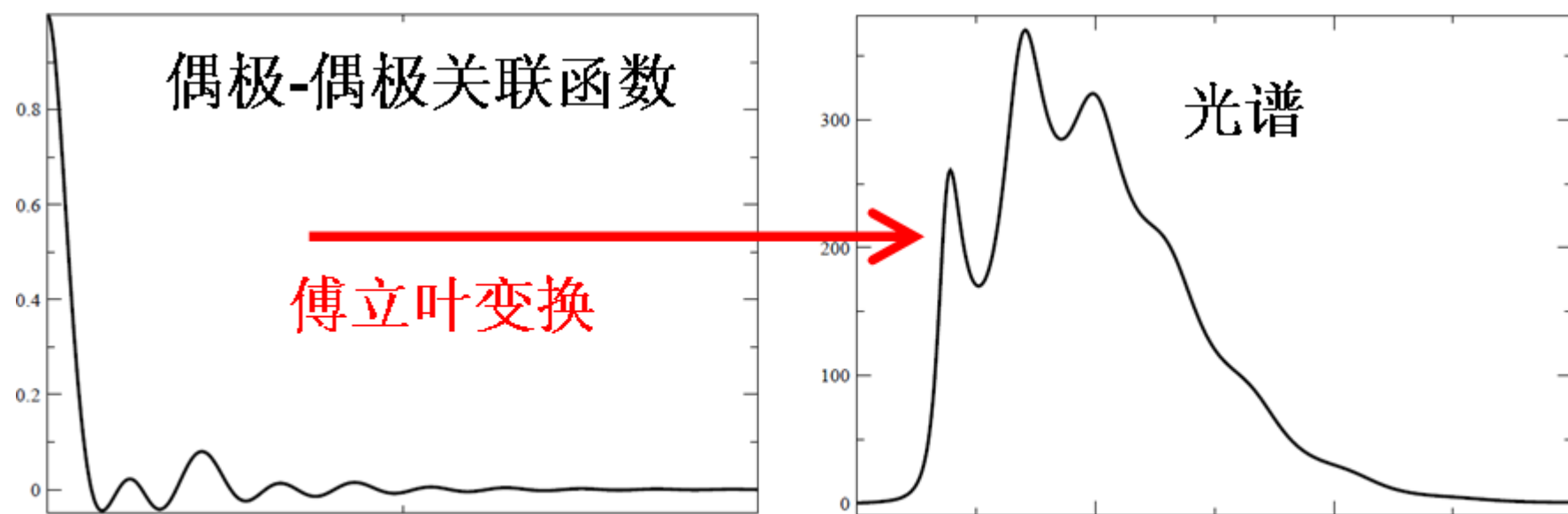
$$\hat{\mu}(t) = e^{\frac{iHt}{\hbar}} \hat{\mu} e^{-\frac{iHt}{\hbar}}$$

$$H = H_g |g\rangle\langle g| + H_e |e\rangle\langle e|, \quad \hat{\mu} = \mu(|g\rangle\langle e| + |e\rangle\langle g|)$$

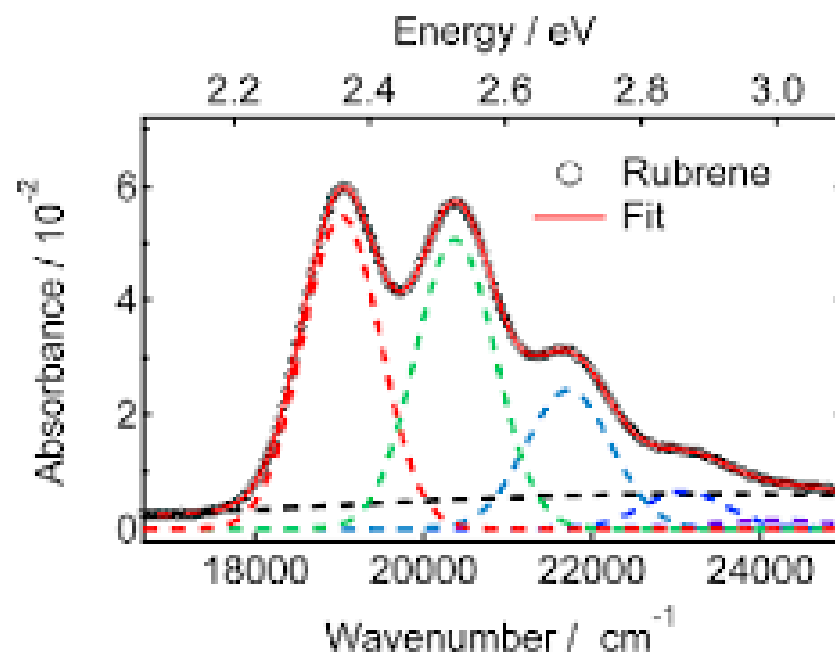
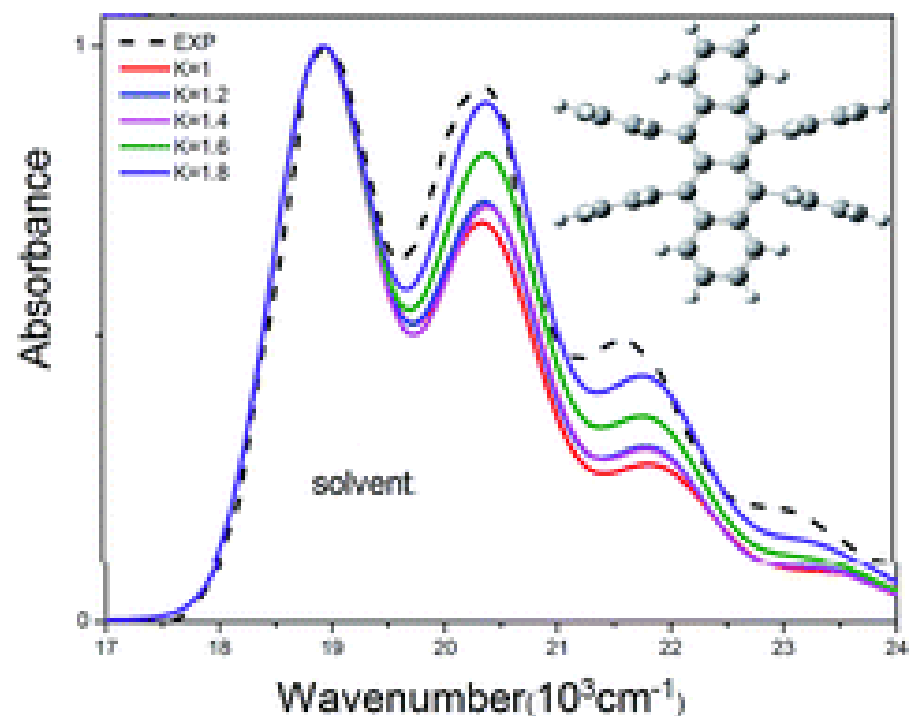
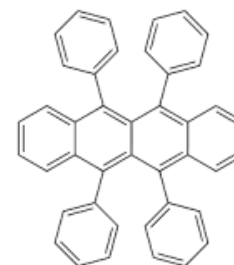
$$\tilde{\alpha}_{abs}(\omega_L) = \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \langle \hat{\mu} \hat{\mu}(t) \rangle_g$$

