《高等物理化学》

（凝聚相）化学动力学部分

史强，qshi@iccas.ac.cn, 82616163

（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。

闫亚明，yanyaming@iccas.ac.cn， 62564822
柳燕莺，liuyanying@iccas.ac.cn， 62564822

2018.12.13， Lecture 5

1. 上节内容回顾
2. 分子间激发态：激子、Excimer和Exciplex
3. 光谱部分：光与物质相互作用
4. 光谱的展宽和线型
5. 分子振动光谱：简正模式
6. 小结

1.1费米黄金规则（含时微扰FGR）

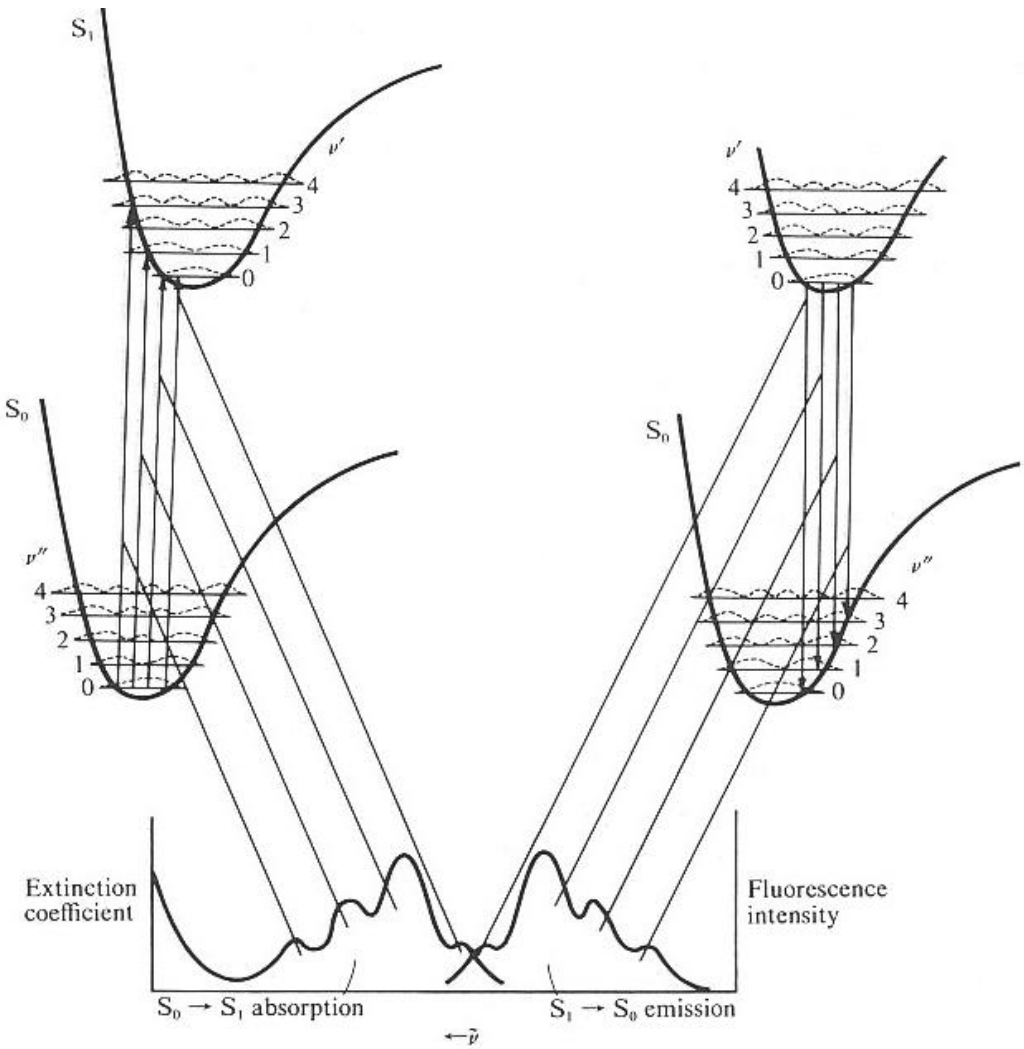
分立能级形式

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

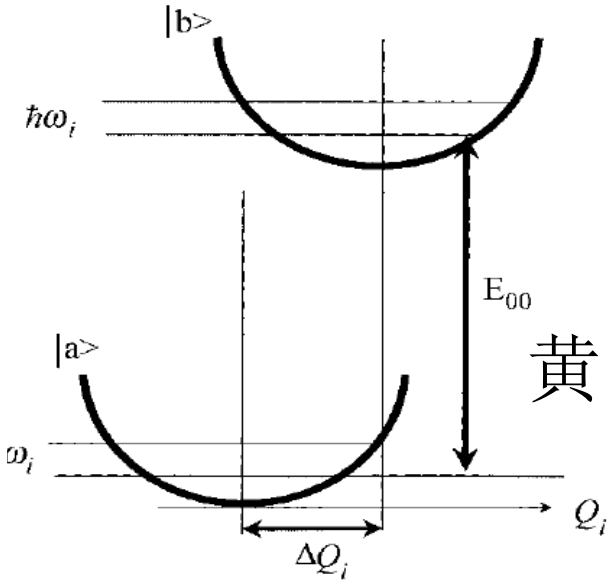
关联函数形式

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

1.2：吸收和发射光谱



$$|\langle \chi_{bv_i'} | \chi_{a0_i} \rangle|^2 = \frac{S_i^{v_i'}}{v_i'!} e^{-S_i}$$



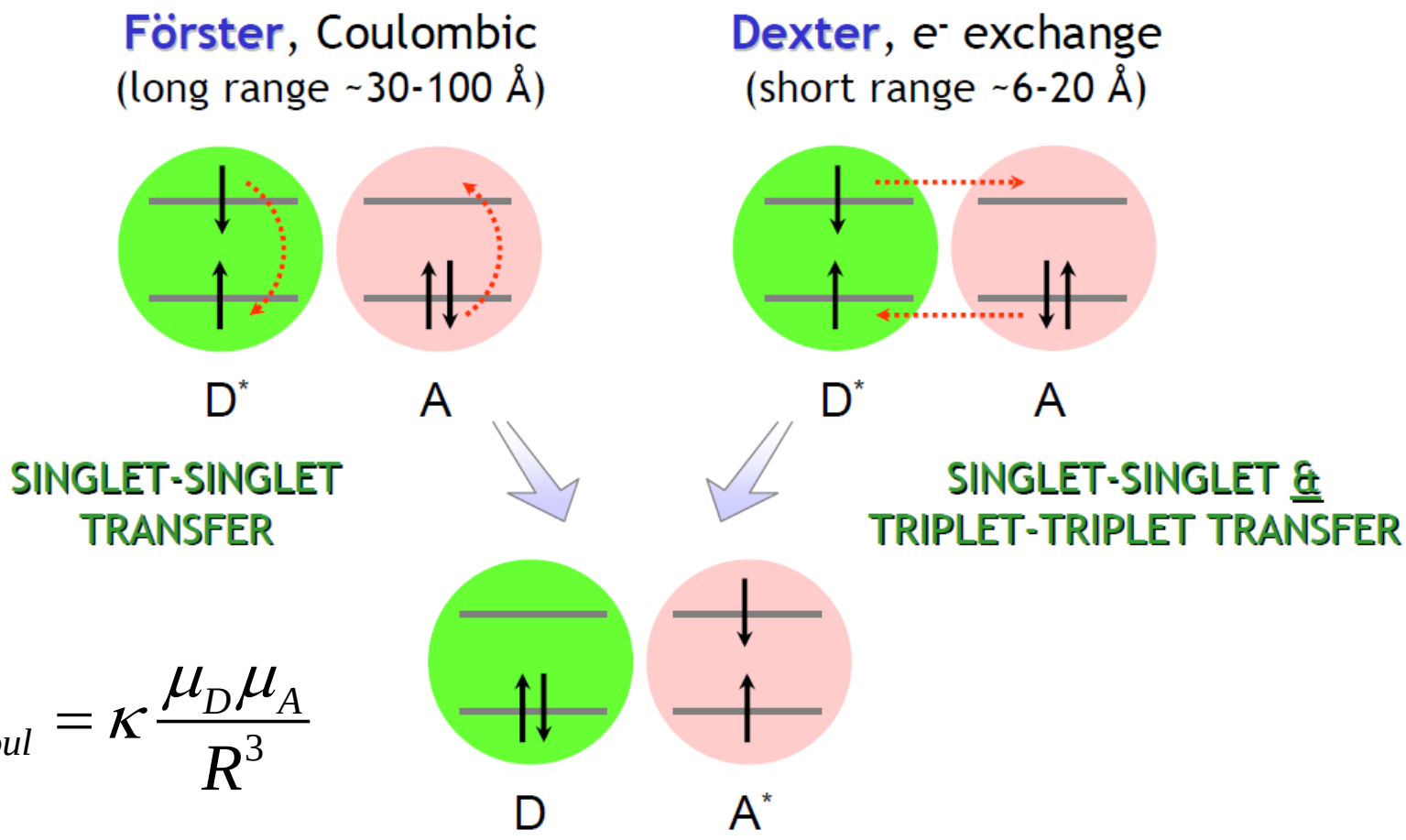
$$S_i = \frac{\omega_i}{2\hbar}\Delta Q_i^2$$

黄昆因子

(a)

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

1.3：激发态传能机制

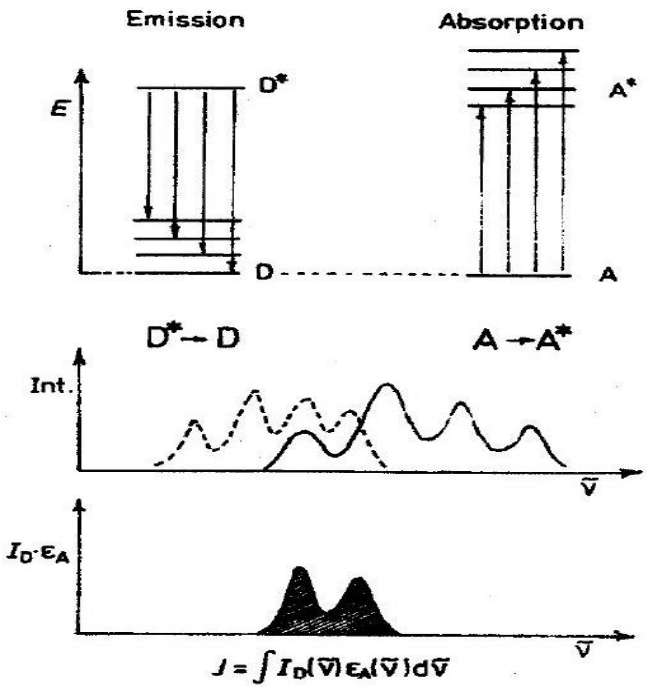


$$K_{coul} = \kappa \frac{\mu_D \mu_A}{R^3}$$

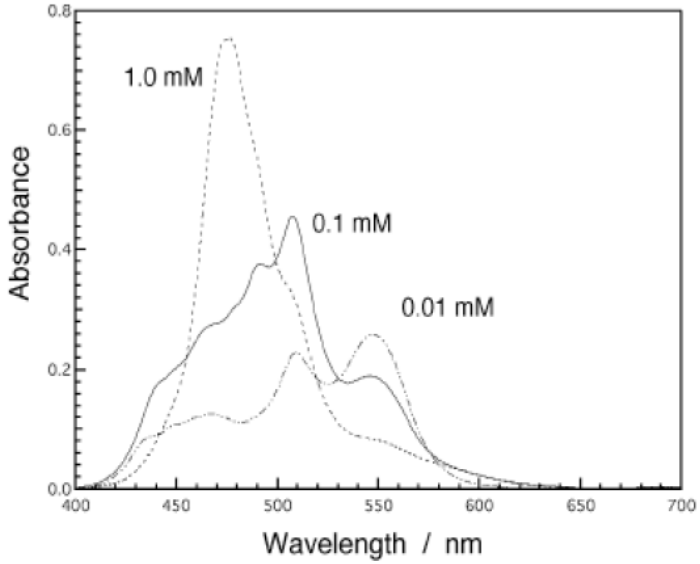
1.4：Förster传能公式

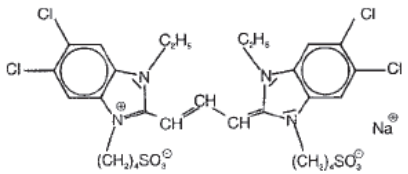
$$k_{D^*A\to DA^*} = const \times \frac{1}{R^6}\int_{-\infty}^{+\infty}\frac{d\omega}{\omega^4} I_{ems}^{D}(\omega)\alpha_{abs}^{A}(\omega)$$

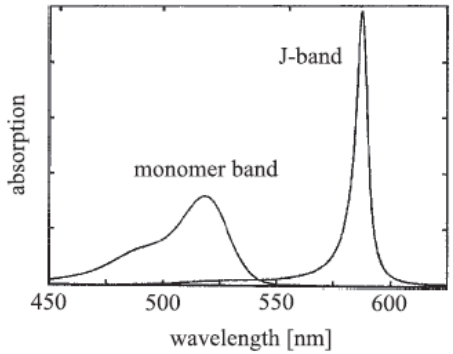
- 与距离的6次方成反比
- 与给体发射和受体吸收光谱重叠成正比

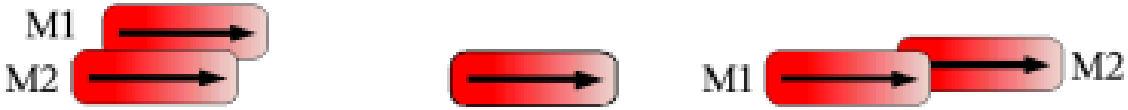


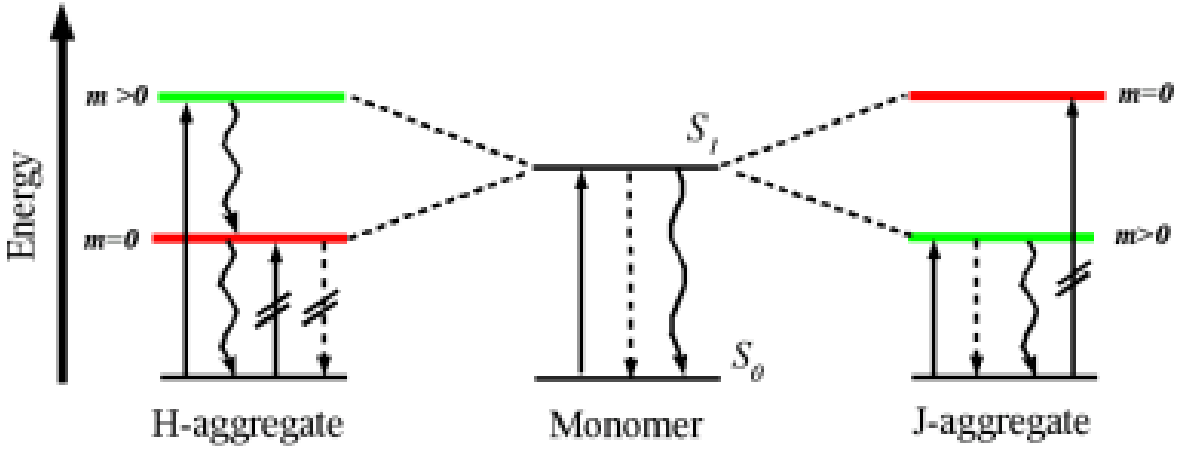
1.5：J-和H-聚集体


1.0 mM
0.1 mM
0.01 mM
Absorbance
Wavelength / nm
0.0
0.2
0.4
0.6
0.8
400
450
500
550
600
650
700


