

# 《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**。

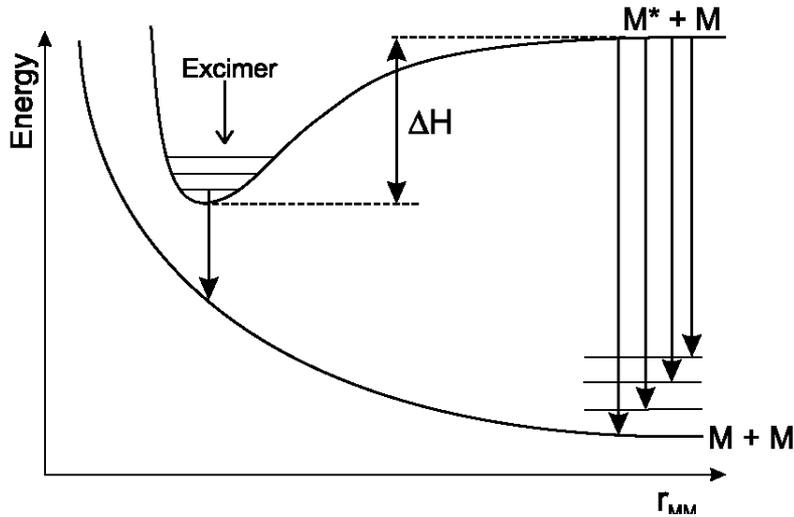
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# 2018.12.20, Lecture 6

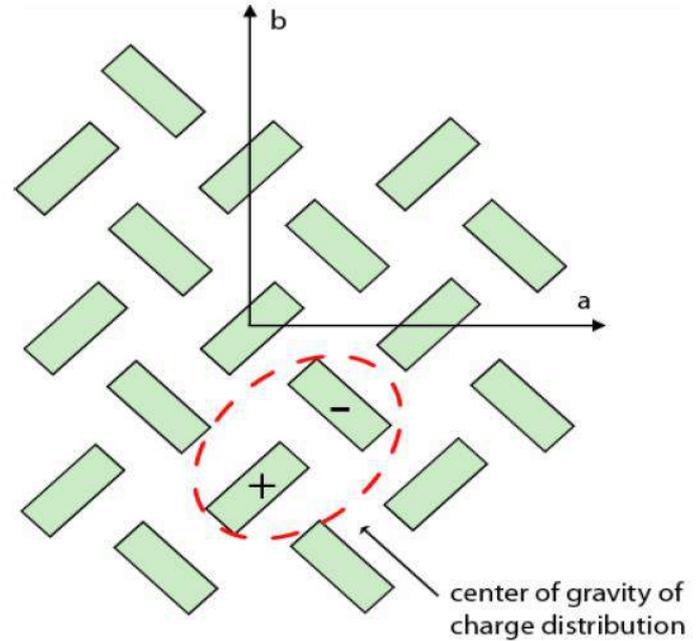
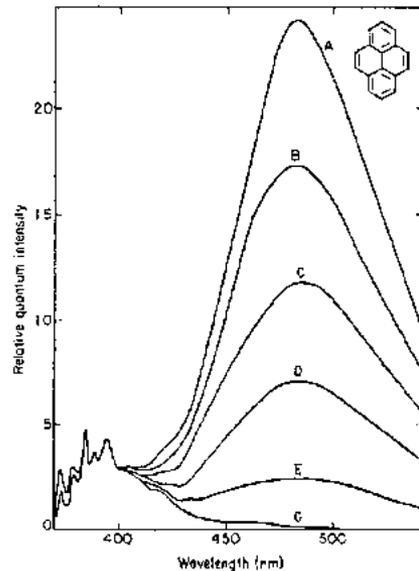
1. 上节内容回顾
2. 二阶响应函数：表面和频光谱
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4. Pump-Probe光谱（瞬态吸收）
5. 其它三阶光谱方法
6. 小结
7. 凝聚相动力学部分总结

# 1.1: 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

# 1.2: 光与物质相互作用

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

**宏观现象:**  $\chi^{(1)}$ ,  $\chi^{(2)}$ ,  $\chi^{(3)}$

一阶极化率: 吸收、发射、拉曼、...

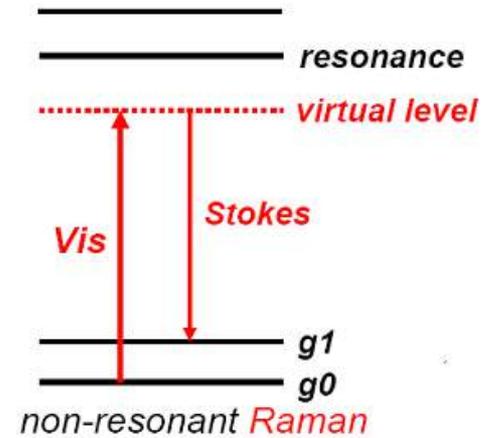
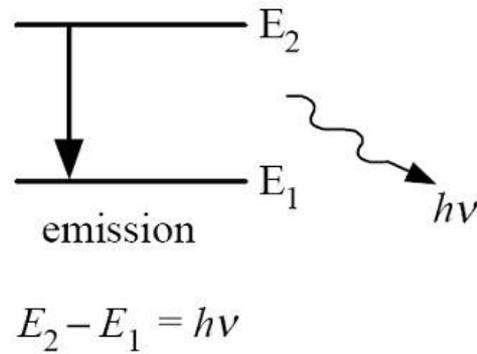
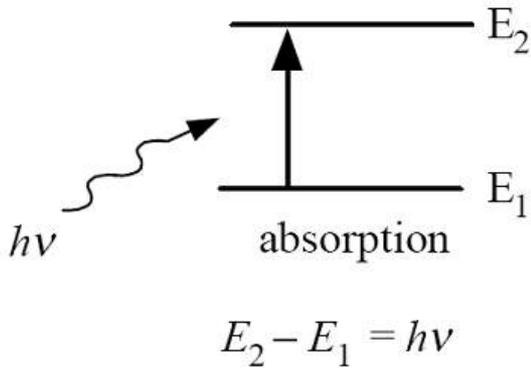
二阶: 表面和频谱、双光子吸收、...

三阶: 泵浦-探测、光子回声、2D光谱、...

**微观哈密顿量: 电场和偶极矩相互作用 (一般情况)**

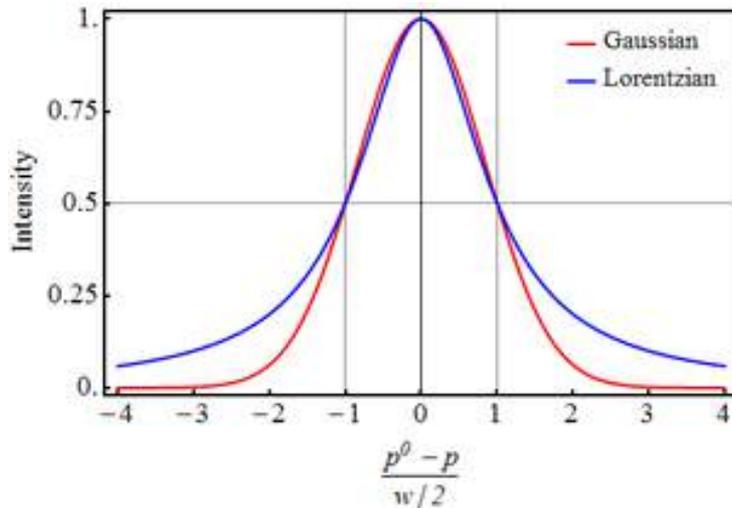
$$H_{light-mol} = -\mathbf{E}(\mathbf{X}_m, t) \cdot \hat{\boldsymbol{\mu}}_m$$