$$\tilde{I}_{ems}(\omega_L) = \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \langle \hat{\mu}(t) \hat{\mu} \rangle_e = \int_{-\infty}^{\infty} dt e^{i\omega_L t} \langle \hat{\mu} \hat{\mu}(t) \rangle_e$$

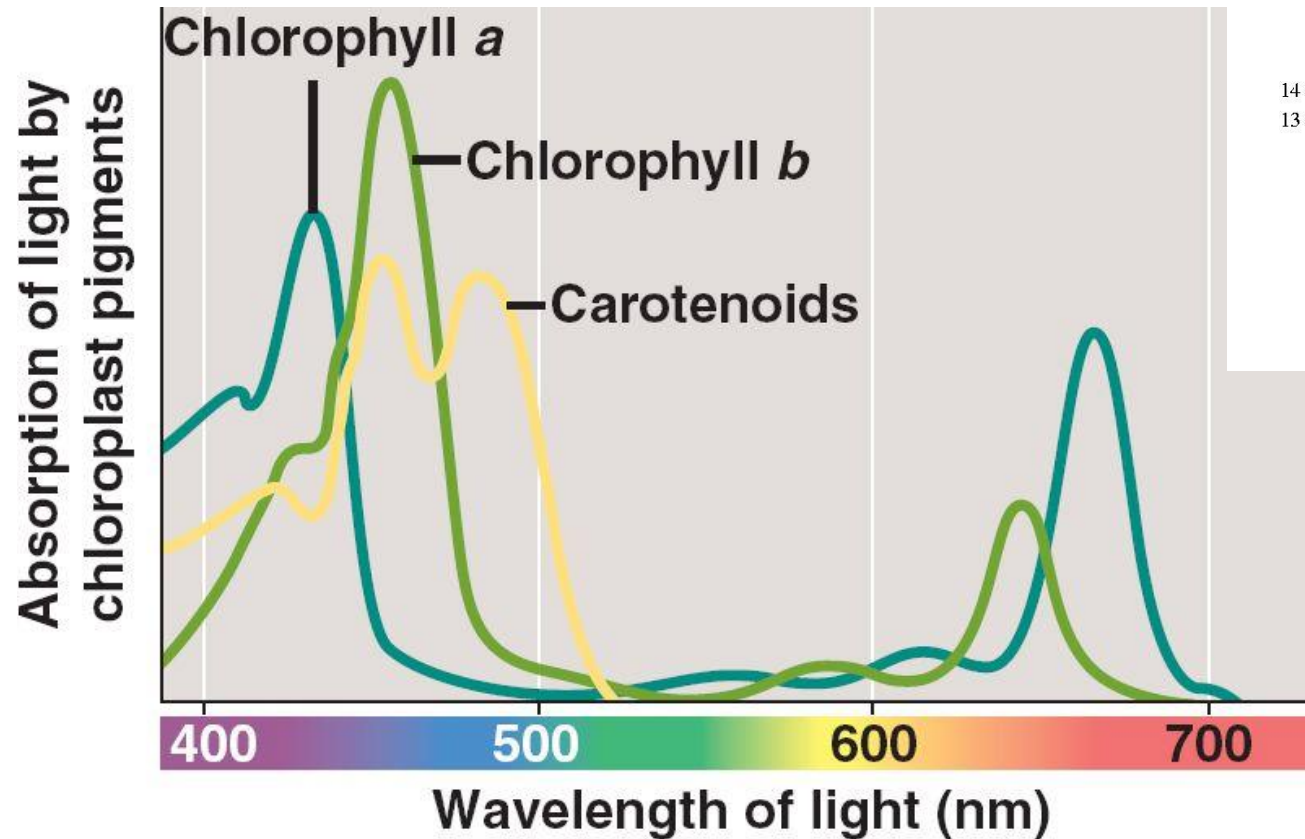
关联函数形式的FGR



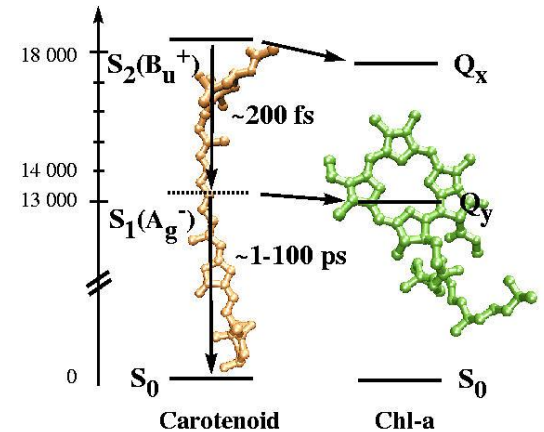
例子1：并苯类分子



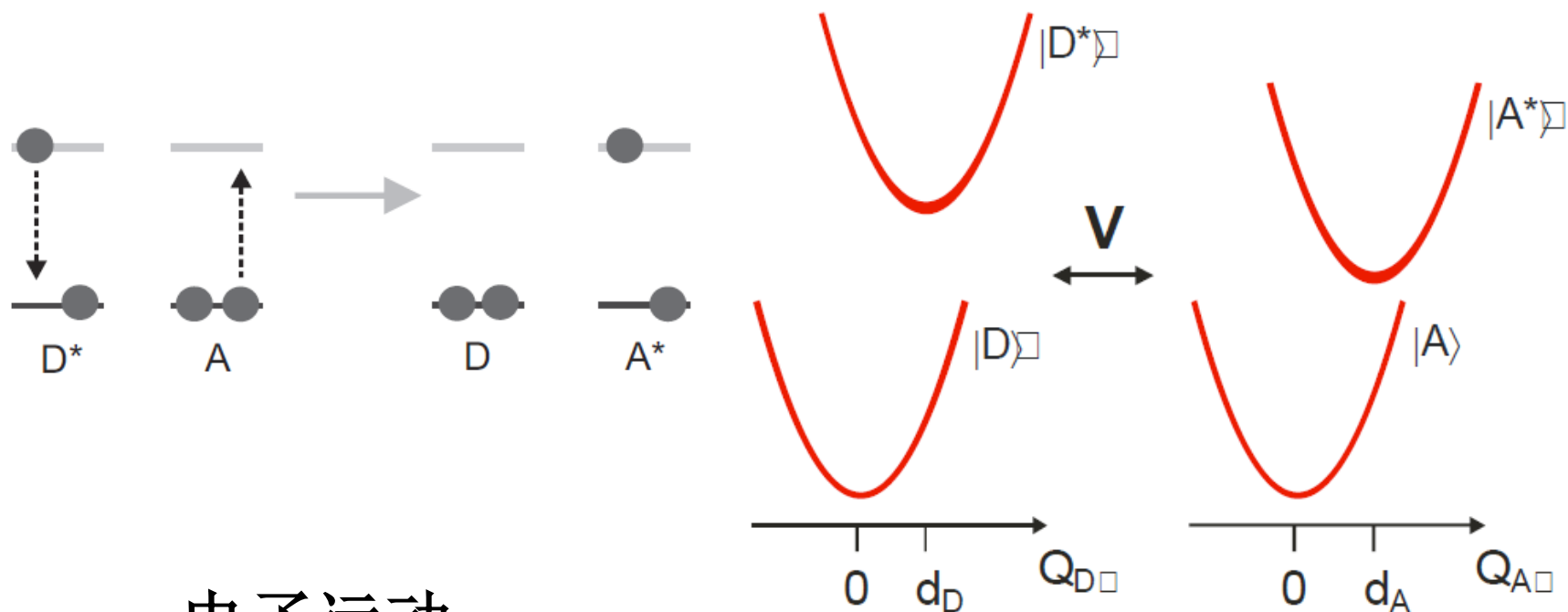
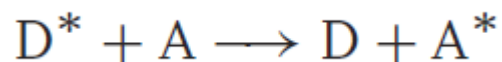
例子2：光合作用体系



Energy Level Scheme and Lifetimes



3. 激发态能量转移：电子与原子核耦合运动



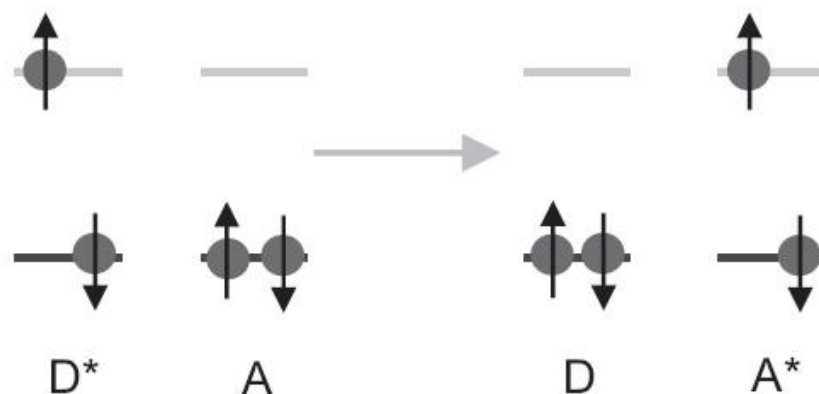
电子运动

电子态的变化伴随着
核构型的变化

激发态能量转移的耦合项

- 初态和末态的电子构型

假设 (1) Singlet-Singlet 转移; (2) 波函数可以用单行列式表示;



$$\Psi_r = |\Psi_{\text{core}} \phi_D \bar{\phi}_D^* \phi_A \bar{\phi}_A| \quad \Psi_p = |\Psi_{\text{core}} \phi_D \bar{\phi}_D \phi_A \bar{\phi}_A^*|$$

波函数正常写法表示 α 自旋, 上横线表示 β 自旋

$$H_{rp} = \langle \Psi_r | H | \Psi_p \rangle$$