Cl
Cl
Cl
Cl
C_2H_5
C_2H_5
N
N
CH
CH
CH
CH
N
N
$(CH_2)_4SO_3^-$
$(CH_2)_4SO_3^-$
Na^+


J-band
monomer band
absorption
450
500
550
600
wavelength [nm]


M1
M2
M1
M2


Energy
m >0
m=0
S_1
S_0
m=0
m>0
H-aggregate
Monomer
J-aggregate

本次课主要内容

1. 上节内容回顾
2. 分子间激发态：Excimer和Exciplex, Exciton
3. 光谱部分：光与物质相互作用
4. 光谱的展宽和线型
5. 分子振动光谱：简正模式
6. 小结

2. Excimer, Exciplex, exciton

Excimers（excited dimer）are dimers in the excited state 激-基缔合物；Exciplexs（excited complex）are excited state complexes激-基复合物

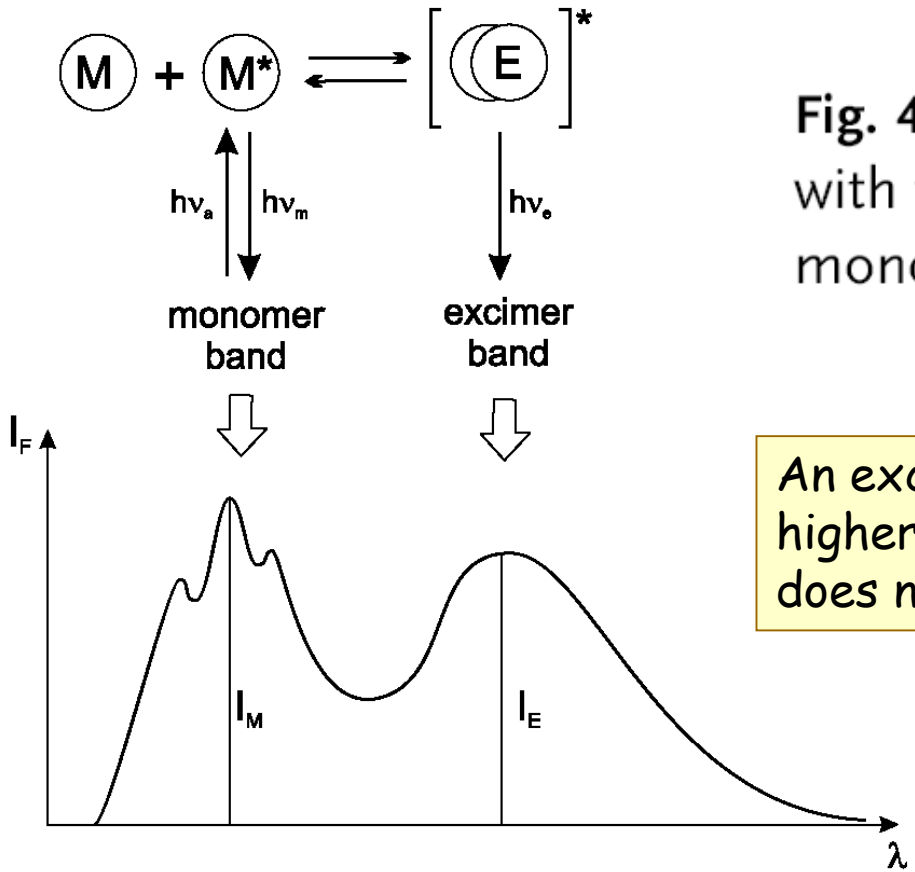


Fig. 4.6. Excimer formation, with the corresponding monomer and excimer bands.

An excimer is located at wavelengths higher than that of the monomer and does not show vibronic bands.

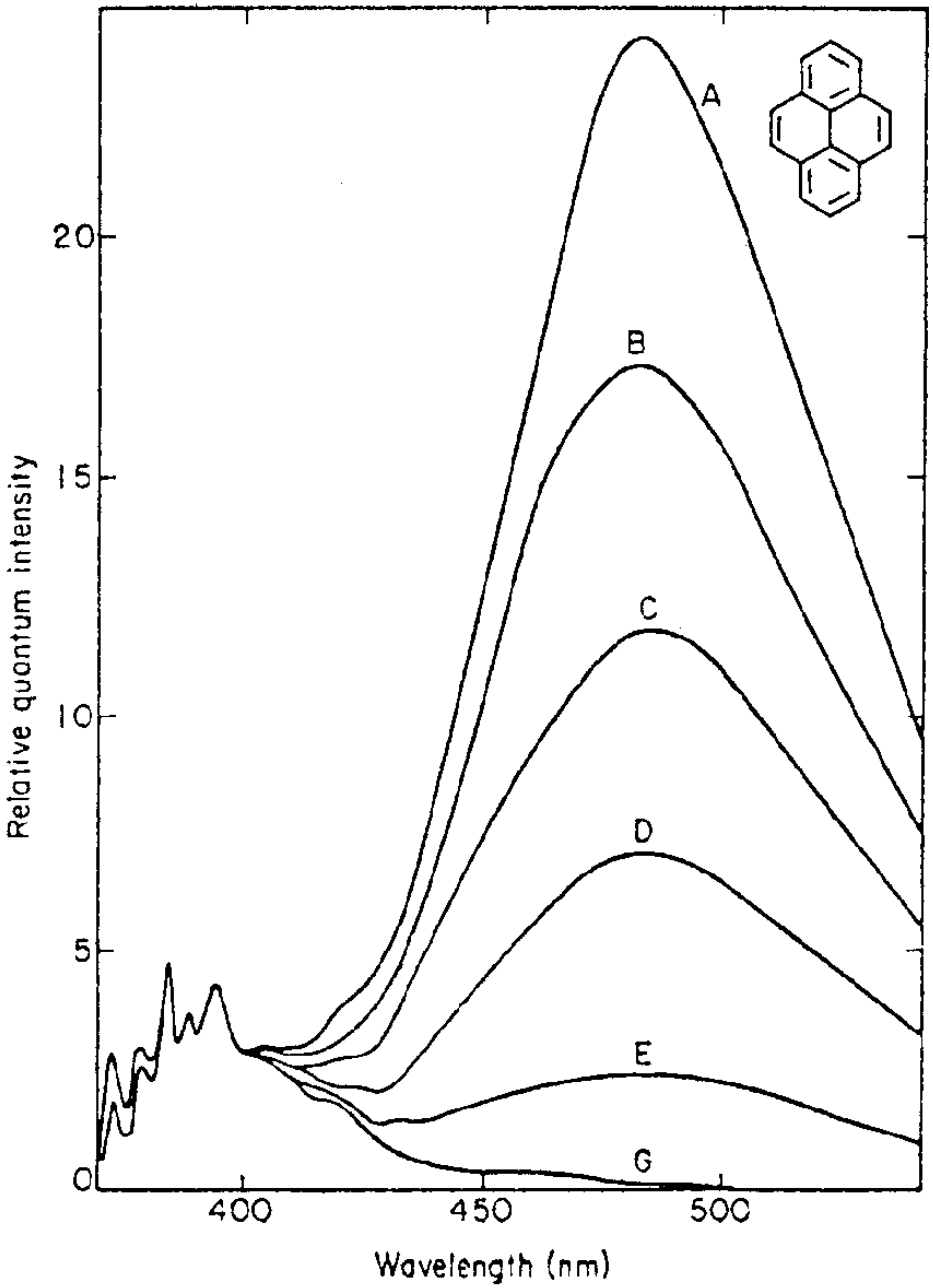
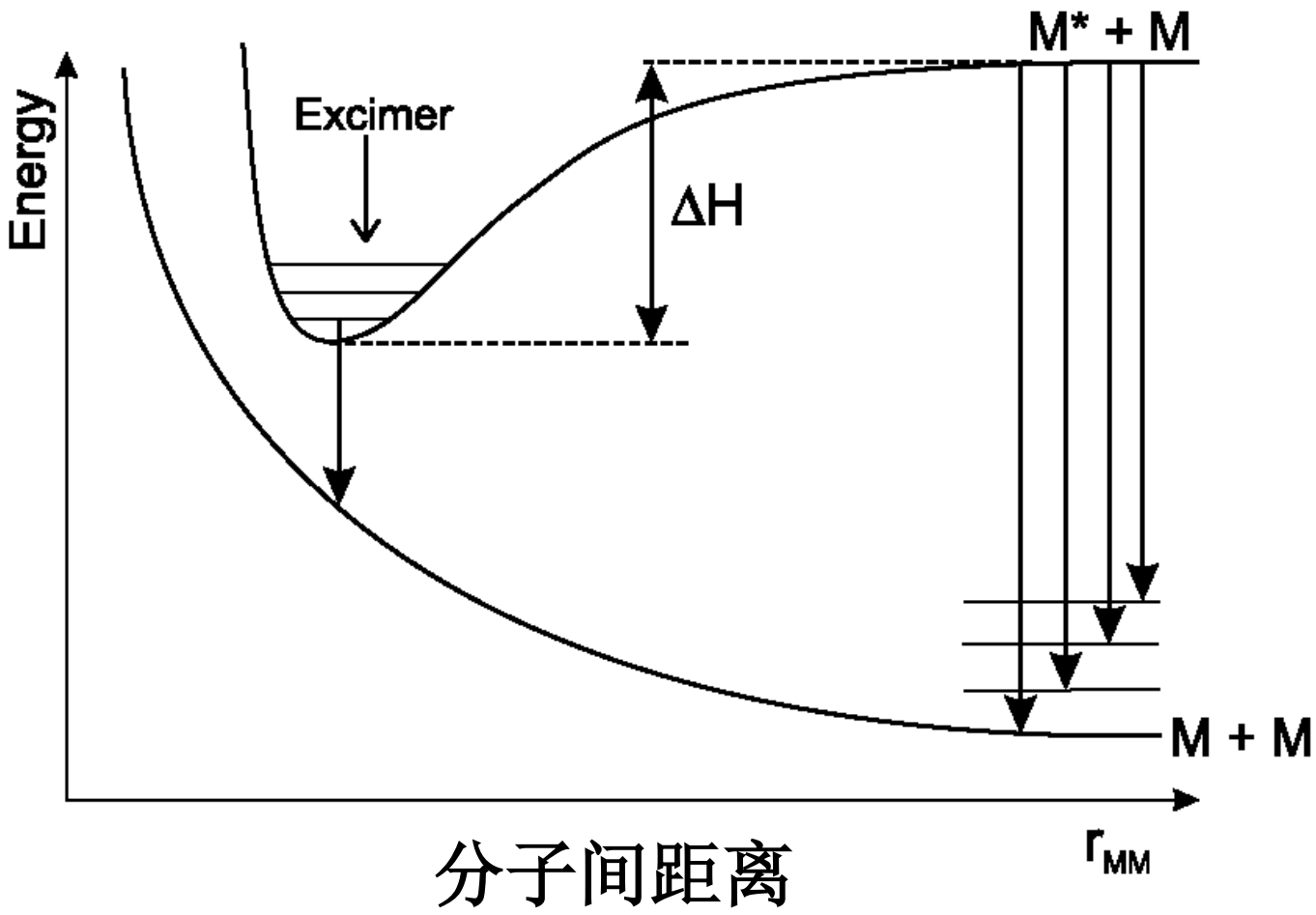


Fig. 4.7. Fluorescence spectra of pyrene at various concentrations in cyclohexane. A: 10^{-2} mol L^{-1}; B: 7.75×10^{-3} mol L^{-1}; C: 5.5×10^{-3} mol L^{-1}; D: 3.25×10^{-3} mol L^{-1}; E: 10^{-3} mol L^{-1}; G: 10^{-4} mol L^{-1} (from Birks and Christophorou, (1963) Spectrochim. Acta, **19**, 401).