# 一阶极化率相关的过程



# 1.3: 光谱的线型和线宽

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

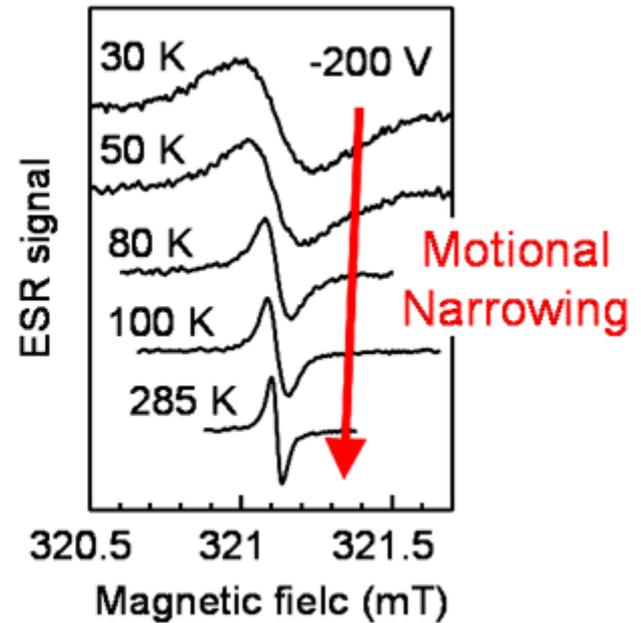
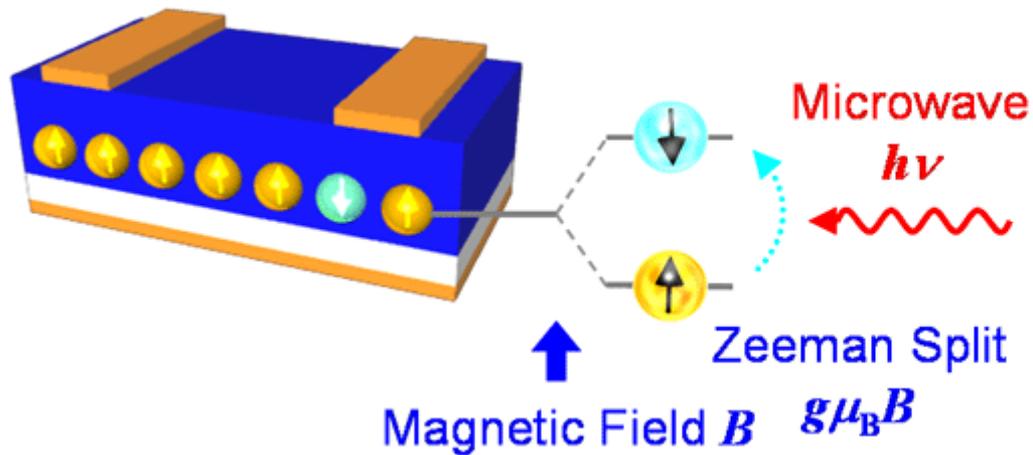


- 寿命展宽,  $T_1$
  - 碰撞展宽,  $T_2$
  - 非均匀展宽 (高斯)
- 均匀展宽  
洛伦兹

KUBO线型理论, 统一描述跃迁频率高斯涨落下的线型,  
静态极限、运动变窄 (Motional Narrowing)

可解模型: 位移谐振子模型, FGR

# Example: ESR光谱



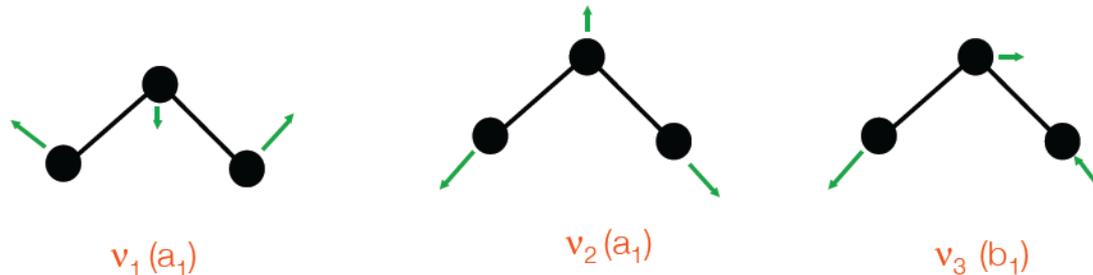
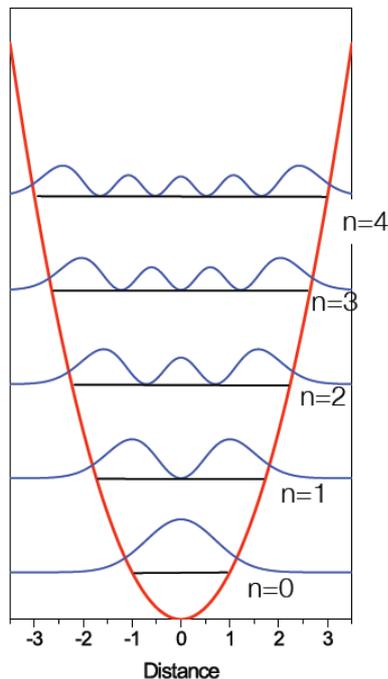
# 1.4: 振动光谱

双原子分子:

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

2. 非谐性 (Morse 振子)

3. 多原子分子: 简正模式 (正则模式)



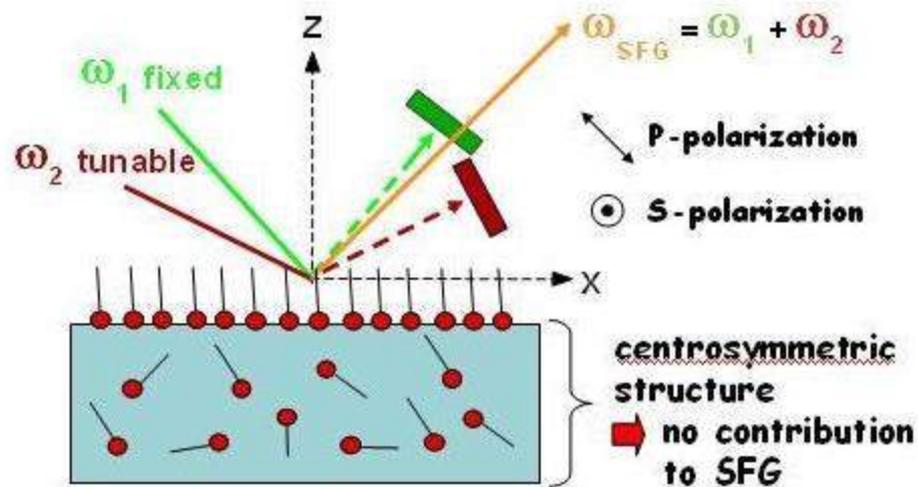
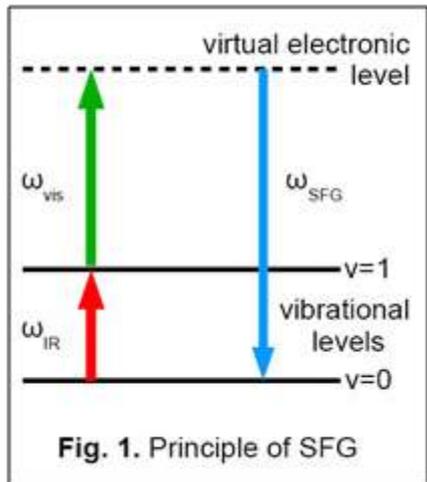
4. 强度/选择定则

偶极矩/极化率导数的平方,  
最强峰对应  $n \rightarrow n+1/n-1$  跃迁

5. 共振拉曼 (强度增强、测量黄昆因子)、  
**SERS** (利用纳米粒子表面,  $10^6-10^{10}$ )

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## 2: 表面和频光谱



和频谱：出射光的频率等于两束入射光频率之和  
两束光都是激光，信号有特定的方向

表面和界面的结构、取向和动力学

# 表面和频谱信号

$$S(\omega) \propto |\chi_{\text{eff}}^{(2)}|^2 I_1(\omega_1) I_2(\omega_2),$$

$$\vec{\chi}_{\text{eff}}^{(2)} = [\vec{F}(\omega) \cdot \hat{e}] \cdot \vec{\chi}^{(2)} : [\vec{F}(\omega_1) \cdot \hat{e}_1][\vec{F}(\omega_2) \cdot \hat{e}_2],$$

实验室坐标

**F: Fresnel factor, 与入射、出射构型、介电常数等有关的张量**

$$\chi_{ijk} = N_s \sum_{\xi, \eta, \zeta} \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta}) \rangle \alpha_{\xi\eta\zeta}^{(2)}$$