$$H = \underbrace{h_d^{(1)} + h_a^{(1)}}_{\text{单体部分, 电子与D/A核的作用}} + \underbrace{h^{(2)}}_{\text{两体部分, 电子之间的相互作用}}$$

单体部分，
电子与**D/A**
核的作用

两体部分，
电子之间的
相互作用

（例如：Szabo & Ostland, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory）

假设：（1）单体部分的交叉影响可以忽略

（2）**Core**轨道不受前线轨道的影响 （3）**Donor**和**Acceptor**内层轨道没有重叠

$$\begin{aligned}
 H_{rp} &= \langle \bar{\phi}_D^* \bar{\phi}_A || \bar{\phi}_D \bar{\phi}_A^* \rangle \\
 &\equiv \sum_s \sum_{s'} \int d\mathbf{r} d\mathbf{r}' \left(\frac{1}{\sqrt{2}} \begin{vmatrix} \bar{\phi}_D^*(\mathbf{r}) & \bar{\phi}_A(\mathbf{r}') \\ \bar{\phi}_D(\mathbf{r}) & \bar{\phi}_A(\mathbf{r}') \end{vmatrix} \right) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left(\frac{1}{\sqrt{2}} \begin{vmatrix} \bar{\phi}_D(\mathbf{r}) & \bar{\phi}_A^*(\mathbf{r}') \\ \bar{\phi}_D(\mathbf{r}) & \bar{\phi}_A^*(\mathbf{r}') \end{vmatrix} \right) \\
 &= H_{rp}^{\text{Coulomb}} - H_{rp}^{\text{Dexter}}
 \end{aligned}$$