Excimer来源于分子间相互作用



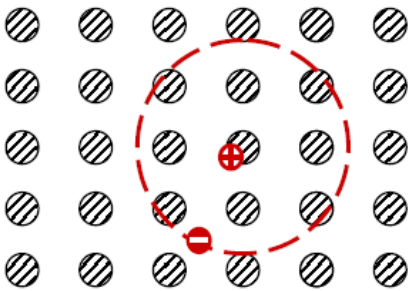
Exciton：凝聚相中的激发态

Excitons
(bound electron-hole pairs)

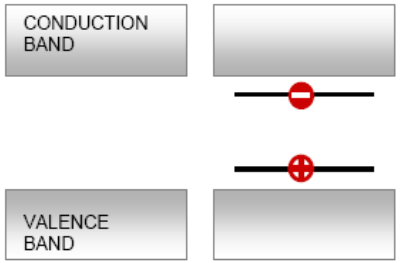
treat excitons as chargeless particles capable of diffusion,

also view them as excited states of the molecule

Wannier exciton
(typical of inorganic semiconductors)



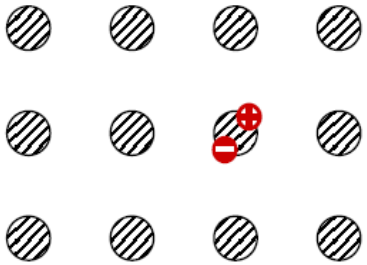
SEMICONDUCTOR PICTURE



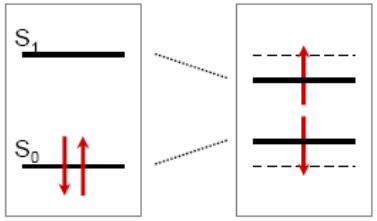
GROUND STATE WANNIER EXCITON

binding energy ~10meV
radius ~100Å

Frenkel exciton
(typical of organic materials)



MOLECULAR PICTURE



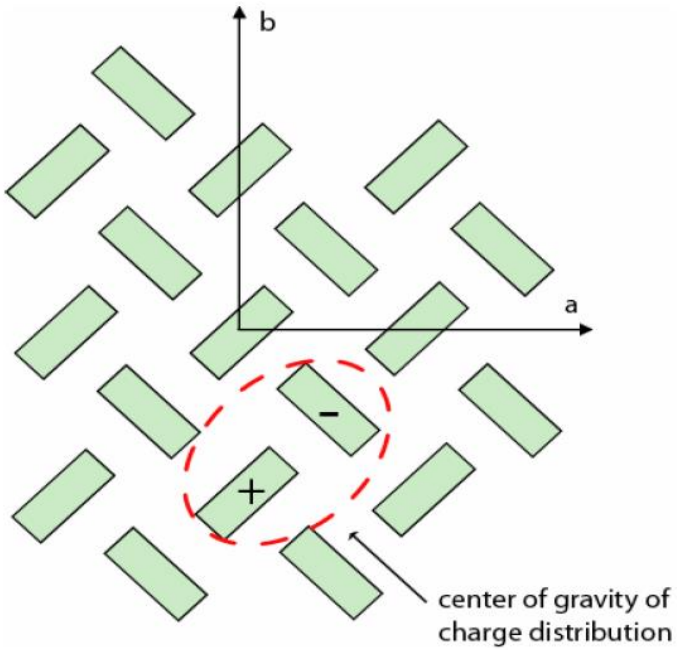
GROUND STATE FRENKEL EXCITON

binding energy ~1eV
radius ~10Å

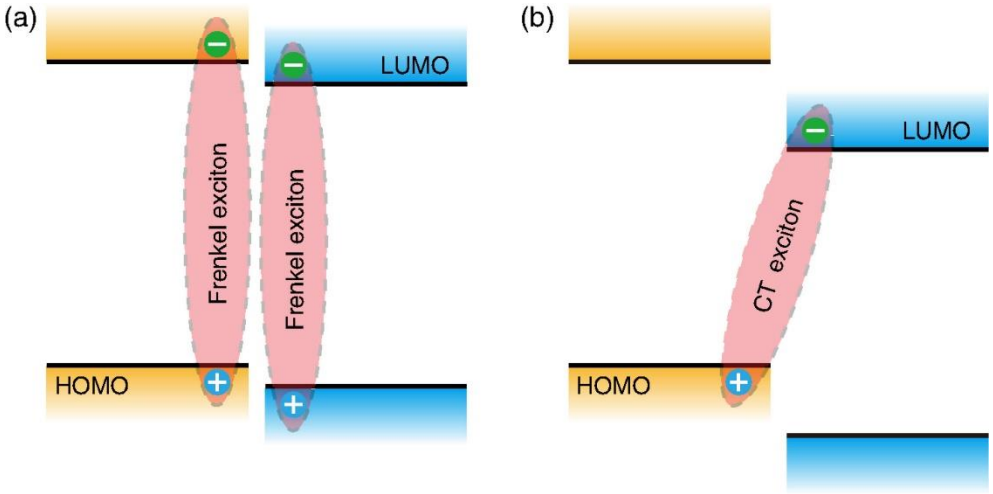
Charge Transfer (CT) Exciton
(typical of organic materials)

Electronic Processes in Organic Crystals and Polymers by M. Pope and C.E. Swenberg

Charge-transfer exciton

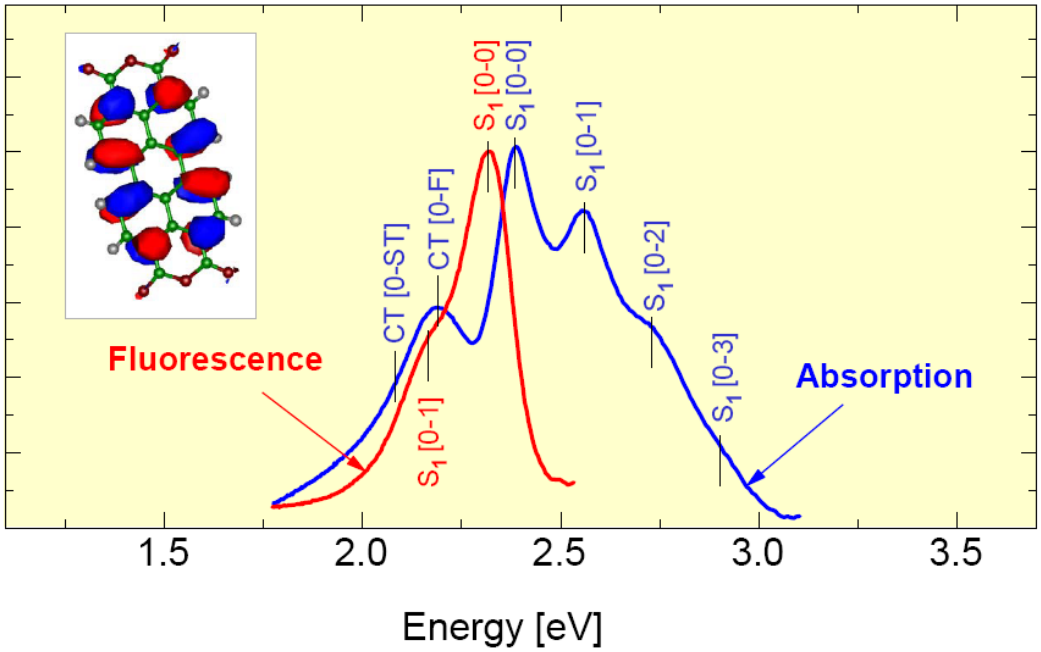


相同种类分子间



不同分子的界面

CT激子的光谱特征



PTCDA Solution (~ 2μM in DMSO

3. 分子光谱

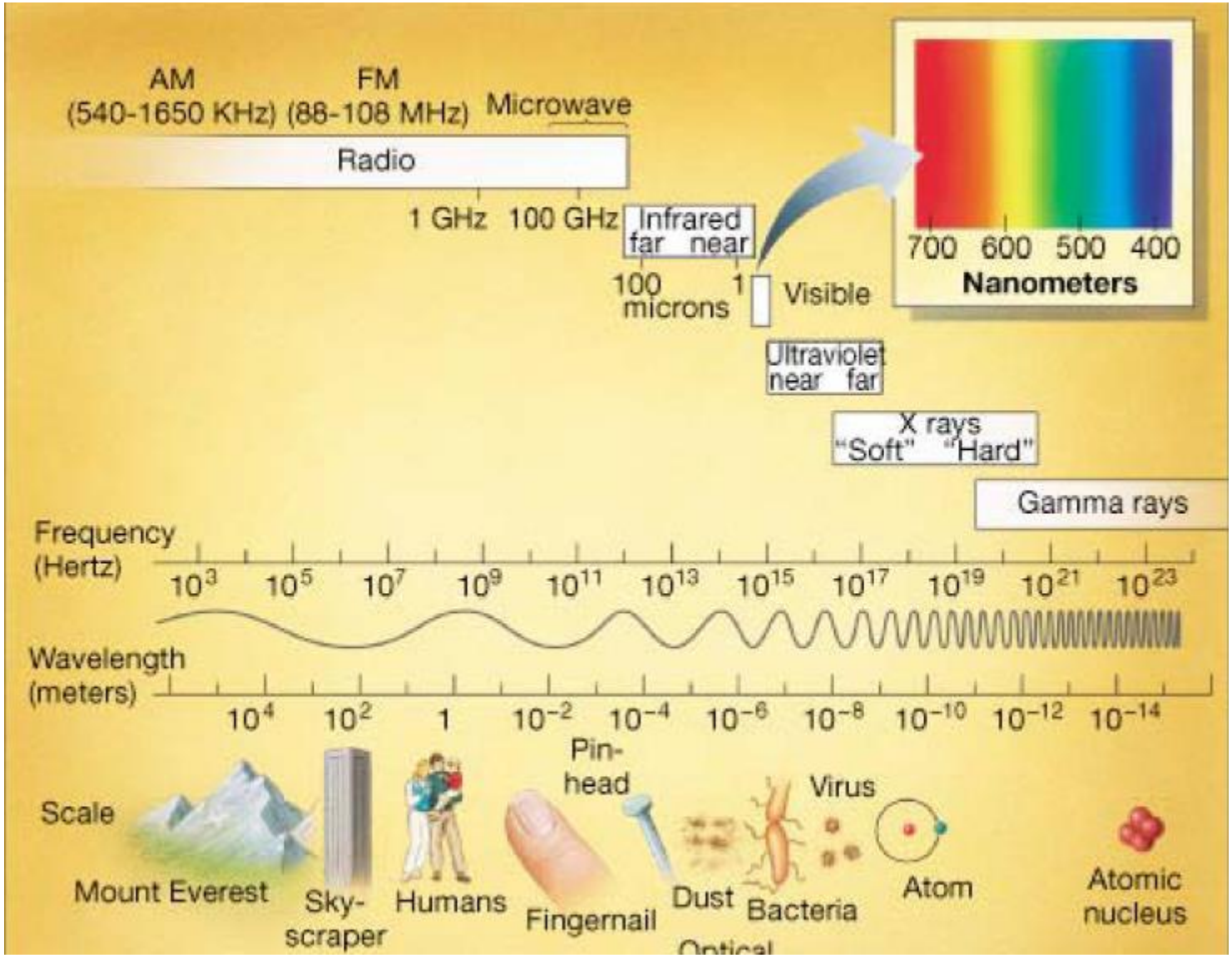
光谱是探测分子结构和动力学非常重要的手段

其他手段：质谱（质量），电子、中子、STM

能量尺度：0.01eV-10eV

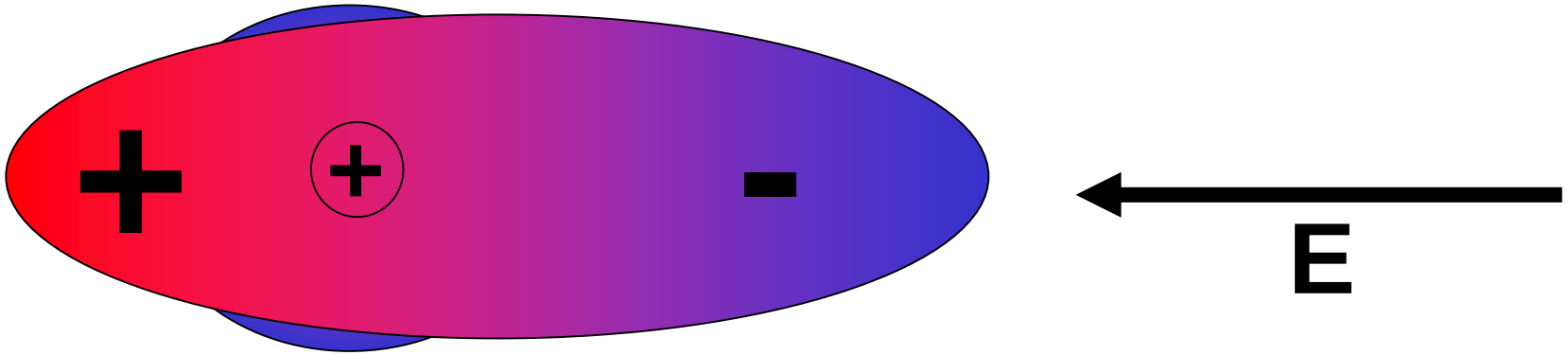
时间尺度：10^{-15}s-1000s，分子原子核运动尺度

电磁波的时间和空间尺度



光与物质相互作用：宏观现象

$$P = \varepsilon_0\left(\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots\right)$$



分子极化 **P**： Dipole moment per unit volume

$\chi^{(1)}$，$\chi^{(2)}$，$\chi^{(3)}$ **一阶、二阶、三阶极化率**

频率依赖、方向依赖…

Process

$\chi^{(1)}$

- Linear absorption
- Spontaneous emission (Fluorescence)
- Reflection
- Elastic scattering
- Inelastic scattering: Raman-scattering
- Diffraction

$\chi^{(2)}$

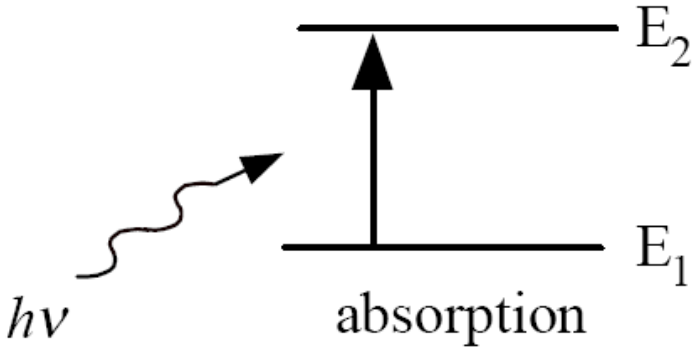
- Second harmonic generation (SHG)
- Sum-frequency generation (SFG)
- Difference-frequency generation (DFG)
- Optical parametric amplification
- Two-photon absorption (TPA)

$\chi^{(3)}$

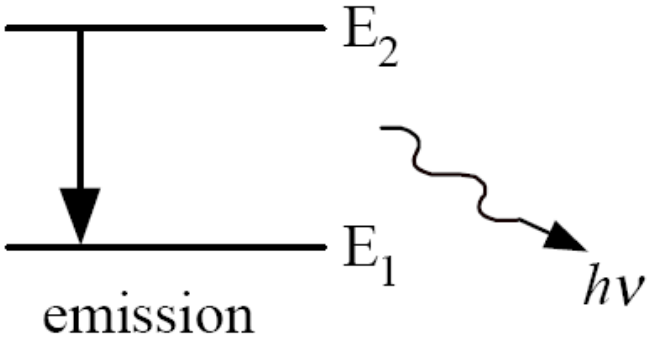
- Third harmonic generation (THG)
- CARS (Coherent Anti-Stokes-Raman-Scattering)