分子坐标

取向平均

分子性质

分子动力学模拟

量子化学计算

# 和频光谱是表面敏感的技术

对于中心对称的体系，E1和E2同时反向，P也反向

$$\chi^{(2)} = 0$$

在表面或界面，中心对称被打破  $\chi^{(2)} \neq 0$

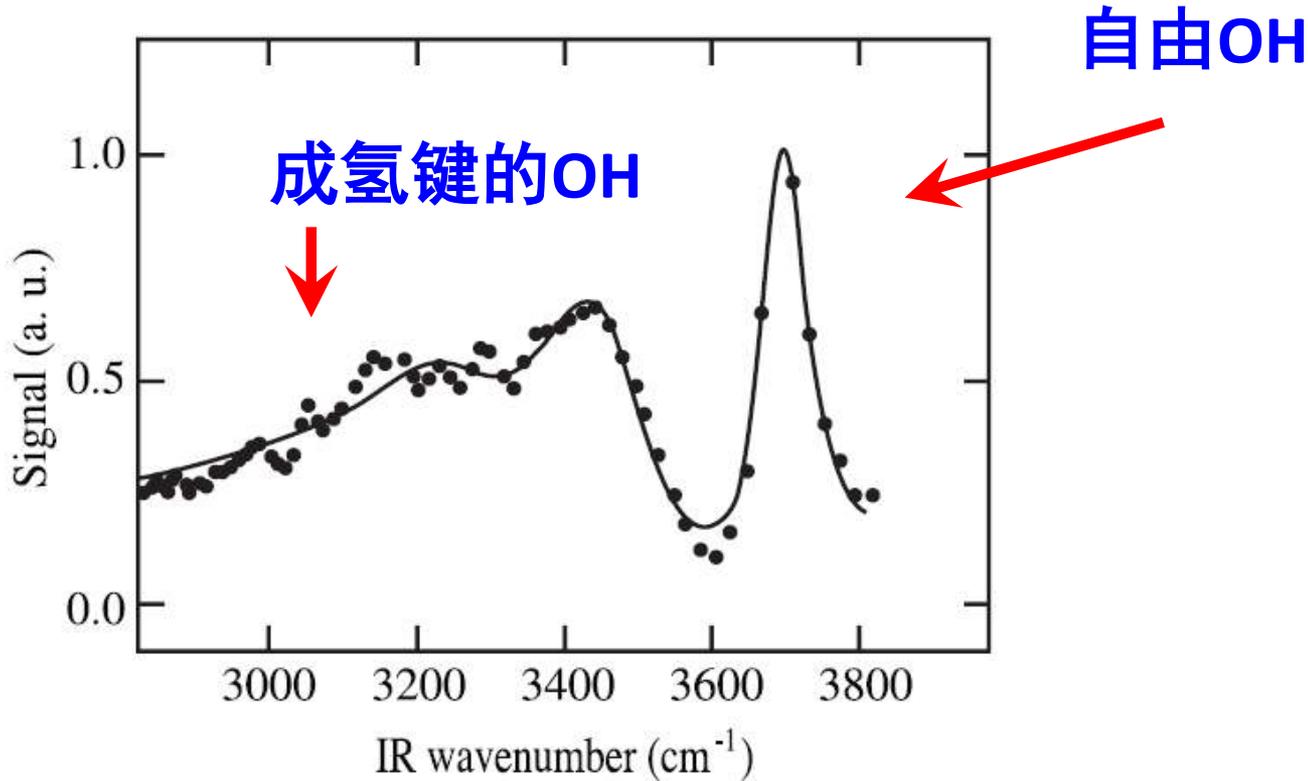
类似的，手性物质、非中心对称的晶体，二阶极化率也不为0

由于没有体相的贡献，表面和频谱的信号一般也比较弱

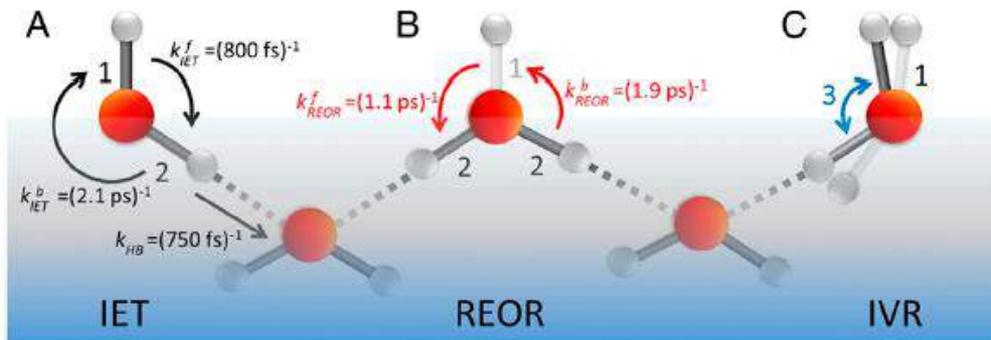
$$\alpha_{abc}^{(2)} = \frac{2}{\hbar} \sum_{\kappa} \frac{\langle 0^{\kappa} | \partial \mu_{gg}^c / \partial q^{\kappa} | 1^{\kappa} \rangle \langle 1^{\kappa} | \partial \alpha_g^{ab} / \partial q^{\kappa} | 0^{\kappa} \rangle}{(\omega_{10}^{\kappa} - \omega_{\text{ir}} - i\Gamma_{10}^{\kappa})}$$