两个轨道组成的反对称波函数（行列式）

$$H_{rp}^{\text{Coulomb}} = \int d\mathbf{r} d\mathbf{r}' \underbrace{\phi_D^*(\mathbf{r}) \phi_D(\mathbf{r})}_{\text{Coulomb}} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \underbrace{\phi_A^*(\mathbf{r}') \phi_A(\mathbf{r}')}_{\text{Coulomb}}$$

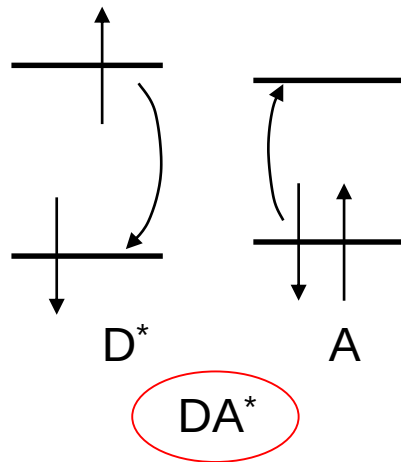
同一积分变量的波函数（中心）在同一个分子上，通过长程作用相联系

$$H_{rp}^{\text{Dexter}} = \int d\mathbf{r} d\mathbf{r}' \underbrace{\phi_D^*(\mathbf{r}) \phi_A^*(\mathbf{r})}_{\text{Exchange}} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \underbrace{\phi_D(\mathbf{r}') \phi_A(\mathbf{r}')}_{\text{Exchange}}$$

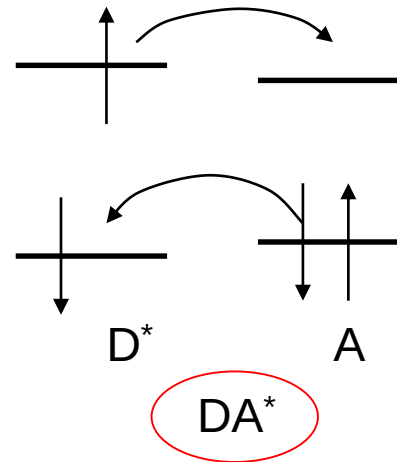
交换项，**Exchange**

同一积分变量的波函数（中心）在不同分子上，需要波函数重叠才有作用

库仑项和交换项



Coulomb Term

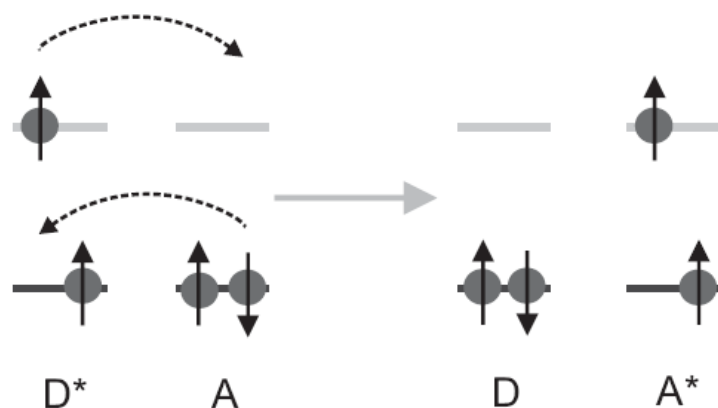


Exchange Term

$$H_{rp} = \langle \Psi_r | H | \Psi_p \rangle = H_{rp}^{\text{Coulomb}} - H_{rp}^{\text{Dexter}}$$

库仑项是长程项 ($1/r^3$)，交换项是短程项 (e^{-ar})

三重态能量转移只有交换项



$$\Psi_r = |\Psi_{\text{core}} \phi_D \phi_D^* \phi_A \bar{\phi}_A|$$

$$\Psi_p = |\Psi_{\text{core}} \phi_D \bar{\phi}_D \phi_A \phi_A^*|$$

$$H_{rp}^T = - \int d\mathbf{r} d\mathbf{r}' \phi_D^*(\mathbf{r}) \phi_A^*(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_D(\mathbf{r}') \phi_A(\mathbf{r}')$$

库仑项的计算

$$\int d\mathbf{r}d\mathbf{r}' \phi_D^*(\mathbf{r})\phi_D(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_A^*(\mathbf{r}')\phi_A(\mathbf{r}')$$

Transition Density Cube (TDC)