- Pump-probe
- Photon-echo
- 2D spectra

吸收与发射光谱

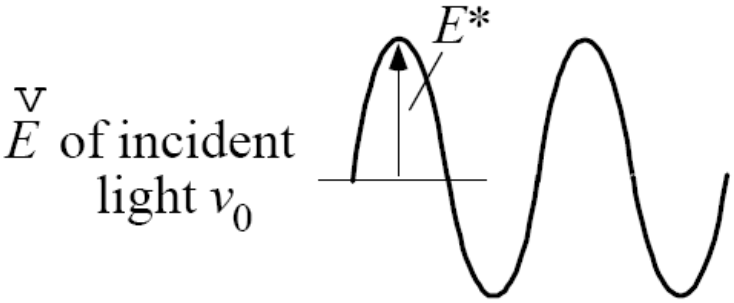


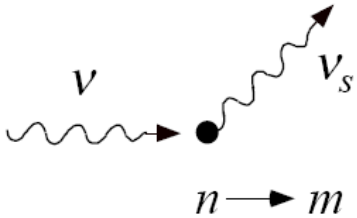
$$E_2 - E_1 = h\nu$$

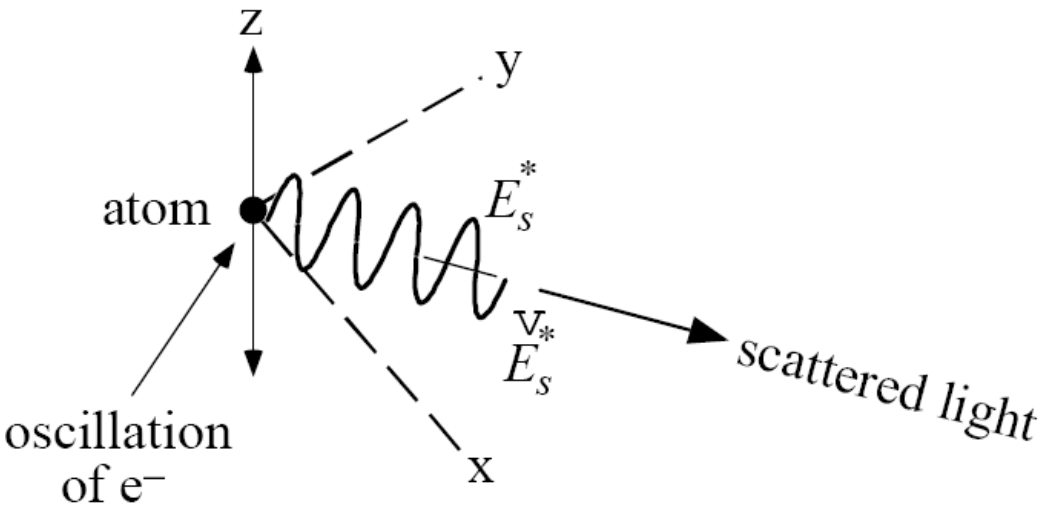


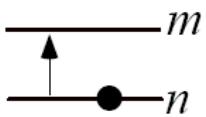
$$E_2 - E_1 = h\nu$$

散射（Scattering）

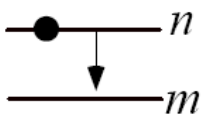








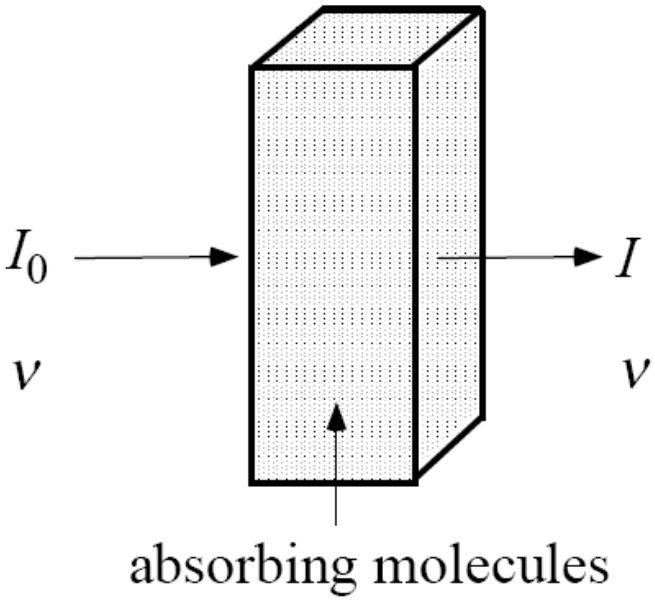
Stokes



anti-Stokes

拉曼散射（Nobel Prize 1930）

Beer-Lambert定律



$$I = I_0 \exp[-\alpha(\omega)Cl]$$

摩尔消光系数　浓度　光程

线性光谱：信号强度正比于光强
非线性光谱：信号强度正比于光强的高次幂

光与物质相互作用：哈密顿量

$$H_{light-mol} = -\boldsymbol{E}(\boldsymbol{X}_m, t) \bullet \hat{\mu}_m$$

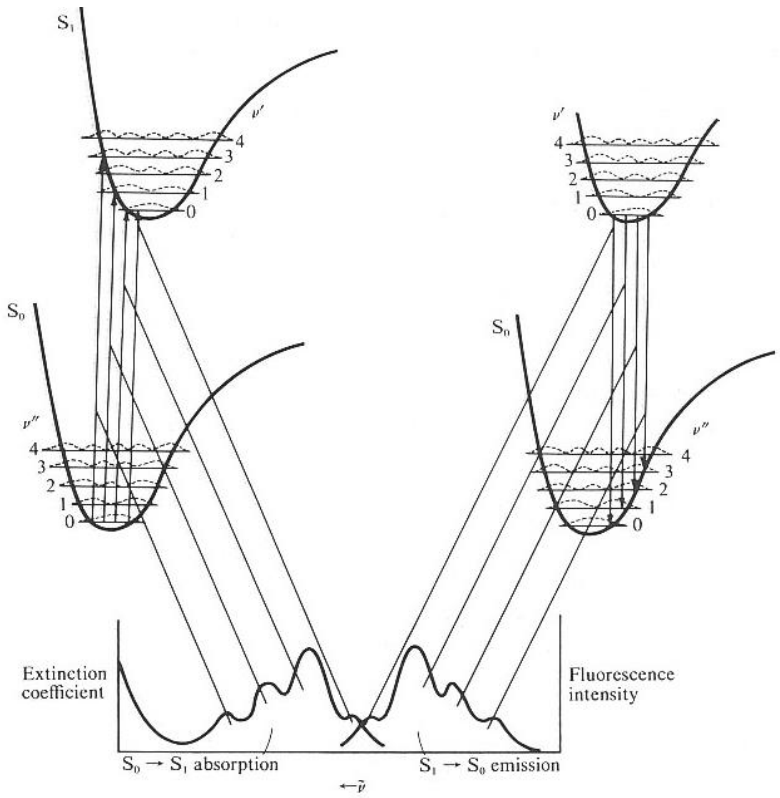
$$\hat{\boldsymbol{\mu}}_m = \sum_{u \in m} q_u \boldsymbol{x}_u = -\sum_j e\boldsymbol{r}_j^{(m)} + \sum_n e z_n^{(m)} \boldsymbol{R}_n^{(m)}$$

1 和电场的相互作用，磁场要弱很多
2 电磁波波长远大于分子的尺度，四极矩贡献很小
3 偶极矩算符包括了原子核和电子的贡献

$$e^{-i\boldsymbol{k}\bullet\boldsymbol{x}} \approx e^{-i\boldsymbol{k}\bullet\boldsymbol{x}_m}[1 - i\boldsymbol{k}\bullet(\boldsymbol{x} - \boldsymbol{x}_m) - \ldots]$$

电子态吸收发射光谱

- 波长区域：近红外、可见、紫外

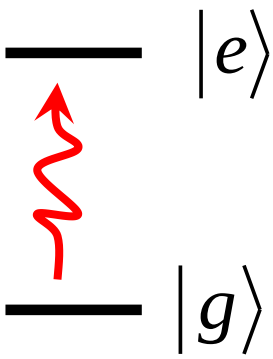


光谱的线宽？

吸收光谱的线型

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

初始状态： $|g\rangle$

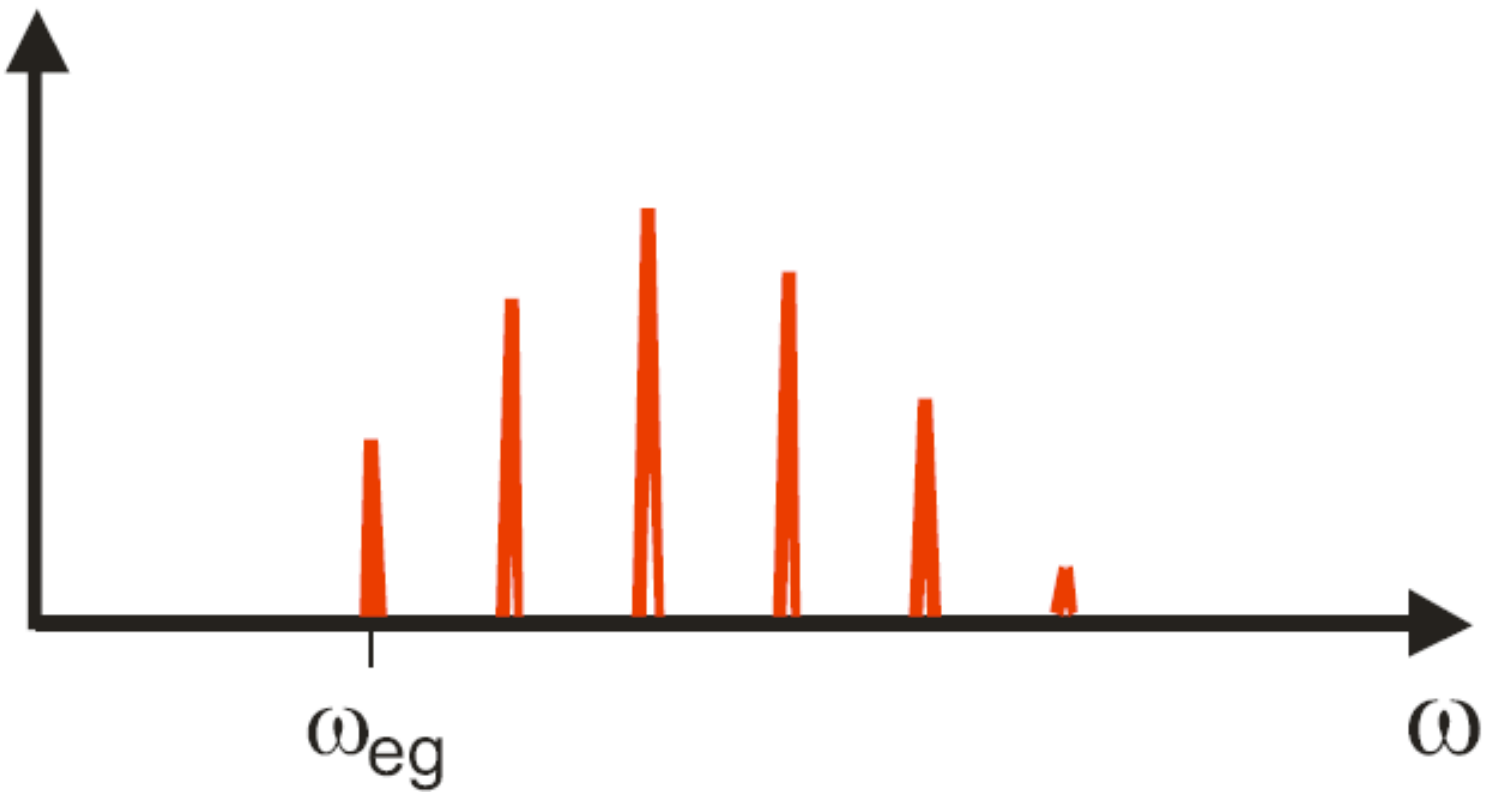


$$C(t) = \langle \mu\mu(t) \rangle_g = \mu_{eg}^2 \langle A(t) \rangle$$

$$\frac{dA(t)}{dt} = i(\omega_e - \omega_g) A(t)$$

1. 理想情况：ω_{eg} 是常数，能级寿命无限

$$\tilde{\alpha}_{abs}(\omega_L) = \delta(\omega_L - \omega_{eg})$$



2. 能级寿命有限（寿命展宽，T_1过程）

$$\frac{dA(t)}{dt} = i(\omega_e - \omega_g)A(t) - \frac{1}{2}\gamma A(t)$$

γ^{-1} 是激发态能级寿命，T_1

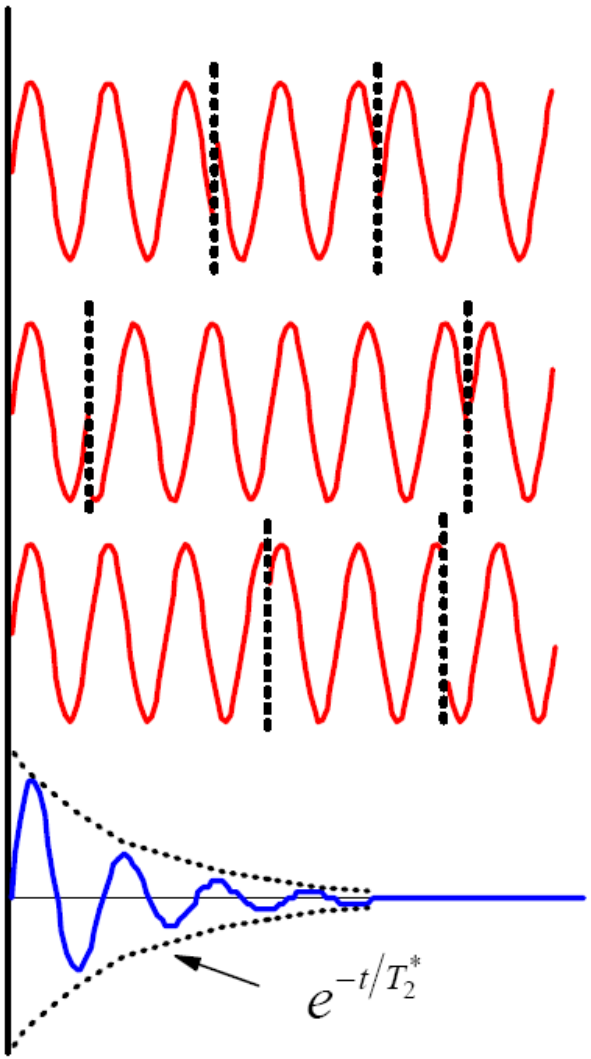
$$\tilde{\alpha}_{abs}(\omega_L) \propto \frac{1}{\left(\omega_L - \omega_{eg}\right)^2 + \frac{1}{4}\gamma^2}$$