**SFG能探测到的振动模式需要同时红外和拉曼活性  
信号与光的偏振方向、分子的取向有很大关系  
可以通过不同偏振组合来得到分子在表面的取向，  
以及分子的（固有）二阶极化率张量**

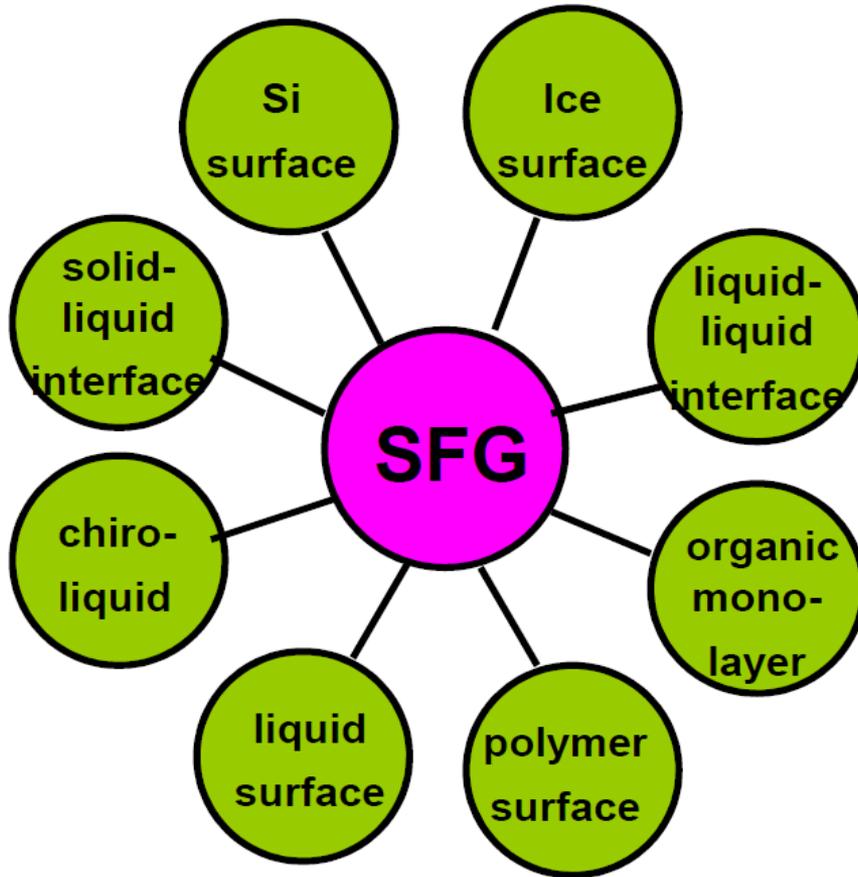
# 水的表面和频光谱



Y. R. Shen  
沈元壤

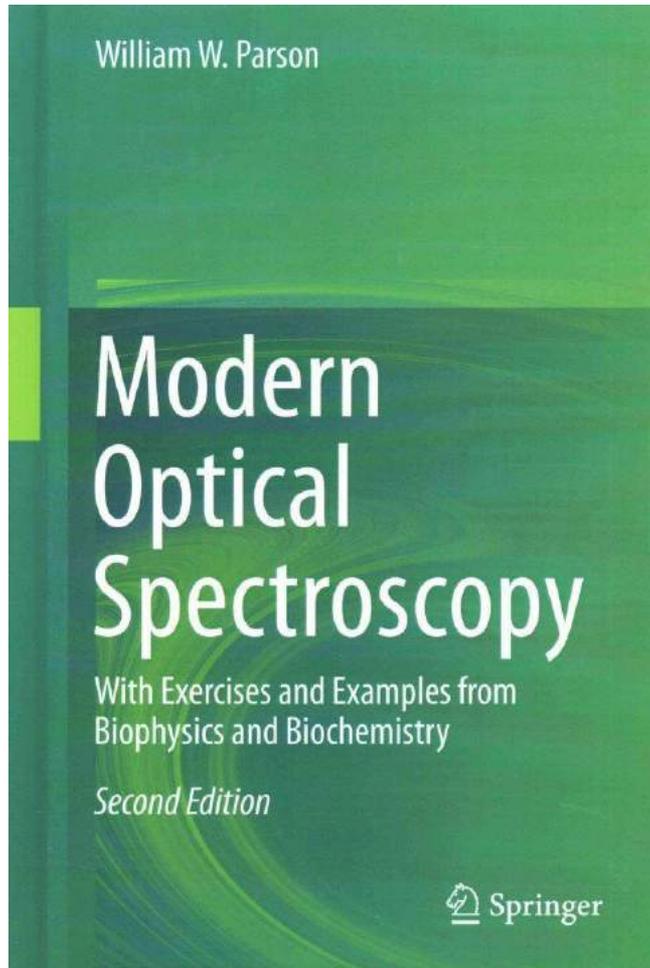


# 其它领域的应用



1. 材料表面，高分子
  2. 环境问题
  3. 生物体系，蛋白质-生物膜体系
  4. 催化体系
- ...

### 3. 时间分辨光谱：参考书



主要光谱技术、能量转移等



非常偏理论，时间域方法

# 化学动力学中的时间尺度

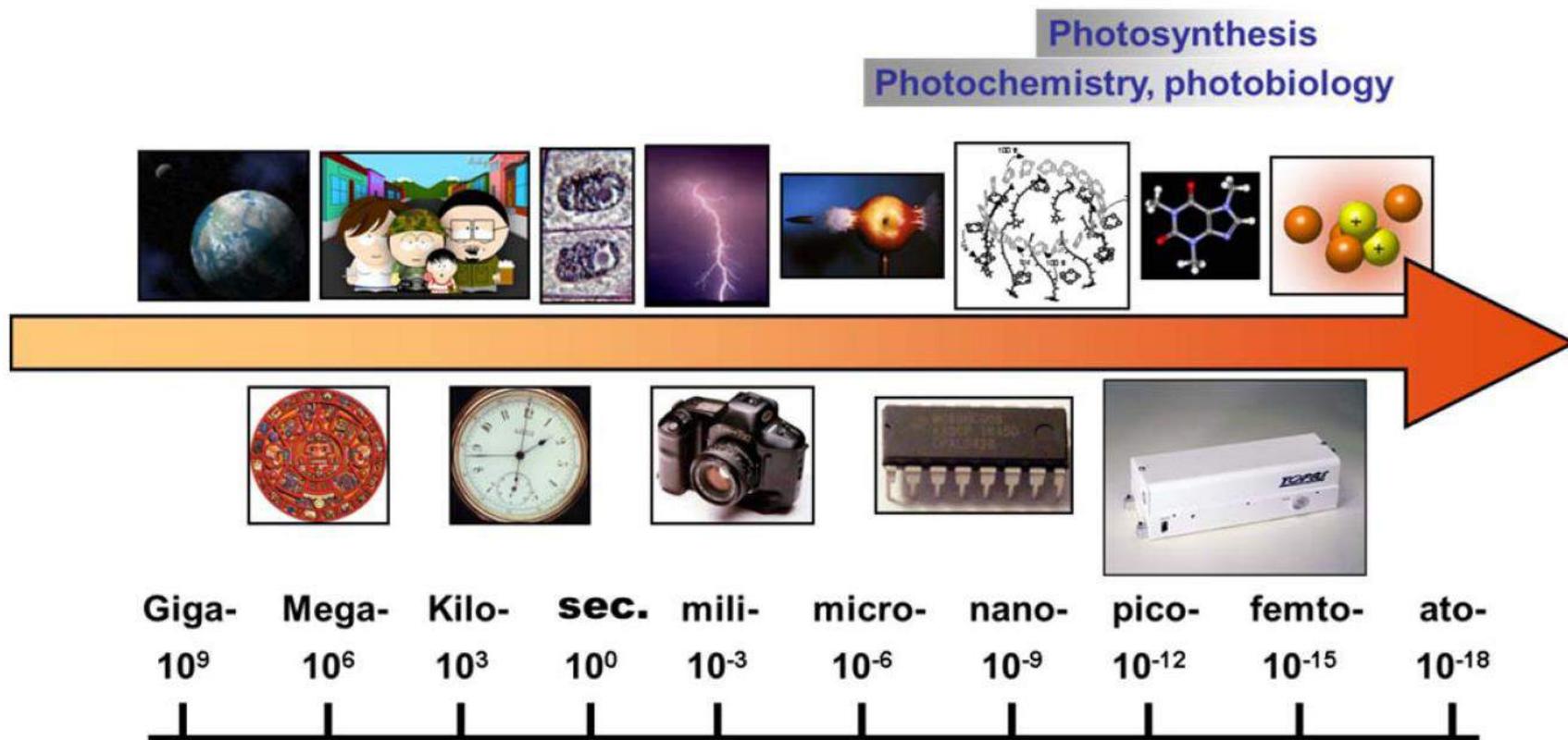
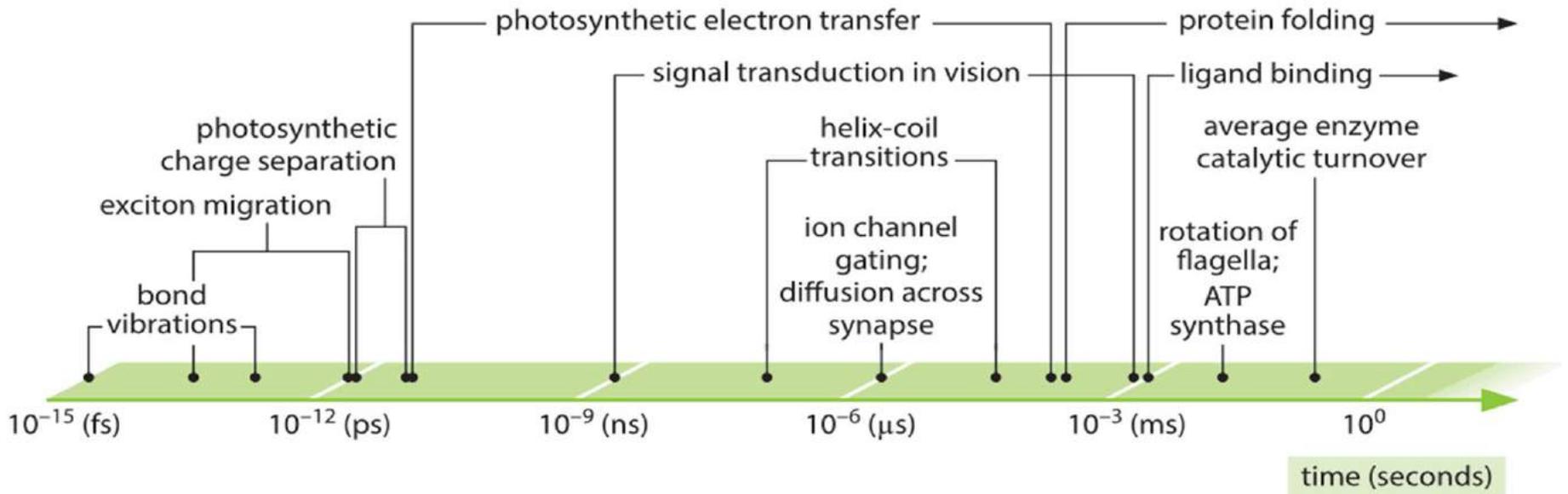


Fig. 1. Different natural processes, their timescales and instruments for following them.