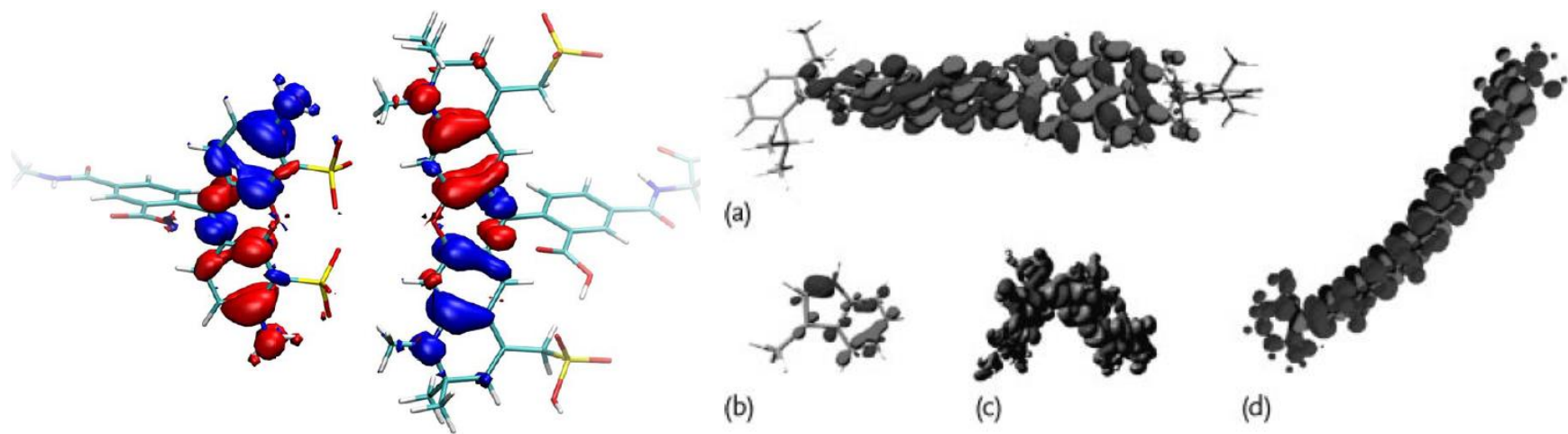
用量化程序计算三维格点上的跃迁密度

$$\rho_D(\mathbf{r}) = \phi_D^*(\mathbf{r})\phi_D(\mathbf{r})$$

$$\rho_A(\mathbf{r}') = \phi_A^*(\mathbf{r}')\phi_A(\mathbf{r}')$$

$$H_{rp}^{\text{Coulomb}} = \int d\mathbf{r}d\mathbf{r}' \frac{\rho_D(\mathbf{r})\rho_A(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

TDC的一些例子



偶极-偶极近似

$$\int d\mathbf{r} d\mathbf{r}' \phi_D^*(\mathbf{r}) \phi_D(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_A^*(\mathbf{r}') \phi_A(\mathbf{r}') \quad (1)$$

$$\mathbf{x} = \mathbf{r} - \mathbf{r}_0, \quad \mathbf{x}' = \mathbf{r}' - \mathbf{r}'_0$$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{|\mathbf{r}_0 + \mathbf{x} - \mathbf{r}'_0 - \mathbf{x}'|}$$

$$\approx \frac{1}{|\mathbf{r}_0 - \mathbf{r}'_0|} + \frac{(\mathbf{x} - \mathbf{x}') \cdot (\mathbf{r}_0 - \mathbf{r}'_0)}{|\mathbf{r}_0 - \mathbf{r}'_0|^3} - \frac{(\mathbf{x} - \mathbf{x}')^2}{2|\mathbf{r}_0 - \mathbf{r}'_0|^3} + \frac{3[(\mathbf{x} - \mathbf{x}') \cdot (\mathbf{r}_0 - \mathbf{r}'_0)]^2}{2|\mathbf{r}_0 - \mathbf{r}'_0|^5}$$

代入 (1) 求积分

只有 $\mathbf{x}$ 和 $\mathbf{x}'$ 的交叉项才不为0：不同的轨道是正交的

$$\int d\mathbf{r} \phi_D^*(\mathbf{r}) \phi_D(\mathbf{r}) = 0$$

跃迁偶极矩的定义

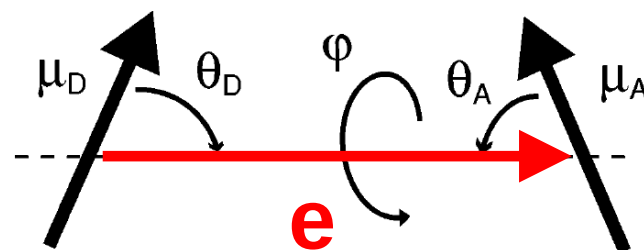
$$\mu_D \equiv \int d\mathbf{r} \phi_D^*(\mathbf{r}) \mathbf{x} \phi_D(\mathbf{r}) = \int d\mathbf{r} \phi_D^*(\mathbf{r}) \mathbf{r} \phi_D(\mathbf{r})$$

$$\mu_A \equiv \int d\mathbf{r} \phi_A^*(\mathbf{r}) \mathbf{x} \phi_A(\mathbf{r}) = \int d\mathbf{r} \phi_A^*(\mathbf{r}) \mathbf{r} \phi_A(\mathbf{r})$$

偶极-偶极近似

$$H_{rp}^{\text{Coulomb}} = \frac{\boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A}{|\mathbf{r}_0 - \mathbf{r}'_0|^3} - \frac{3[\boldsymbol{\mu}_D \cdot (\mathbf{r}_0 - \mathbf{r}'_0)][\boldsymbol{\mu}_A \cdot (\mathbf{r}_0 - \mathbf{r}'_0)]}{|\mathbf{r}_0 - \mathbf{r}'_0|^5}$$