Lorentzian（洛仑兹）线型，均匀展宽，寿命展宽多见于气相光谱

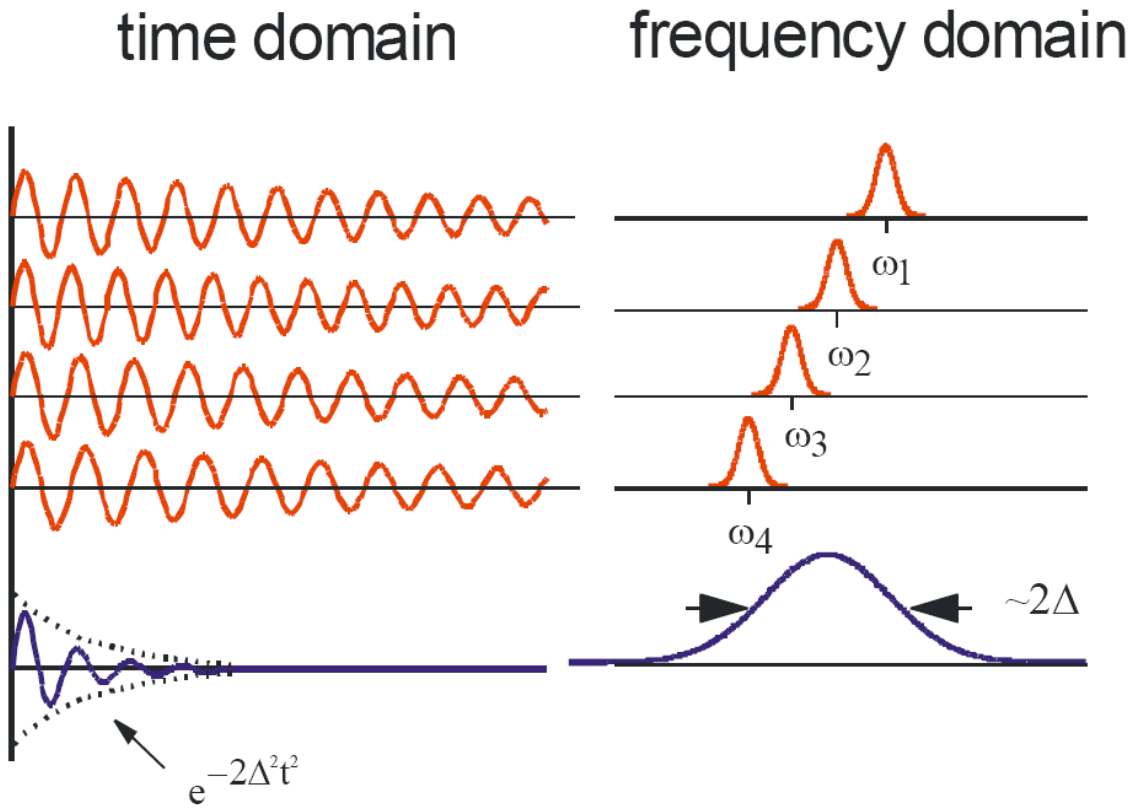
3. 解相过程（Dephasing, T_2过程 ）

第一种情况：碰撞等导致（随机）失去相位，平均的结果导致关联函数的衰减

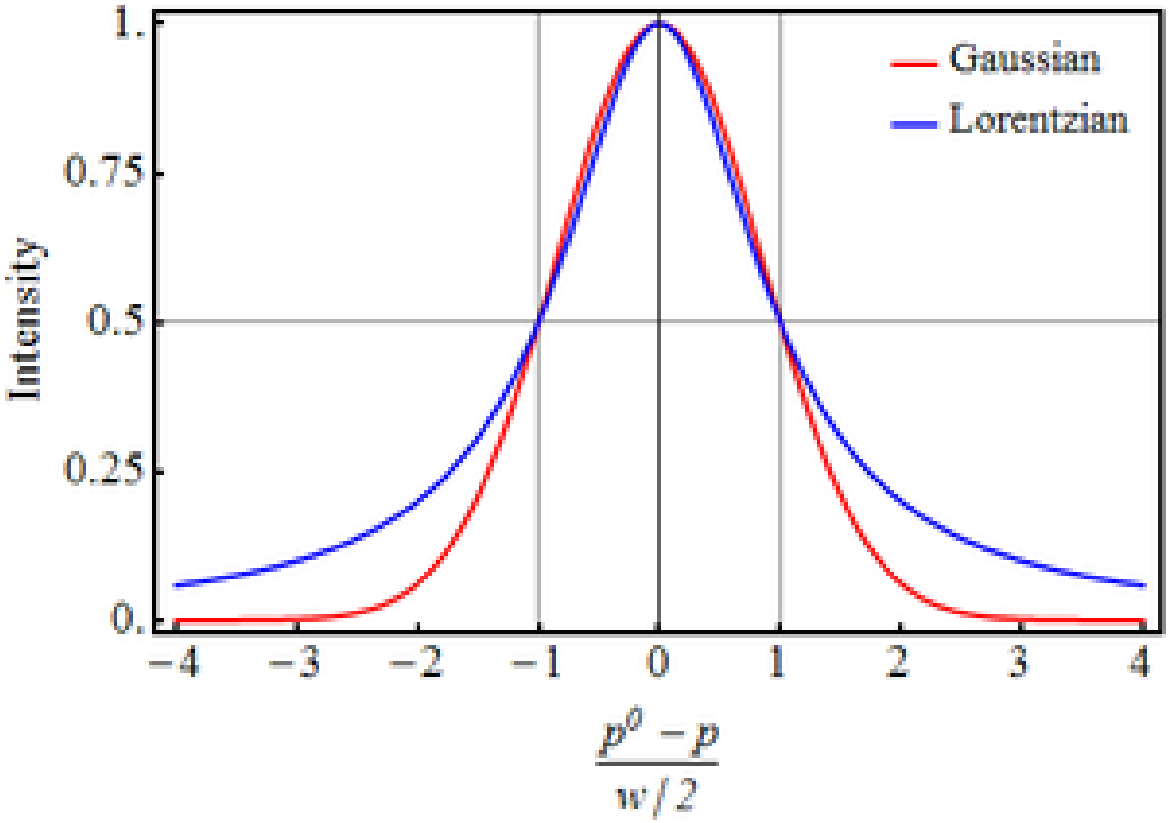
指数形式衰减--〉洛仑兹线型



4. 分子的能级分布：每个分子所处的瞬时的溶剂环境导致跃迁频率并不相同(非均匀加宽)



$$\tilde{\alpha}_{abs}(\omega_L) = \int d\omega_{eg}\delta(\omega_L - \omega_{eg})P(\omega_{eg}) = P(\omega_L)$$


Gaussian
Lorentzian
Intensity
1.
0.75
0.5
0.25
0.
−4
−3
−2
−1
0
1
2
3
4
$\frac{p^0 - p}{w/2}$

4. Kubo线型理论

当基态和激发态能量差随时间变化时

$$\frac{dA(t)}{dt} = i\omega(t)A(t), \quad \omega(t) = \omega_e(t) - \omega_g(t)$$

$$\omega(t) = \omega_0 + \delta\omega(t)$$

$$\overline{\delta\omega(t)} = \langle \delta\omega(t) \rangle = 0$$

$$A(t) = e^{i\omega_0 t} \exp\left\{ i \int_0^t \delta\omega(s)\, ds \right\}$$

$$\langle A(t) \rangle = e^{i\omega_0 t} \phi(t)$$

$$\phi(t) = \left\langle \exp\left\{ i \int_0^t \delta\omega(s)\, ds \right\} \right\rangle$$

$$\phi(t) = \left\langle \exp\left\{ i\int_0^t \delta\omega(s)\,ds \right\} \right\rangle = \exp\left[-\frac{1}{2}\int_0^t ds_1 \int_0^t ds_2 \left\langle \delta\omega(s_1)\,\delta\omega(s_2) \right\rangle \right]$$

$$= \exp\left[-\frac{1}{2}\int_0^t ds_1 \int_0^t ds_2 \psi(s_1 - s_2) \right] = \exp\left[-\int_0^t ds\,(t-s)\,\psi(s) \right]$$

$$\psi(s) = \left\langle \delta\omega(s)\,\delta\omega(0) \right\rangle$$

应用1：指数衰减的关联函数

$$\psi(s) = \langle \delta\omega(s)\delta\omega(0) \rangle = \Delta^2 e^{-s/\tau}$$

频率分布的宽度

频率涨落的时间尺度

$$\phi(t) = \exp\left\{ -\int_0^t (t-s)\psi(s)\,ds \right\}$$

$$= \exp\left\{ -\Delta^2 \int_0^t (t-s) e^{-s/\tau} ds \right\} = \exp\left\{ -\Delta^2 \tau \left(t - \tau \left(1 - e^{-t/\tau} \right) \right) \right\}$$

静态极限:

$$\phi(t) \approx \exp\left\{-\Delta^2\tau\left(t-\tau\left(1-\left(1-\tfrac{t}{\tau}+\tfrac{t^2}{2\tau^2}\right)\right)\right)\right\} = \exp\left\{-\Delta^2 t^2/2\right\}$$

$$I(\omega) = \frac{\sqrt{2\pi}}{\Delta} e^{-(\omega-\omega_0)^2/2\Delta^2}$$

运动变窄（Motional Narrowing）

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, C(t)\, e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-\Delta^2\tau t} e^{-i(\omega-\omega_0)t}$$

$$= \frac{2}{\Delta^2\tau}\frac{\left(\Delta^2\tau\right)^2}{\left(\Delta^2\tau\right)^2+\left(\omega-\omega_0\right)^2} = \frac{2\Delta^2\tau}{\left(\Delta^2\tau\right)^2+\left(\omega-\omega_0\right)^2}$$

可解模型：位移谐振子

$$H_g = \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 \right)$$

$$H_e = E_{eg} + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (x_j - x_j^{(0)})^2 \right)$$

$$C(t) = \left\langle e^{iH_g t} e^{-iH_e t} \right\rangle_g$$

$$C(t) = \exp\left[-\sum_j S_j [(2n_j + 1) - (n_j + 1)e^{i\omega_j t} - n_j e^{-i\omega_j t}] \right]$$

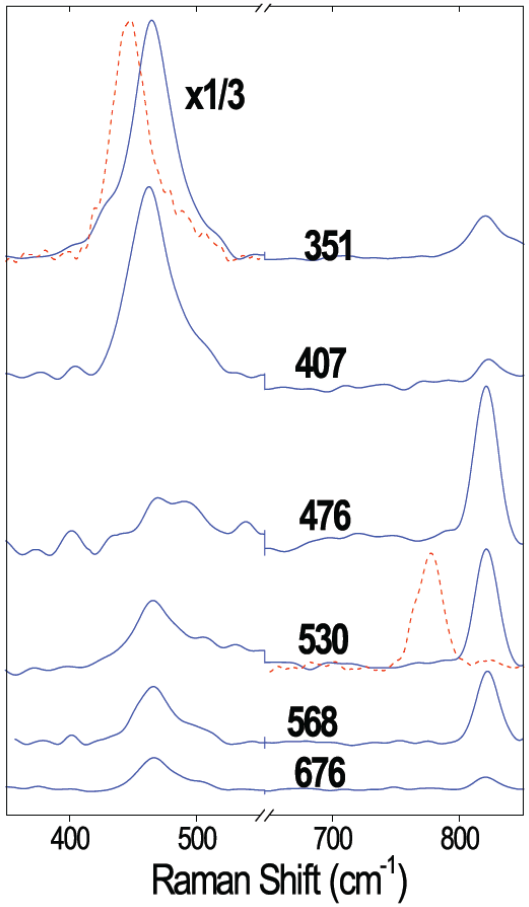
$$C(t) = \exp\left[\int d\omega \frac{J(\omega)}{\omega^2} \left[\coth\left(\frac{\beta\hbar\omega}{2} \right) [\cos\omega t - 1] + i \sin\omega t \right] \right]$$