**振动运动：  $10^{-15}$ - $10^{-12}$ s**

**能量转移：  $10^{-12}$ s- $10^{-9}$ s**

**溶剂化过程：  $10^{-12}$ s- $10^{-9}$ s**

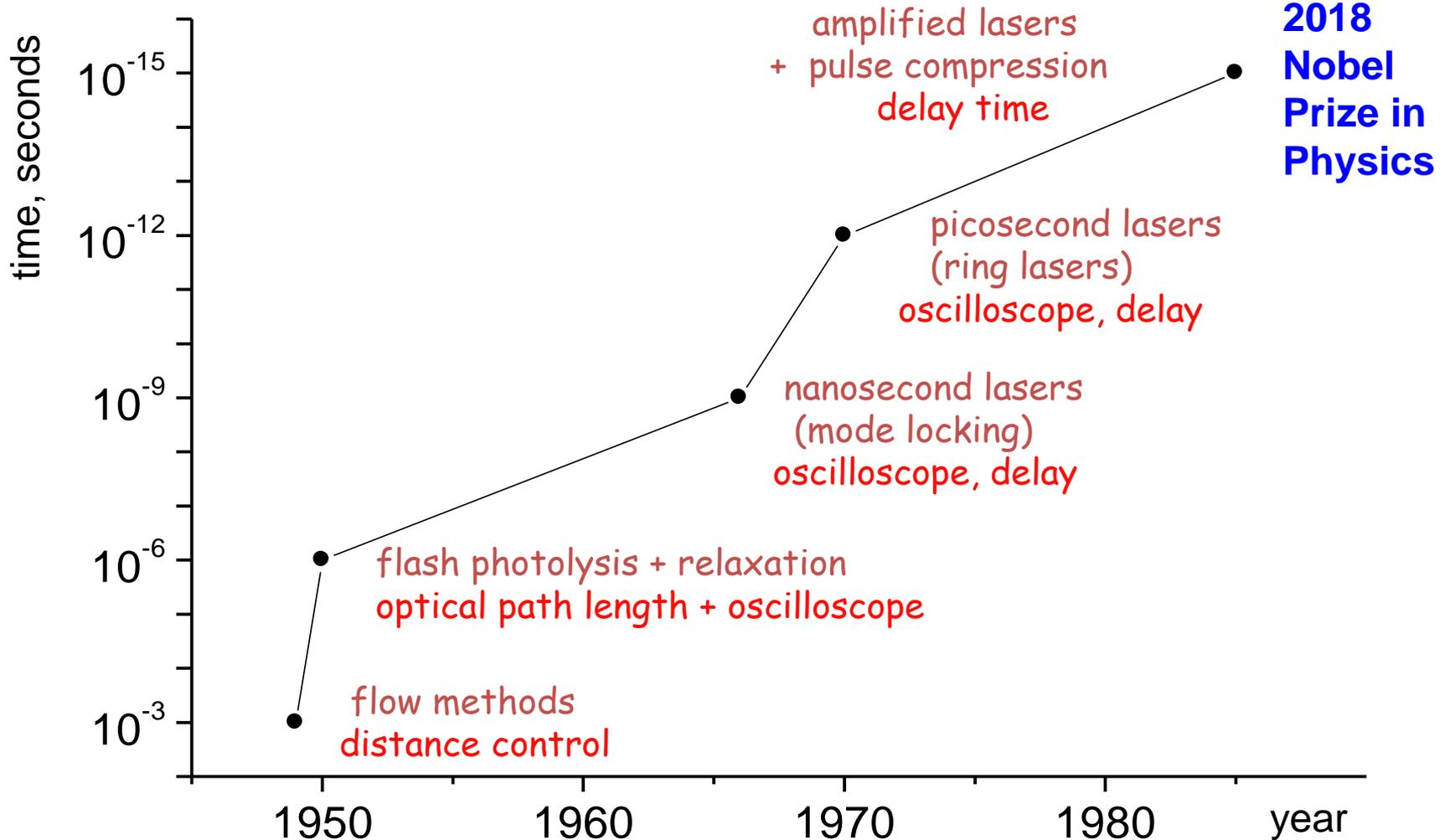
**电子转移：  $10^{-12}$ s  $\rightarrow$  s**

**化学反应：  $10^{-12}$ s  $\rightarrow$  s**

**大分子构象变化：  $10^{-6}$ s  $\rightarrow$  10s**

# 各种实验技术的时间分辨率

$10^{11}$  times increase within 36 years!!

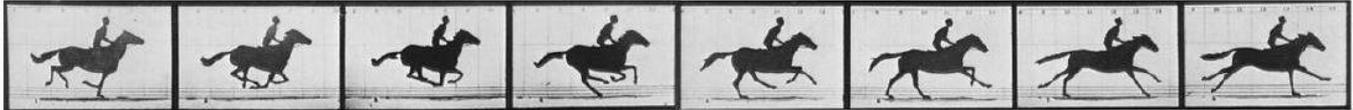


# 时间分辨技术

structure

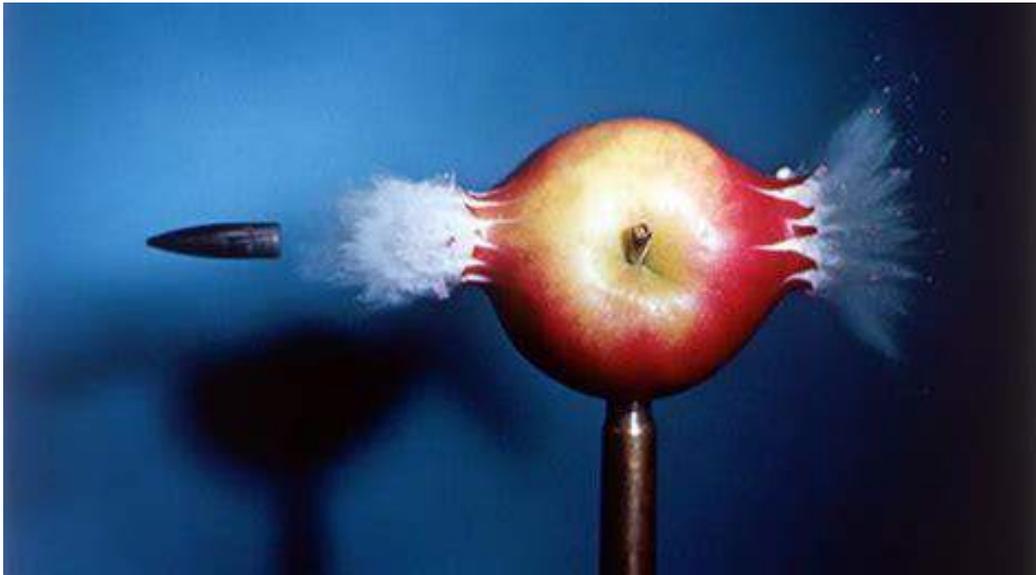


dynamics



kinetics

E. Muybrigde 1887



过程发生时间:  $10^{-4}$ 秒  
分辨率: 微秒 ( $10^{-6}$ s)  
量级

“fast” camera



“slow” camera



# 3.1 电子学延迟：条纹相机

Streak Camera:  
最好分辨率180fs  
激发态寿命

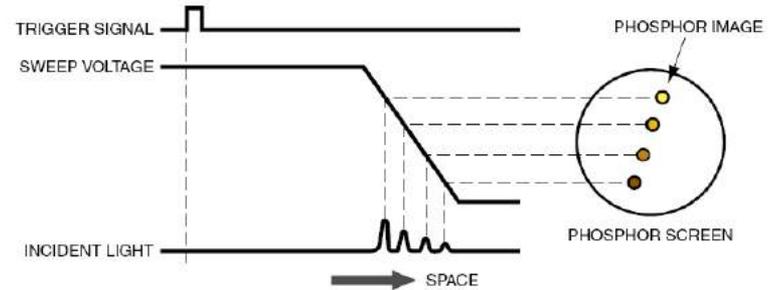


Fig.2 Operation Timing (at time of sweep)