$$= \kappa \frac{\mu_D \mu_A}{|\mathbf{r}_0 - \mathbf{r}'_0|^3}$$



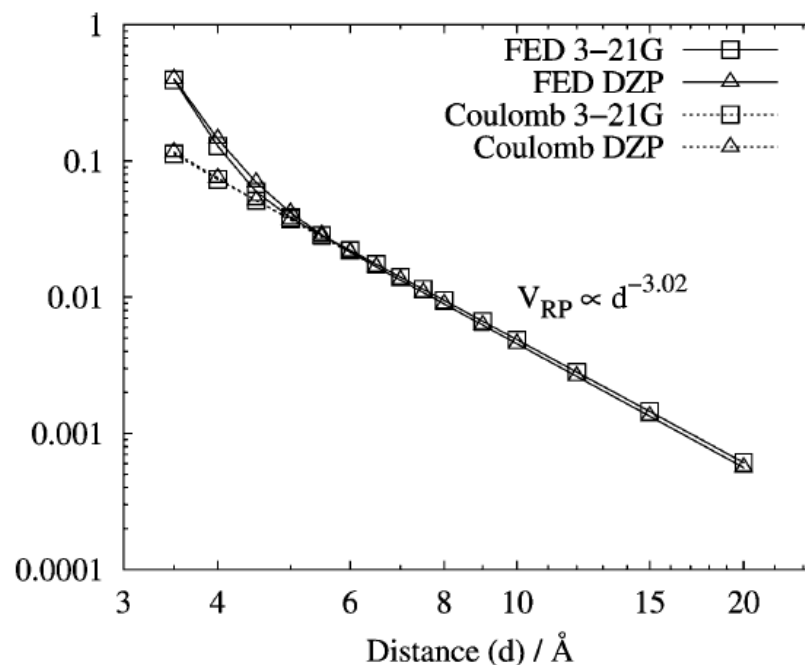
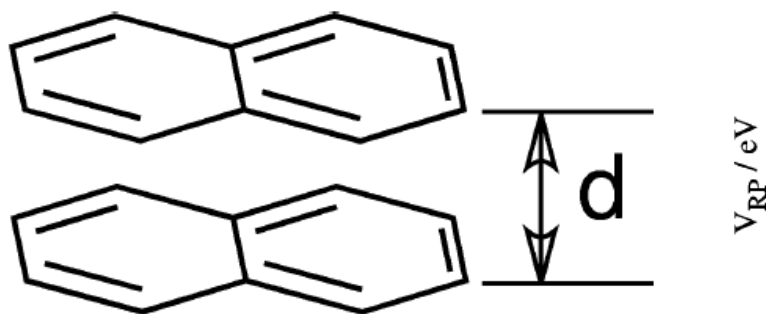
$$\kappa = \underbrace{\mathbf{u}_D \cdot \mathbf{u}_A} - 3(\mathbf{u}_D \cdot \mathbf{e})(\mathbf{u}_A \cdot \mathbf{e})$$

跃迁偶极矩的单位方向向量

两分子中心连线的
单位方向向量

库仑项与交换项的大小

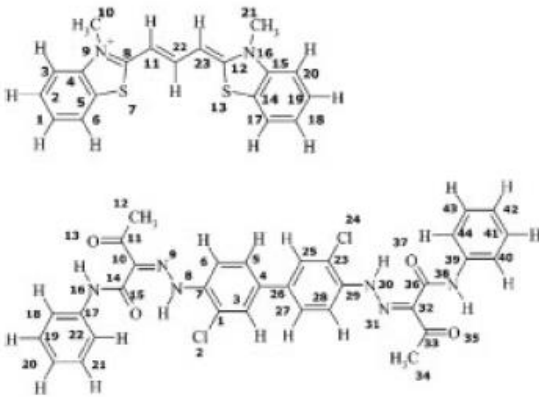
$$H_{rp} = \langle \Psi_r | H | \Psi_p \rangle = H_{rp}^{\text{Coulomb}} - H_{rp}^{\text{Dexter}}$$



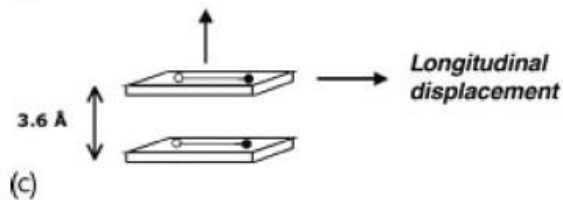
C.-P. Hsu (许昭萍) et al.

J. Phys. Chem. C **2008**, *112*, 1204–1212

TDC与偶极近似的比较



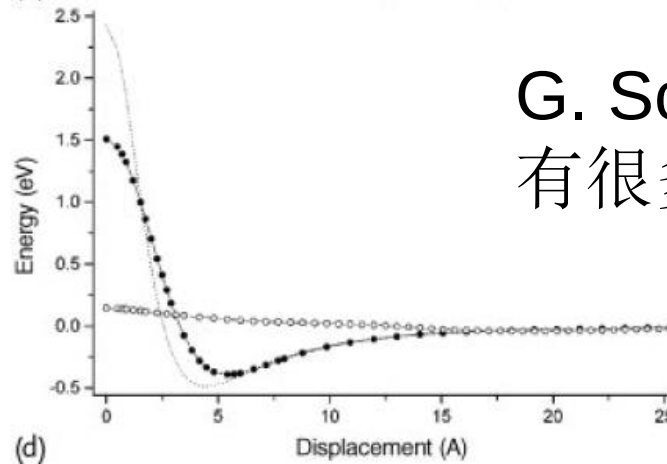
(a)



May & Kuhn Book

偶极-偶极近似在长程是比较准确的，短程情况经常会高估耦合项

(b)



(d)

G. Scholes, 许昭萍, ...
有很多相关工作

4. FÖRSTER公式

$$\begin{aligned}k_{D^*A \rightarrow DA^*} &= \frac{K^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau \left\langle e^{-\frac{i}{\hbar} H_{D^*A} \tau} e^{\frac{i}{\hbar} H_{DA^*} \tau} \right\rangle_{D^*A} \\&= \frac{K^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau \left\langle e^{-\frac{i}{\hbar} H_{D^*} \tau} e^{\frac{i}{\hbar} H_D \tau} \right\rangle_{D^*} \left\langle e^{-\frac{i}{\hbar} H_A \tau} e^{\frac{i}{\hbar} H_{A^*} \tau} \right\rangle_A \\&= \frac{K^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau C_D(\tau) C_A(\tau)\end{aligned}$$

上节课二阶微扰论结果

$$K = \kappa \frac{\mu_D \mu_A}{R^3}$$

$$C_D(\tau) = \left\langle e^{-\frac{i}{\hbar} H_{D^*} \tau} e^{\frac{i}{\hbar} H_D \tau} \right\rangle_{D^*};$$

$$C_A(\tau) = \left\langle e^{-\frac{i}{\hbar} H_A \tau} e^{\frac{i}{\hbar} H_{A^*} \tau} \right\rangle_A$$

$$\tilde{I}_{ems}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega\tau} C_D(\tau) d\tau;$$

$$\tilde{\alpha}_{abs}(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega\tau} C_A(\tau) d\tau$$