自动包含展宽、Stokes位移等

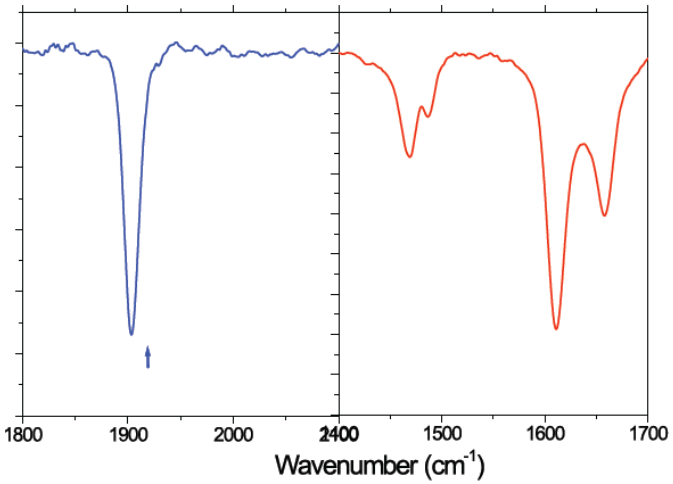
5. 振动光谱

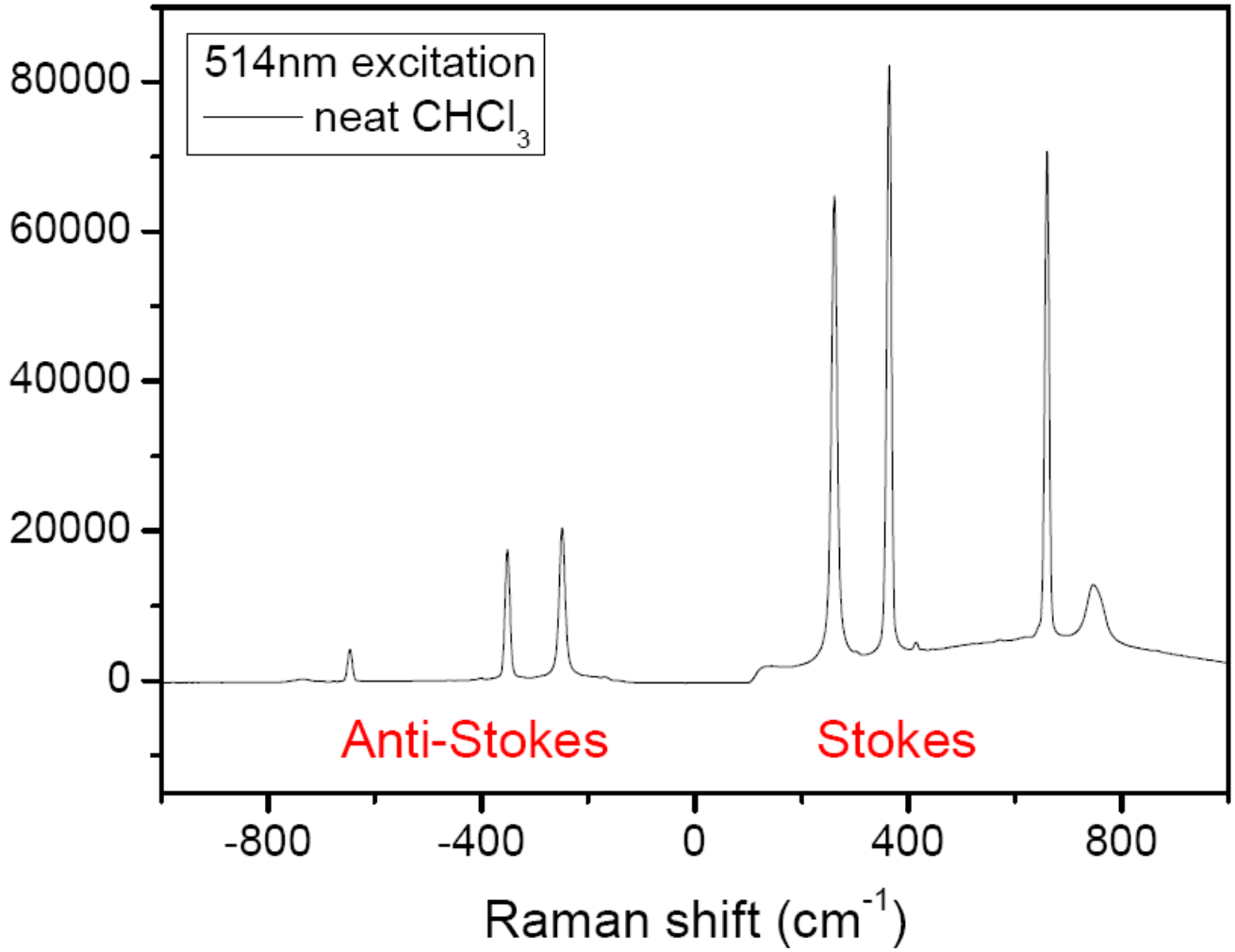
光谱范围：THZ，远红外，红外

Raman

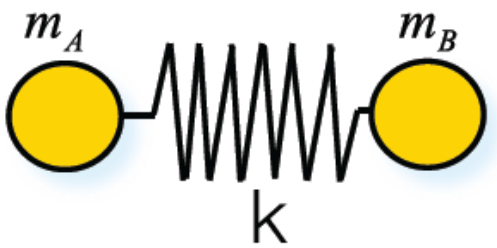


IR

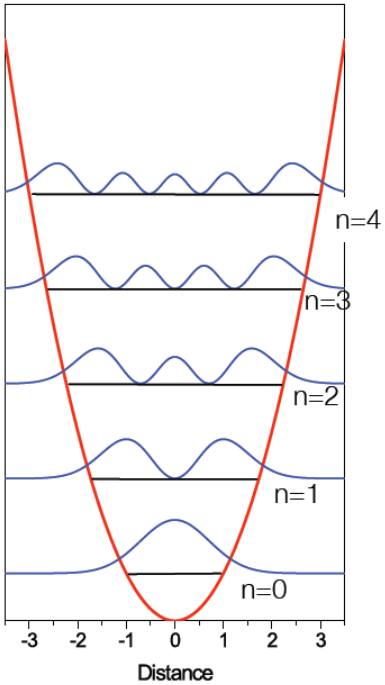



514nm excitation
neat CHCl3
80000
60000
40000
20000
0
Anti-Stokes
Stokes
-800
-400
0
400
800
Raman shift (cm-1)

双原子分子：简谐振子

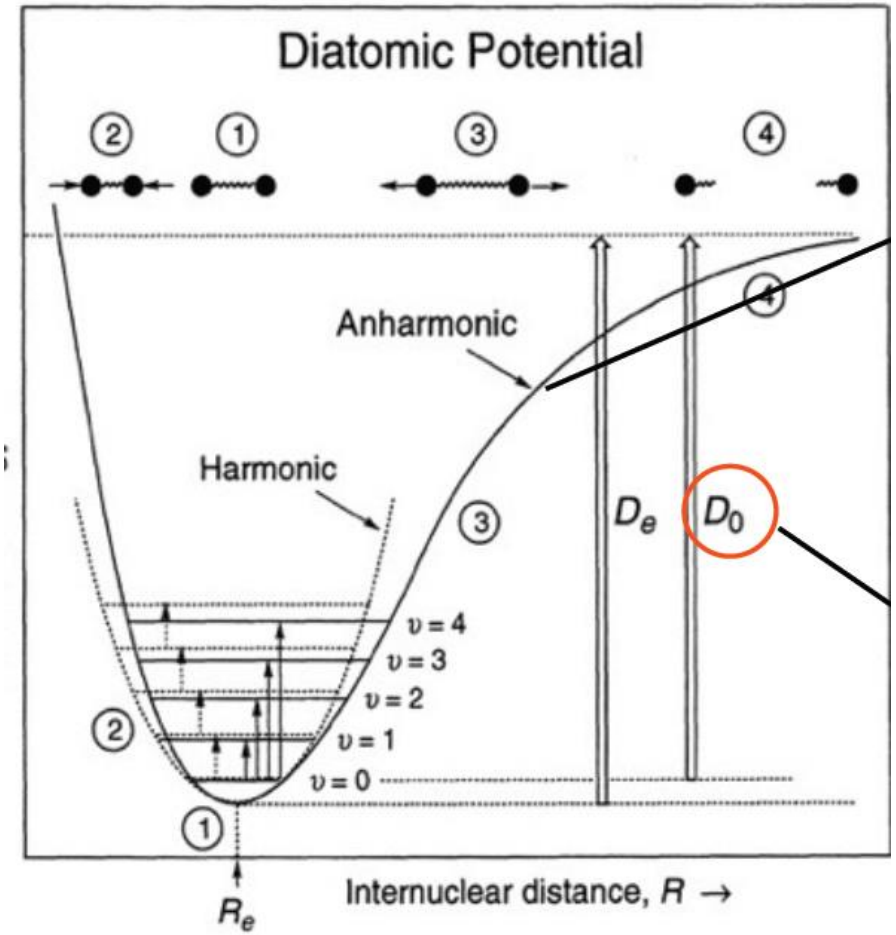


$$m = \frac{m_A m_B}{m_A + m_B}$$



$$\omega = \sqrt{\frac{k}{m}}$$

双原子分子：Morse振子



$$V(R) = D_e\left(1 - e^{-a(R-R_e)}\right)^2$$

$$E_n = h\nu(n+1/2) - \frac{[h\nu(n+1/2)]^2}{4D_e}$$

$$\nu = \frac{a}{2\pi}\sqrt{2D_e/m}$$

$$E_{n+1} - E_n = h\nu - (n+1)\frac{[h\nu]^2}{2D_e}$$

振动的非谐性，总振动能级数有限

多原子分子：Hessian矩阵、简正模式

$$V(\mathbf{x}) = V(\mathbf{x}_0) + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right)_{\mathbf{x}_0} (x_i - x_i^0)$$

$$+ \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\mathbf{x}_0} (x_i - x_i^0)(x_i - x_j^0)$$

Hessian矩阵

$$k_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\mathbf{x}_0}$$

质量加权坐标：

$$q_i = \sqrt{m_i}(x_i - x_i^0)$$

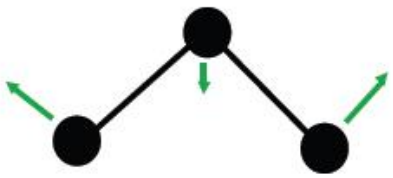
质量加权Hessian矩阵：

$$K_{ij} = \frac{1}{\sqrt{m_i m_j}}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_{\mathbf{x}_0}$$

对角化K矩阵，本征向量即简正振动模式

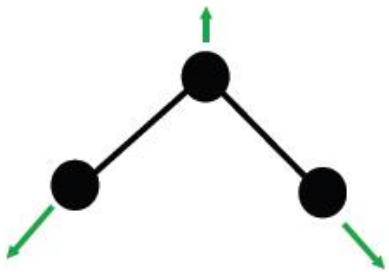
$$H = \frac{1}{2}\sum_i P_i^2 + \frac{1}{2}\sum_i \omega_i Q_i^2$$

水分子：3N-6=3个模式



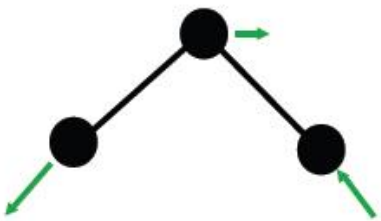
ν_1 (a_1)
Bending

1595 cm^{-1}



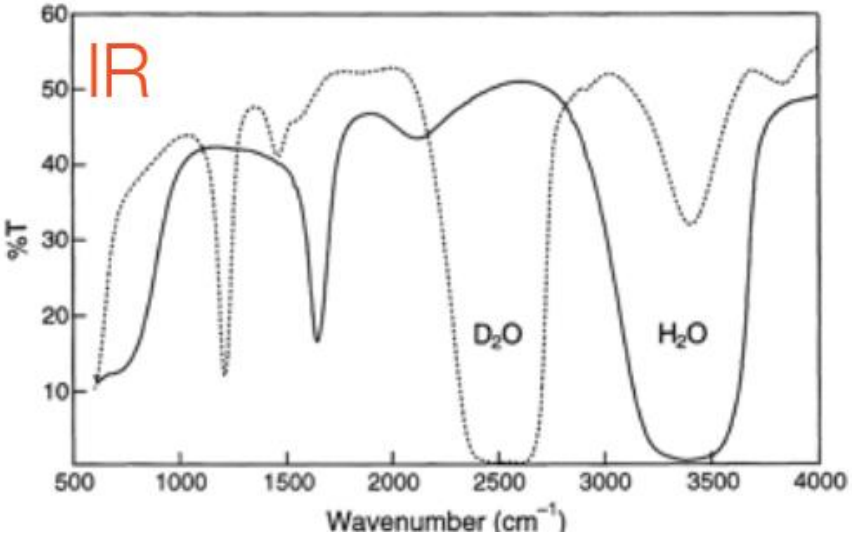
ν_2 (a_1)
Symmetric Stretch

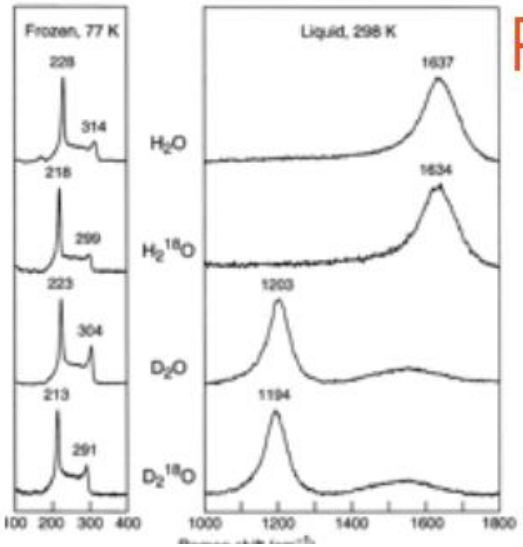
3652 cm^{-1}



ν_3 (b_1)
Asymmetric Stretch

3756 cm^{-1}





CO_2：3N-5=4个模式

ν_3 (σ_g^+)	ν_2 (σ_g^+)	ν_1 (π_u)	ν_1 (π_u)
Antisymmetric Stretch	Symmetric Stretch	Out of plane Bending	In plane Bending
2349 cm^{-1}	1337 cm^{-1}	667 cm^{-1}	667 cm^{-1}

„Doubly Degenerate“ Vibration

常见基团的振动频率

Group	Compound Class	Frequency Range (cm^{-1})
C-H	Alkanes	2965-2850
	$-CH_3$	1450
		1380
	$-CH_2$	1465
	Alkenes	3095-3010
		700-1000
	Alkines	~3300
C-C	Alkanes	700-1200
C=C	Alkenes	1680-1620
C≡C	Alkines	2260-2100
C=O	Ketones	1725-1705
	Aldehydes	1740-1720
	Carbonic Acids	1725-1700
	Esters	1750-1730
	Amides	1700-1630
	Anhydrides	1850-1800
C-O	Any	1300-1000
-O-H	Alcohols, isolated	3650-3590
	Alcohols, H-bonded	3400-3200
	Carbonic Acids	3300-2500
-N-H	Primary Amines	~3500
	Secondary Amines	3500
C≡N	Nitriles	2260-2240