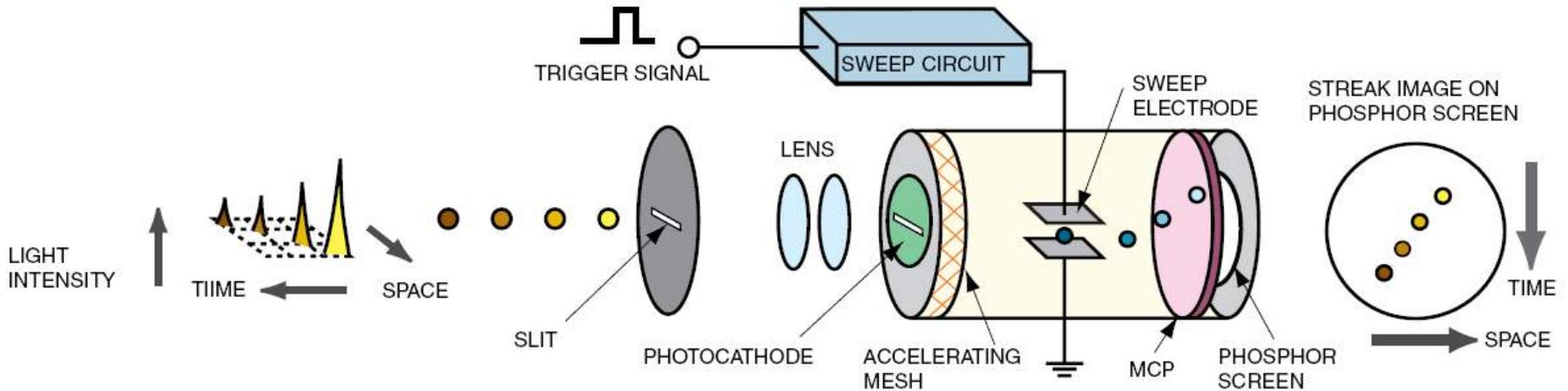
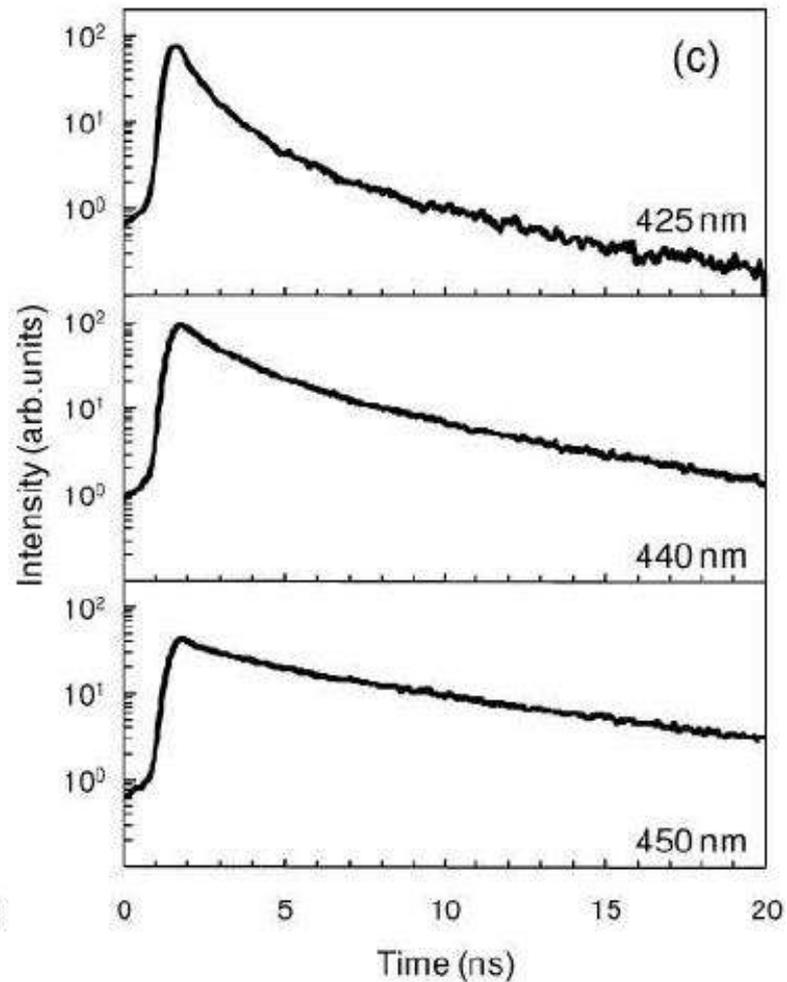
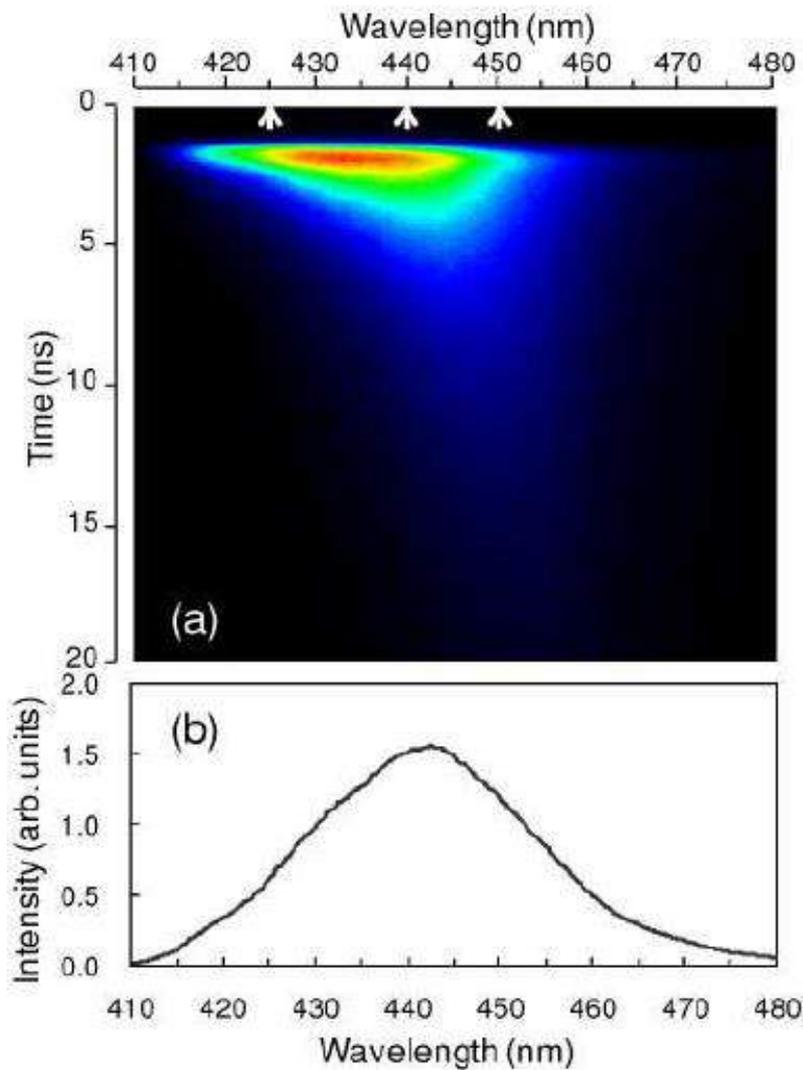


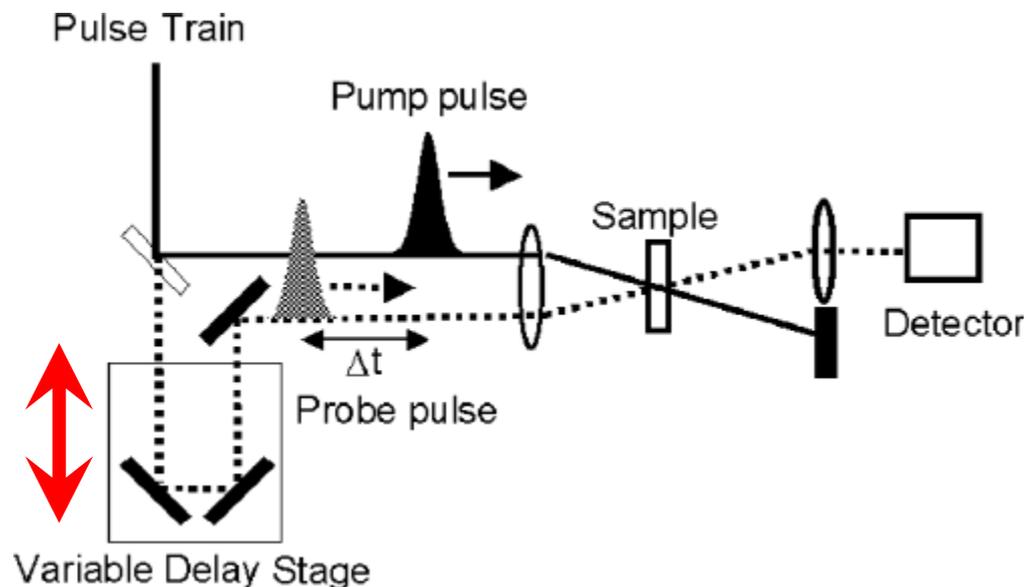
Fig.1 Operating Principle of the Streak Tube