傅里叶变换
的反变换

$$C_A(\tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega\tau} \tilde{\alpha}_{abs}(\omega) d\omega$$

$$\begin{aligned}
k_{D^*A \rightarrow DA^*} &= \frac{K^2}{\hbar^2} \int_{-\infty}^{\infty} d\tau C_D(\tau) C_A(\tau) \\
&= \frac{K^2}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\tau C_D(\tau) \int_{-\infty}^{+\infty} e^{i\omega\tau} \tilde{\alpha}_{abs}(\omega) d\omega \\
&= \frac{K^2}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega \tilde{I}_{ems}(\omega) \tilde{\alpha}_{abs}(\omega) d\omega
\end{aligned}$$

$$\tilde{I}_{ems}(\omega) \propto I_{ems}(\omega) / \omega^3$$

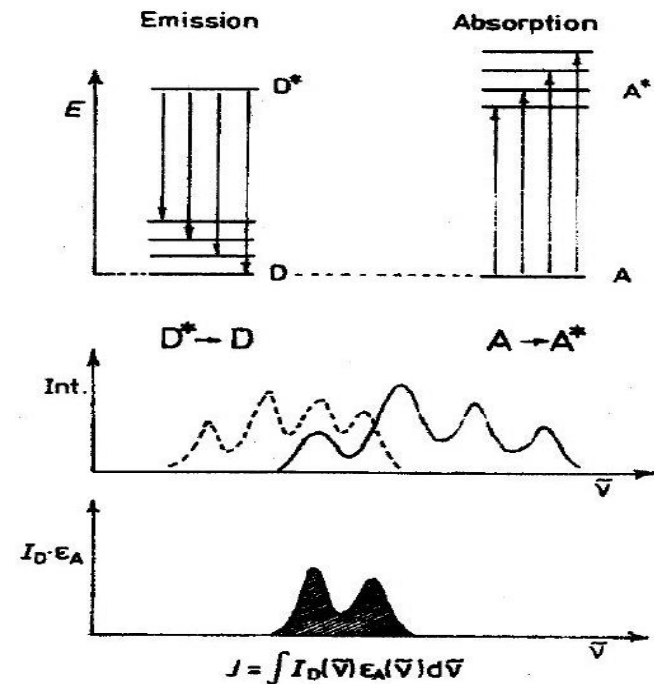
$$\tilde{\alpha}_{abs}(\omega) \propto \alpha_{abs}(\omega) / \omega$$

$$k_{D^*A \rightarrow DA^*} = \text{const} \times \frac{1}{R^6} \int_{-\infty}^{+\infty} \frac{d\omega}{\omega^4} I_{\text{ems}}^D(\omega) \alpha_{\text{abs}}^A(\omega)$$

$$k_{D \rightarrow A} = \frac{9c^4 \kappa_{DA}^2}{8\pi n_{\text{agg}} |X_{DA}^{(0)}|^6} \int_0^\infty \frac{d\omega}{\omega^4} I_D(\omega) \alpha_A(\omega)$$

(May and Kuhn Book)

- 与距离的**6**次方成反比
- 与给体发射和受体吸收光谱重叠成正比



Molecular Ruler

定义一个特征长度 R_F

$$k_{\text{EET}}(R_F) = \frac{1}{\tau_{\text{phot}}^{(D)}} = \int_0^\infty d\omega I_D(\omega),$$


给体的辐射寿命

$$k_{\text{EET}} = \frac{1}{\tau_{\text{phot}}^{(D)}} \left(\frac{R_F}{|X_{\text{DA}}^{(0)}|} \right)^6$$

通过测量能量转移速率可以得到给受体之间的距离

小结1: 费米黄金规则 (FGR)

分立能级形式

$$w_{k'k}(t) = \frac{d}{dt} P_{k'k}(t) = 2\pi \left(\frac{\mu_{k'k} E}{2\hbar} \right)^2 \delta(\omega_{k'k} - \omega_L)$$

关联函数形式

$$\tilde{\alpha}_{abs}(\omega_L) = \int_{-\infty}^{\infty} dt e^{-i\omega_L t} \langle \hat{\mu} \hat{\mu}(t) \rangle_g$$