振动光谱的强度

$$I_{mn} \propto \left|\mu_{mn}\right|^2$$

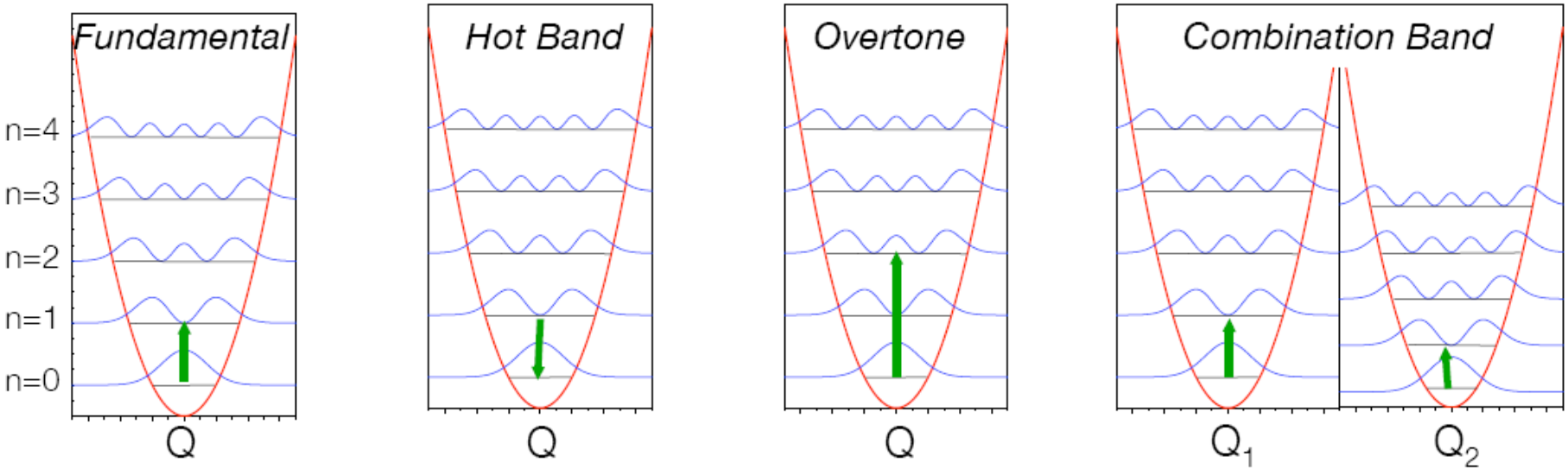
$$\langle m|\mu(R)|n\rangle \approx \langle m|\mu(R_0) + \left.\frac{\partial\mu}{\partial R}\right|_{R_0}(R-R_0)|n\rangle$$

IR：偶极矩导数的平方，最强峰对应n->n+1/n-1跃迁

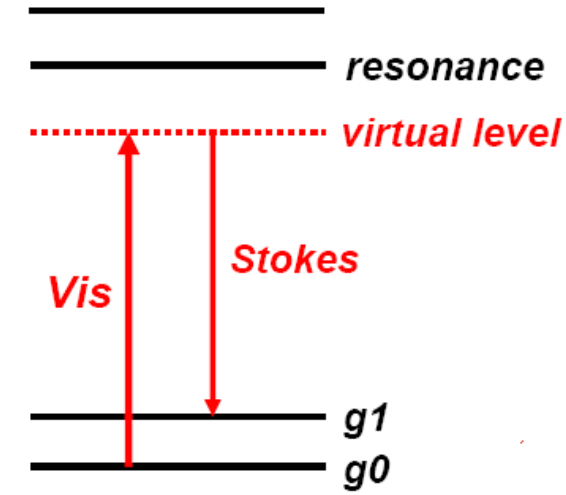
Raman：极化率导数的平方

$$I_{mn} \propto \left|\alpha_{mn}\right|^2 \propto \left|\left.\frac{\partial\mu}{\partial R}\right|_{R_0}\right|^2$$

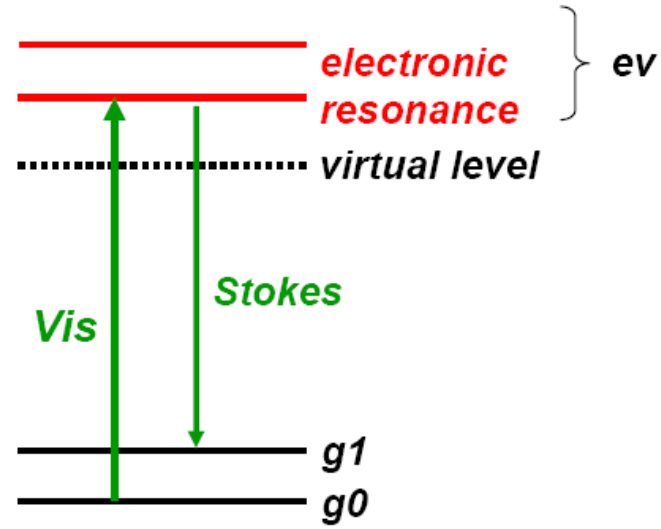
- **Fundamentals** : **$n=0 \rightarrow n'=1$** **$\Delta E=h\nu$**
- „Hot“ Bands : $n=1 \rightarrow n'=n\pm1$ $\Delta E=h\nu$
- Overtones : $n=0 \rightarrow n'=2,3,...$ $\Delta E=2h\nu, 3h\nu,...$
- Combination Bands: $n_1=0, n_2=0 \rightarrow n_1'=1, n_2'=1$ $\Delta E=h\nu_1+h\nu_2$



非共振和共振拉曼光谱



non-resonant Raman



resonant Raman

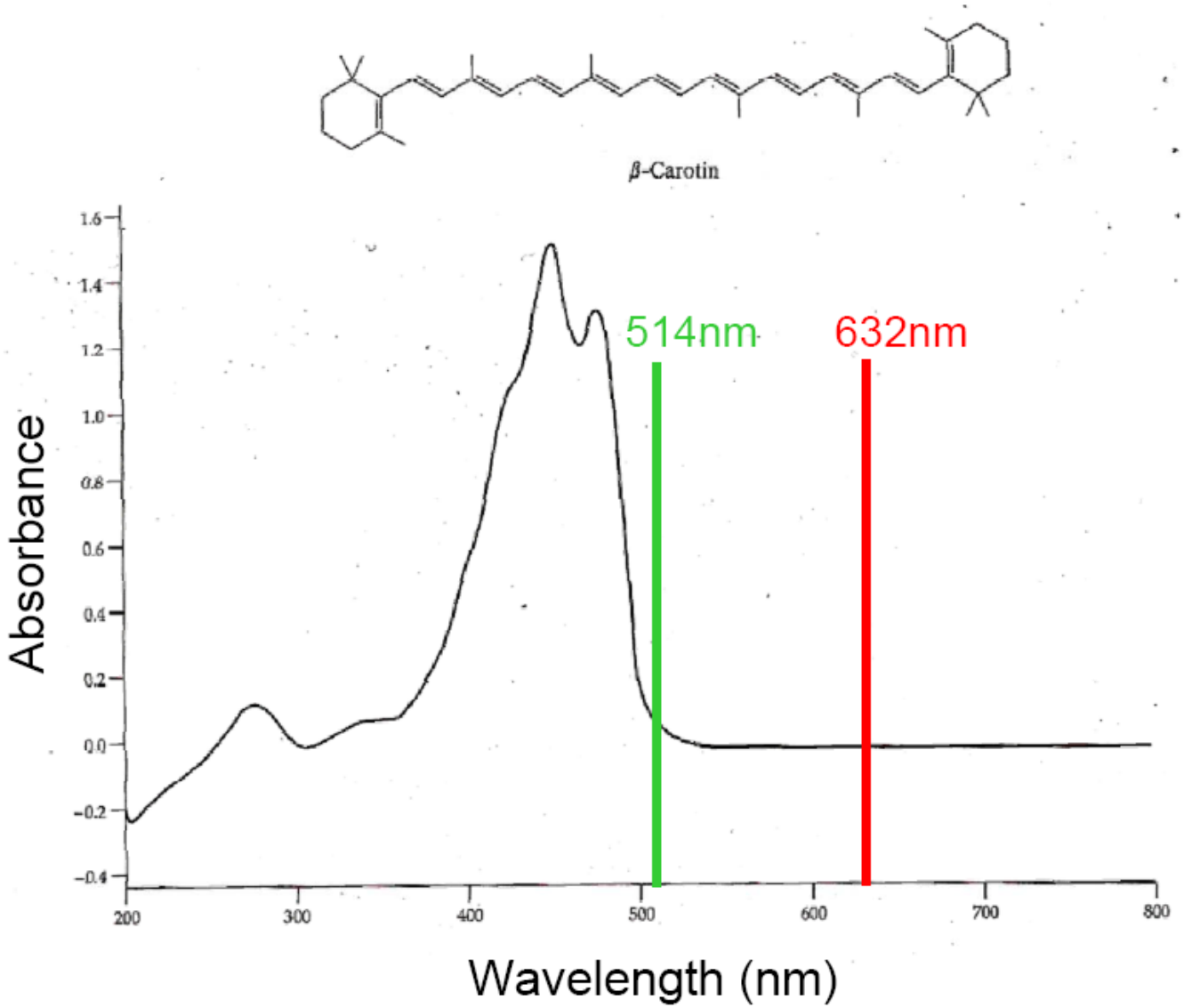
→ Polarizability tensor α (single e state):

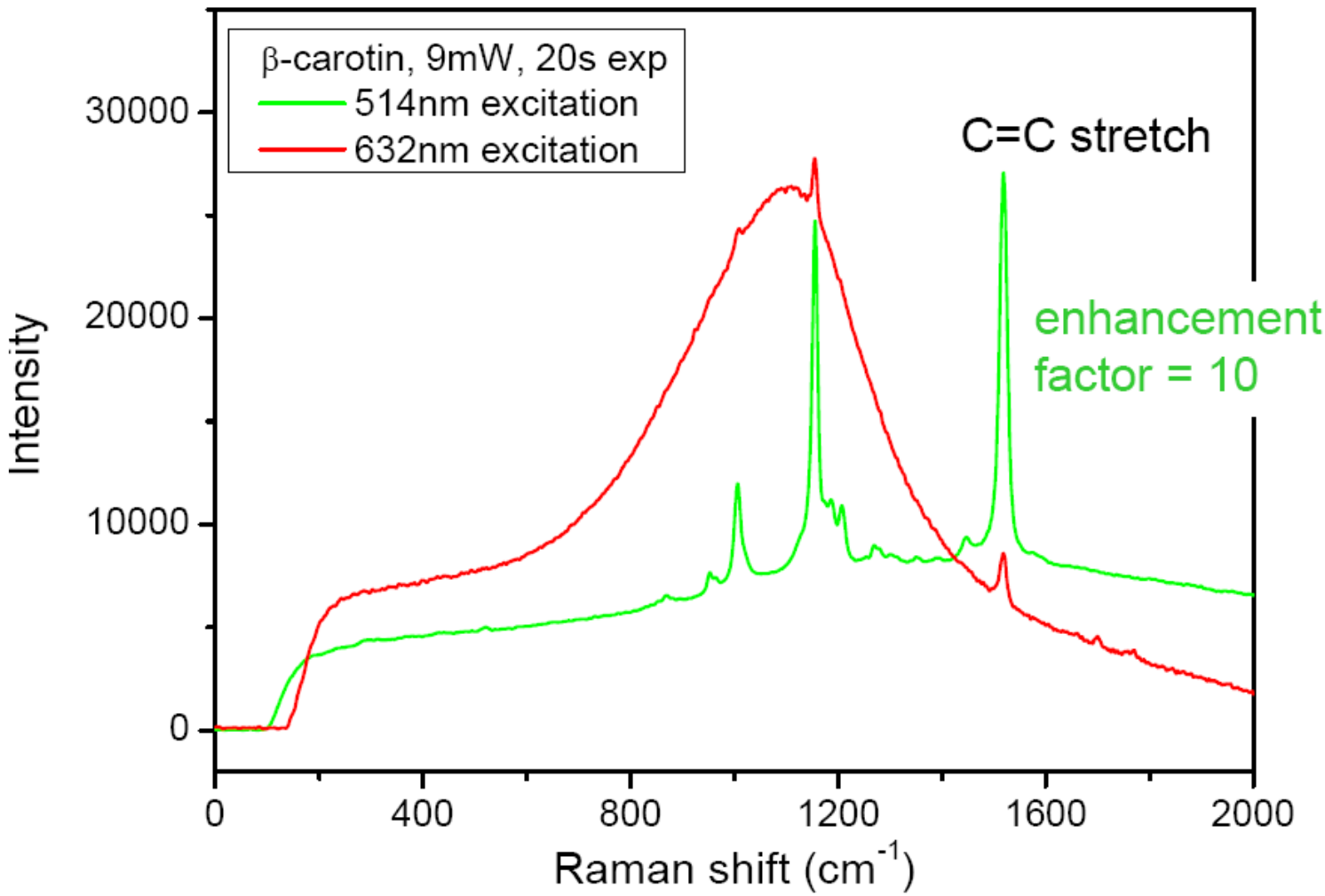
$$\mu = \alpha E$$

$$\alpha_{\alpha\beta} = \frac{1}{\hbar}\sum_{v}\left(\frac{\langle g1|\hat{\mu}_{\alpha}|ev\rangle\langle ev|\hat{\mu}_{\beta}|g0\rangle}{w_{\mathrm{ev,g0}} - w_0 + i\Gamma_{\mathrm{ev}}}\right)$$

$\hat{\mu}_{\alpha}, \hat{\mu}_{\beta}$: Electric dipole moment operator
i.a. with incident/scattered light

非共振：对多个电子态求和，共振：一个最重要电子态


β-Carotin
514nm
632nm
Absorbance
Wavelength (nm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
200
300
400
500
600
700
800


β-carotin, 9mW, 20s exp
514nm excitation
632nm excitation
C=C stretch
enhancement
factor = 10
Intensity
30000
20000
10000
0
0
400
800
1200
1600
2000
Raman shift (cm-1)