**荧光寿命：Time-resolved fluorescence 时间分辨荧光**

## 3.2 光学延迟：超快激光脉冲

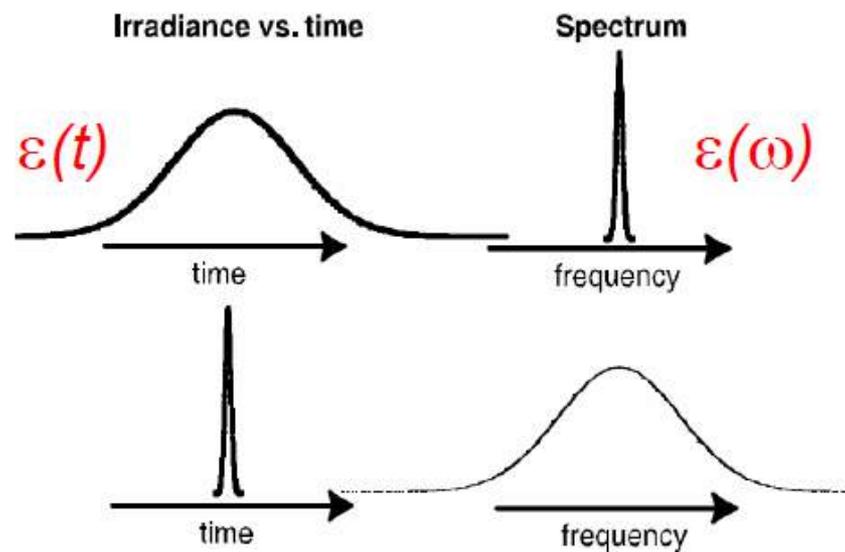
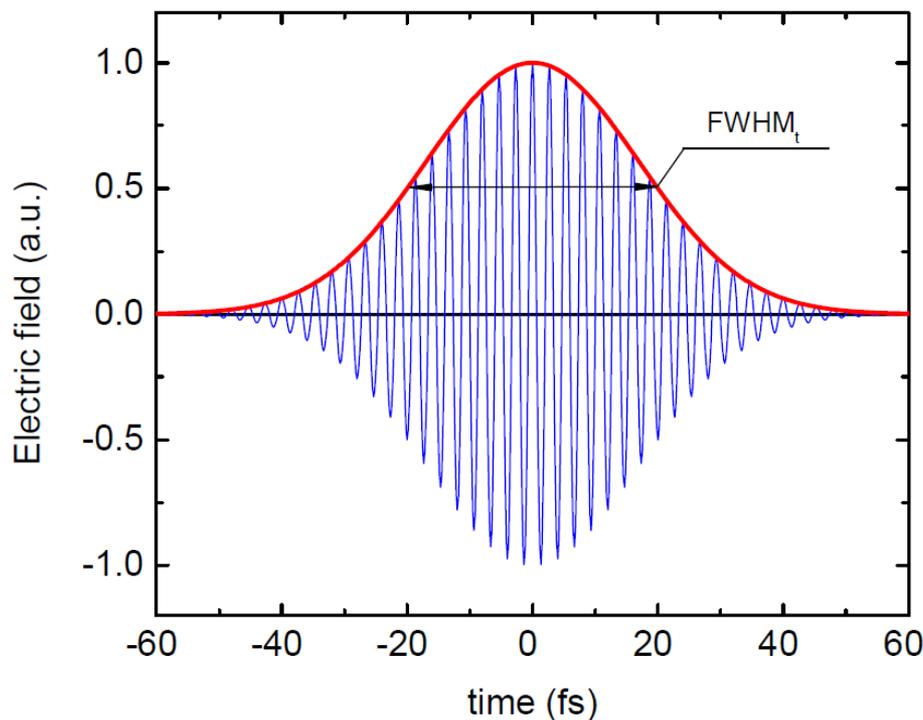
通过调节光程差改变  
时间延迟：



- 需要产生极短的光脉冲
- 信号产生是非线性过程（同时依赖于两个或多个脉冲）

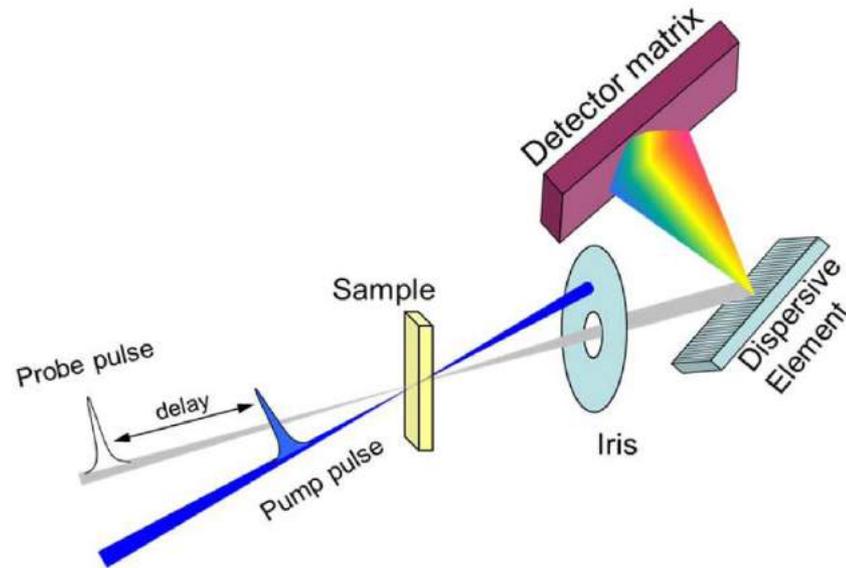
# 超快激光脉冲：时间-频率的不确定关系

$$\Delta\omega\Delta t = 4\ln 2$$



时间分辨率和能量分辨率一般不能兼顾

# 4. Pump-Probe (泵浦-探测)

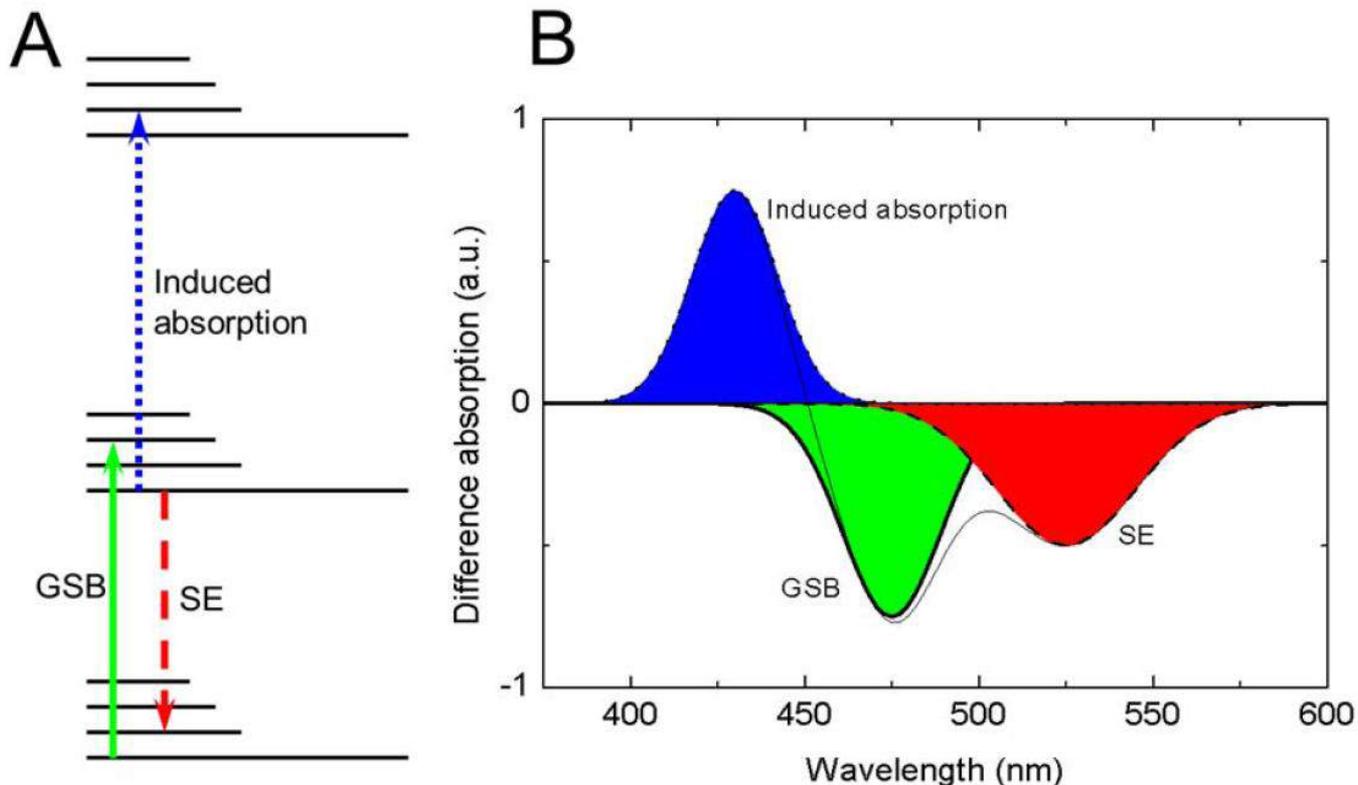


有Pump  $I_{exc} = I_0 \cdot 10^{-A_{exc}}$        $\Delta A \equiv A_{exc} - A_{noexc} = \lg \frac{I_{noexc}}{I_{exc}}$