偶极-偶极关联函数

傅立叶变换



光谱

ET/EET 相互作用-关联函数

积分

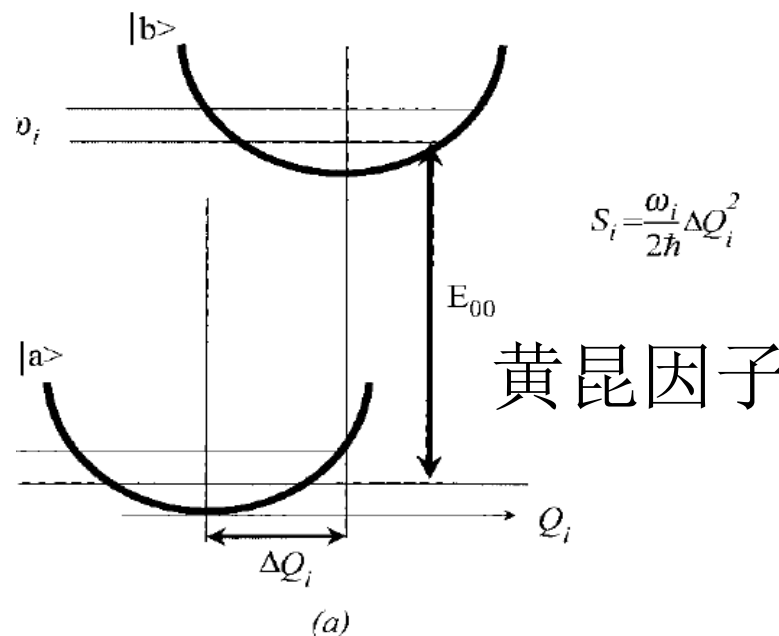
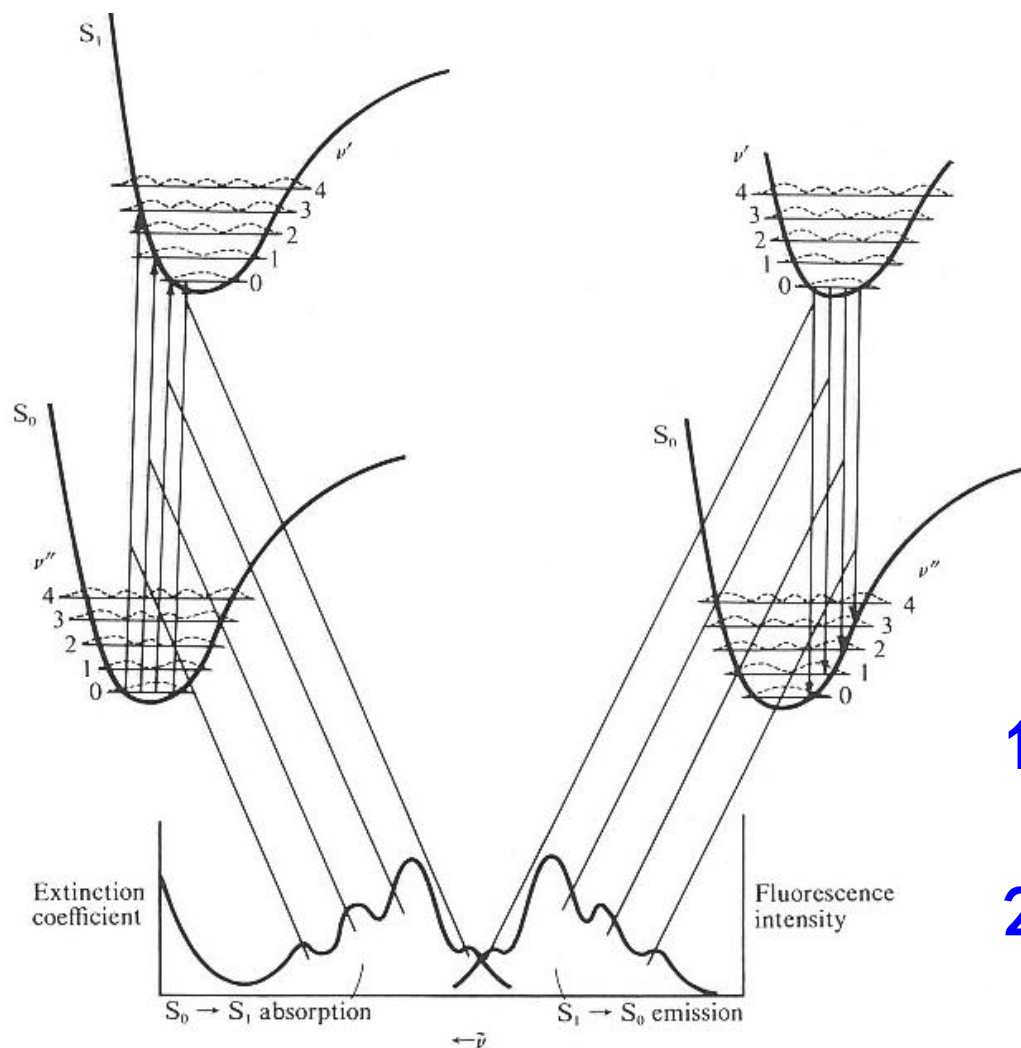


速率

Franck-Condon近似下两者计算的关联函数是一样的

小结2：吸收和发射光谱

$$|\langle \chi_{bv'_i} | \chi_{a0_i} \rangle|^2 = \frac{S_i^{v'_i}}{v'_i!} e^{-S_i}$$

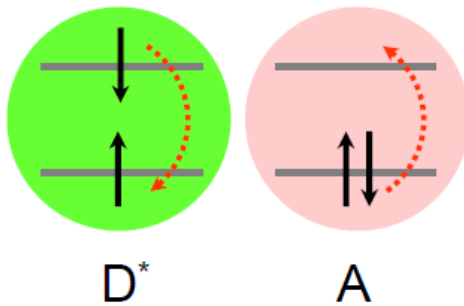


黄昆因子

1. 跃迁偶极矩 (Frank-Condon近似)
2. 波函数重叠 (位移谐振子近似)

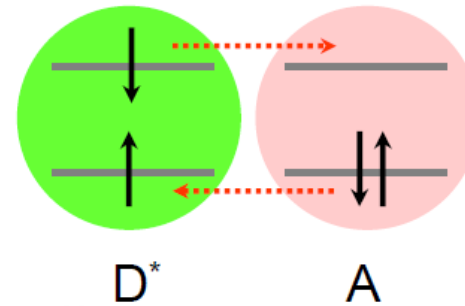
小结3：激发态传能机制

Förster, Coulombic
(long range $\sim 30\text{-}100 \text{ \AA}$)

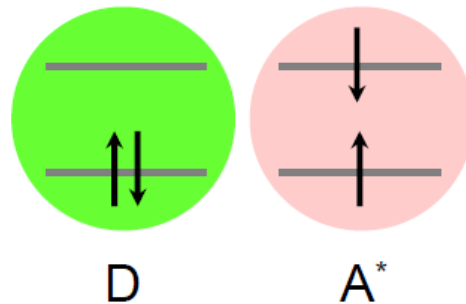


**SINGLET-SINGLET
TRANSFER**

Dexter, e^- exchange
(short range $\sim 6\text{-}20 \text{ \AA}$)



**SINGLET-SINGLET &
TRIPLET-TRIPLET TRANSFER**



小结4: FÖRSTER传能公式

$$k_{D^*A \rightarrow DA^*} = \text{const} \times \frac{1}{R^6} \int_{-\infty}^{+\infty} \frac{d\omega}{\omega^4} I_{\text{ems}}^D(\omega) \alpha_{\text{abs}}^A(\omega)$$

- 与距离的**6**次方成反比
- 与给体发射和受体吸收光谱重叠成正比