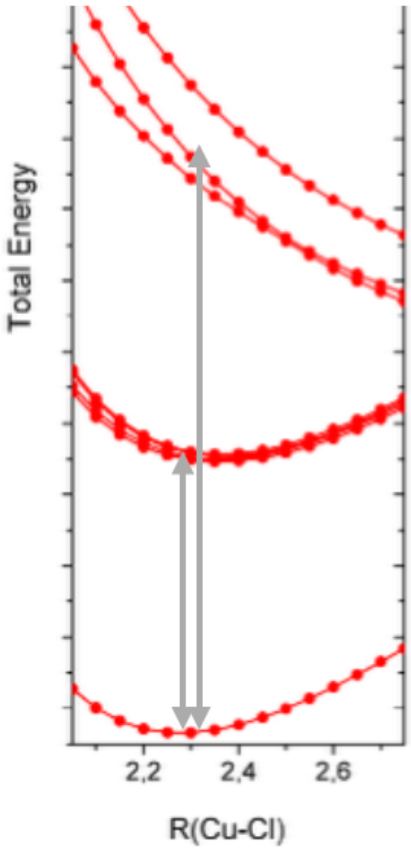
共振拉曼A term

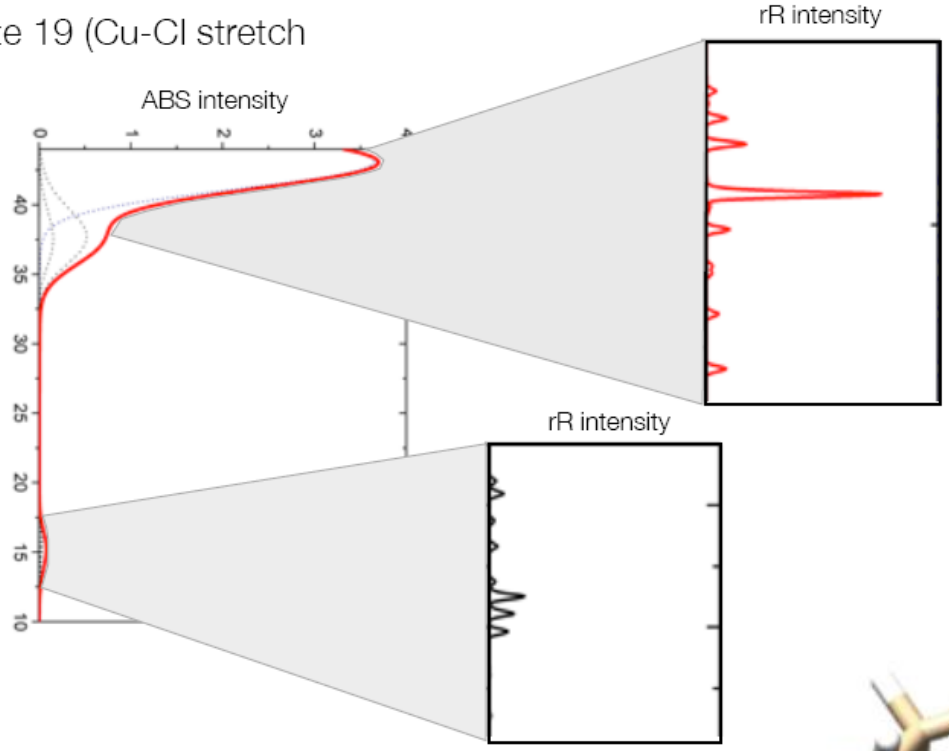
Franck-Condon近似： μ 是常数

$$\langle g1|ev\rangle \approx 1, \quad \langle ev|g0\rangle \propto S$$

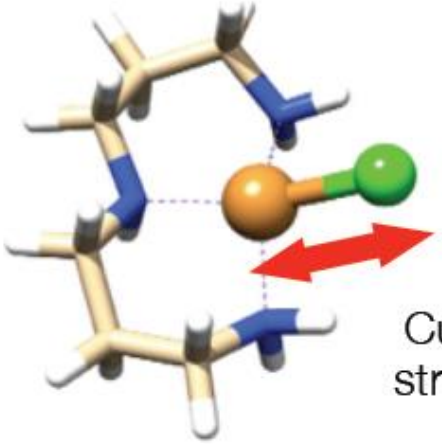
共振Raman强度正比于黄昆因子的平方

Scan along the normal coordinate 19 (Cu-Cl stretch





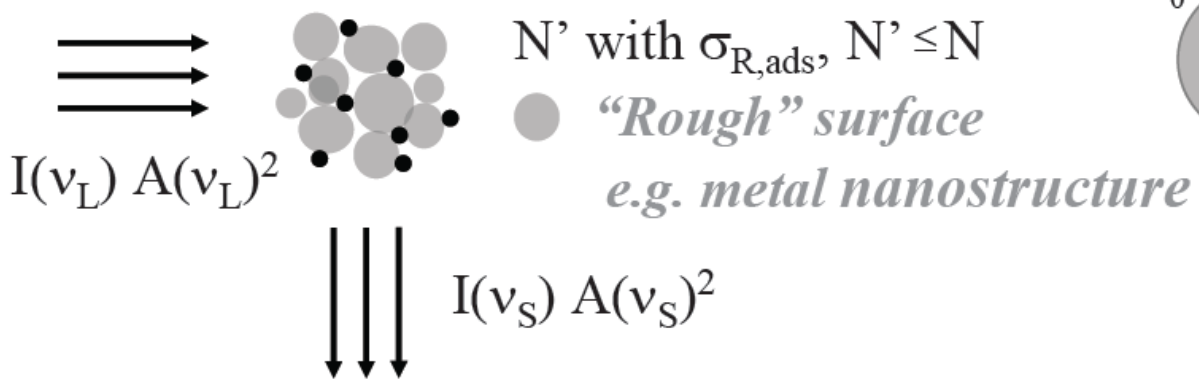
- ✓ d-d excitations have very small excited state
  hence very little rR intensity
- ✓ LMCT excitations have large excited state di
  hence large rR intensities

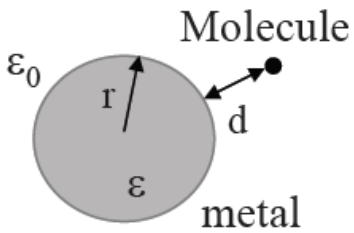


Cu-Cl stretch

表面共振增强拉曼（SERS）

Surface-enhanced Raman scattering





$$I_{SERS}(\nu_S) = N'\ I(\nu_L)\ \mathbf{A(\nu_L)^2\ A(\nu_S)^2}\ \sigma_{R,ads}$$

$$A(\nu) = \frac{E_M(\nu)}{E_0(\nu)}$$

(1) E.m. field enhancement

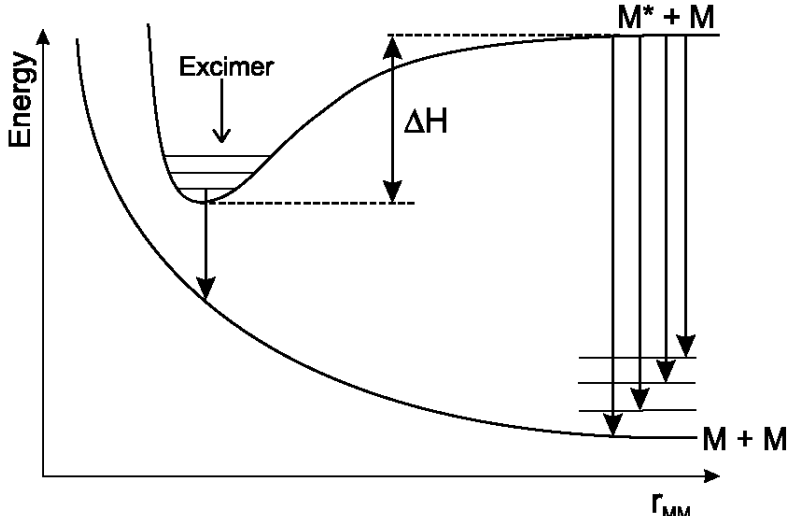
max. ~ 10^6 (isolated Ag,Au)

max. ~ 10^8 (coupled)

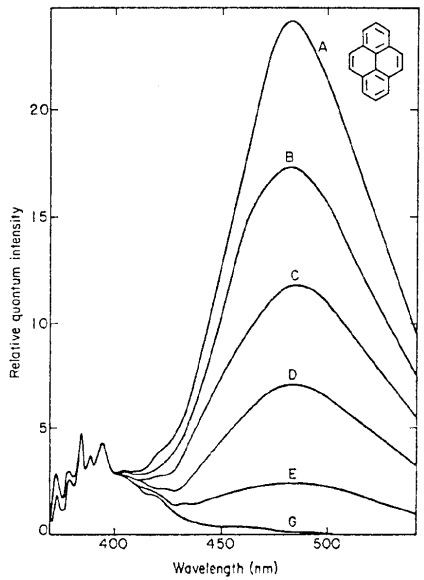
(2) Chemical enhancement

max. 10-100

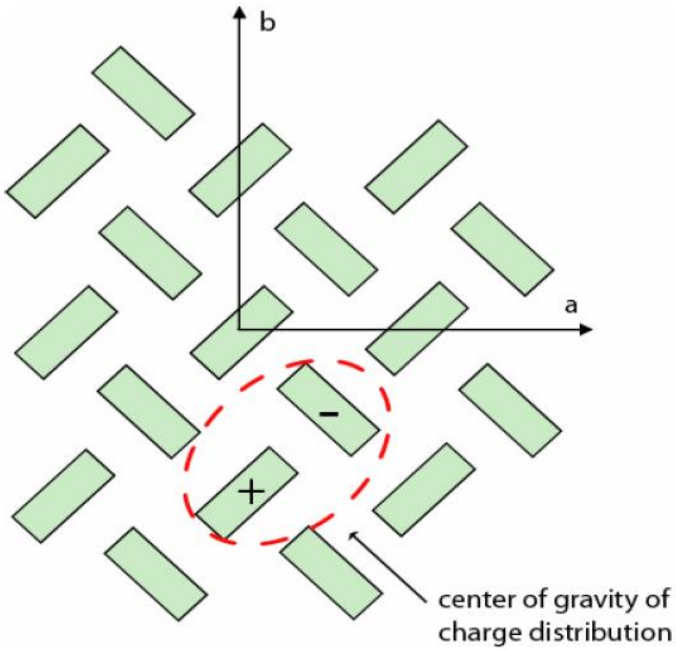
小结1：分子间激发态



分子间距离



发光红移，很宽的发射峰



- 瓦尼尔激子
- 电荷转移激子
- 弗兰克尔激子

小结2：光与物质相互作用

$$P = \varepsilon_0\left(\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots\right)$$

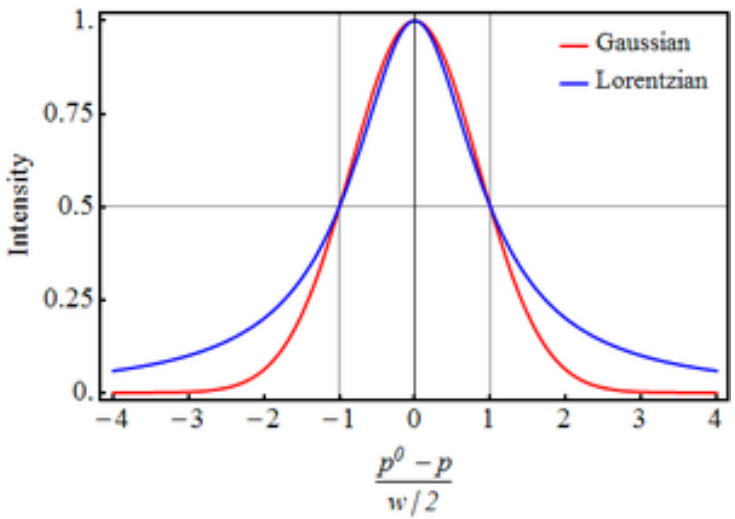
$\chi^{(1)}$，$\chi^{(2)}$，$\chi^{(3)}$ **一阶、二阶、三阶极化率**

$$H_{light-mol} = -\boldsymbol{E}(\boldsymbol{X}_m, t)\bullet\hat{\mu}_m$$

$$\hat{\boldsymbol{\mu}}_m = \sum_{u\in m} q_u \boldsymbol{x}_u = -\sum_j e\boldsymbol{r}_j^{(m)} + \sum_n e z_n^{(m)} \boldsymbol{R}_n^{(m)}$$

小结3：光谱的线型和线宽

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



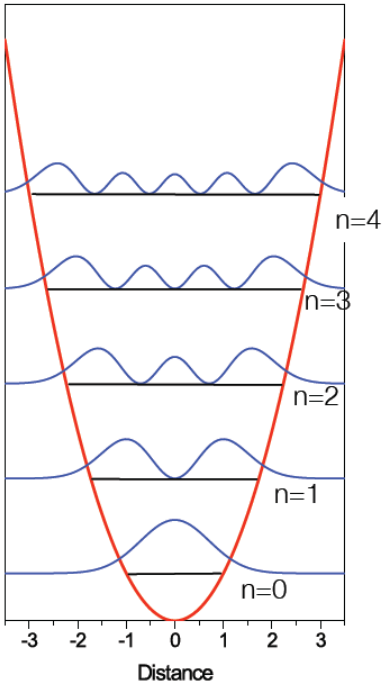
- 寿命展宽，T_1
- 碰撞展宽，T_2
- 非均匀展宽（高斯）

KUBO线型理论，统一描述均匀展宽和，非均匀展宽，

运动变窄（Motional Narrowing）

可解模型：位移谐振子模型，FGR

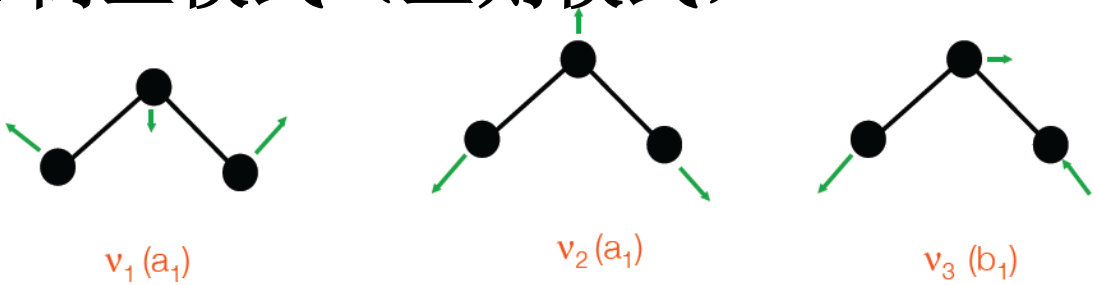
小结4：振动光谱



1. $\omega = \sqrt{\frac{k}{m}}$

2. 非谐性（Morse振子）

3. 简正模式（正则模式）



4. 强度 IR：偶极矩导数的平方，最强峰对应n->n+1/n-1跃迁

5. 共振拉曼、SERS