无Pump  $I_{noexc} = I_0 \cdot 10^{-A_{noexc}}$

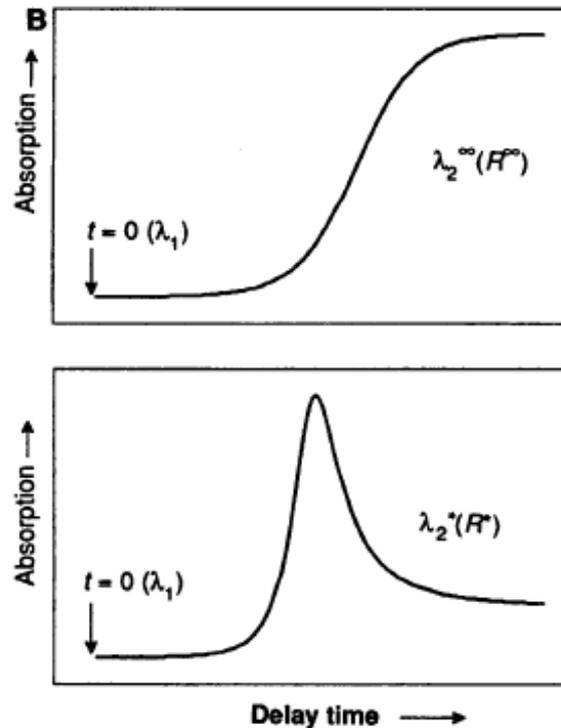
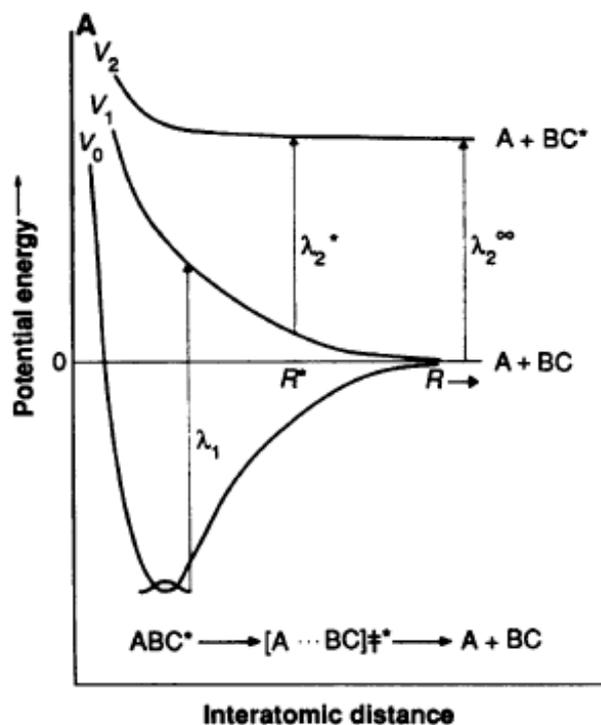
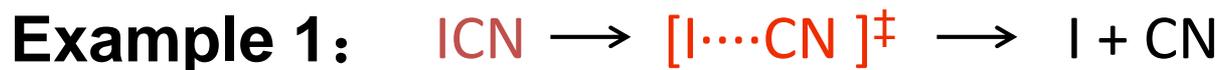
两种条件（有和没有泵浦光）下吸收光谱的差值

# Pump-Probe信号的三个来源



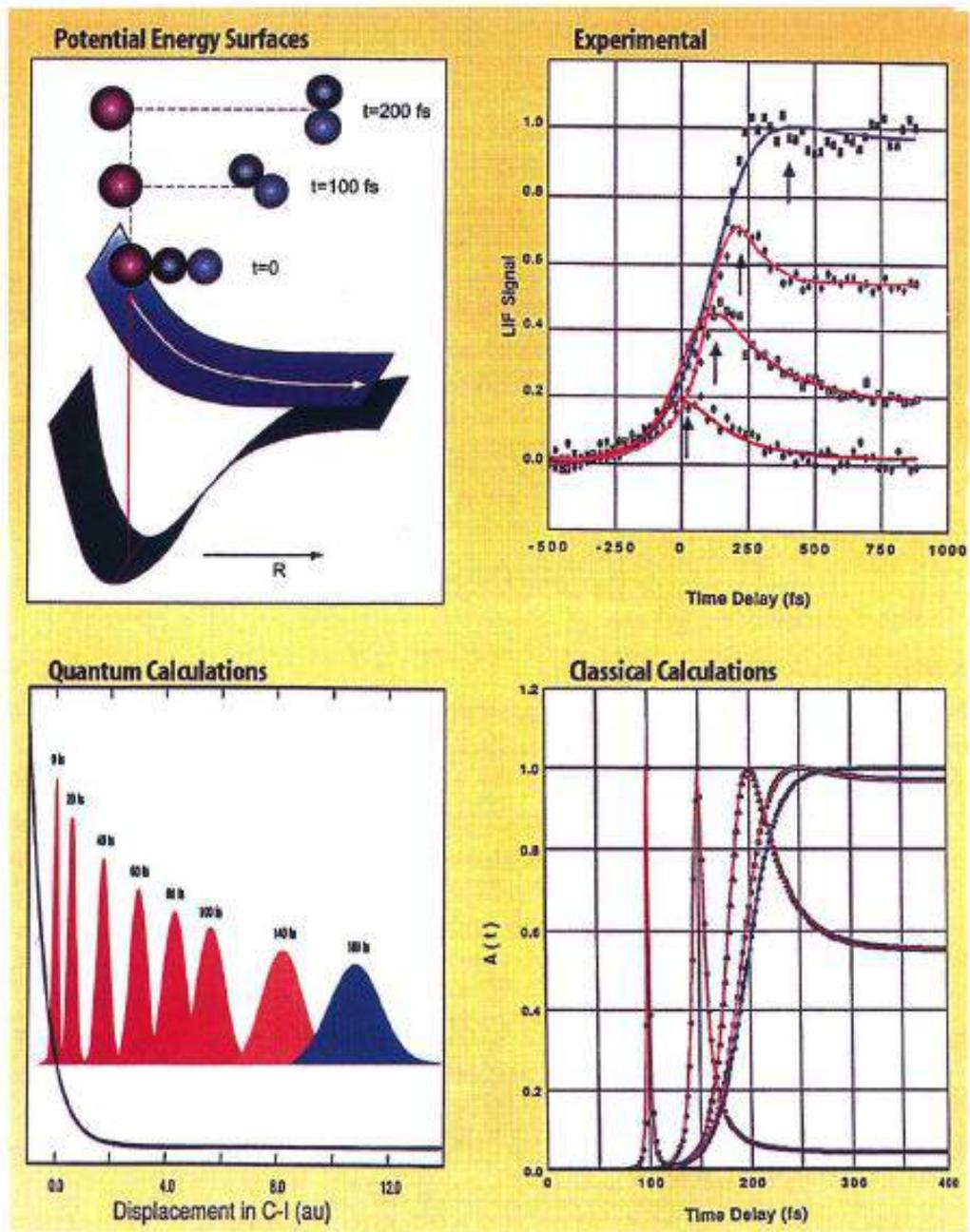
- ESA (蓝) : Excited state absorption 激发态吸收**
- GSB (绿) : Ground state Bleaching 基态漂白**
- SE (红) : Stimulated Emission 受激发射**

# ESA: Transient Absorption, 瞬态吸收

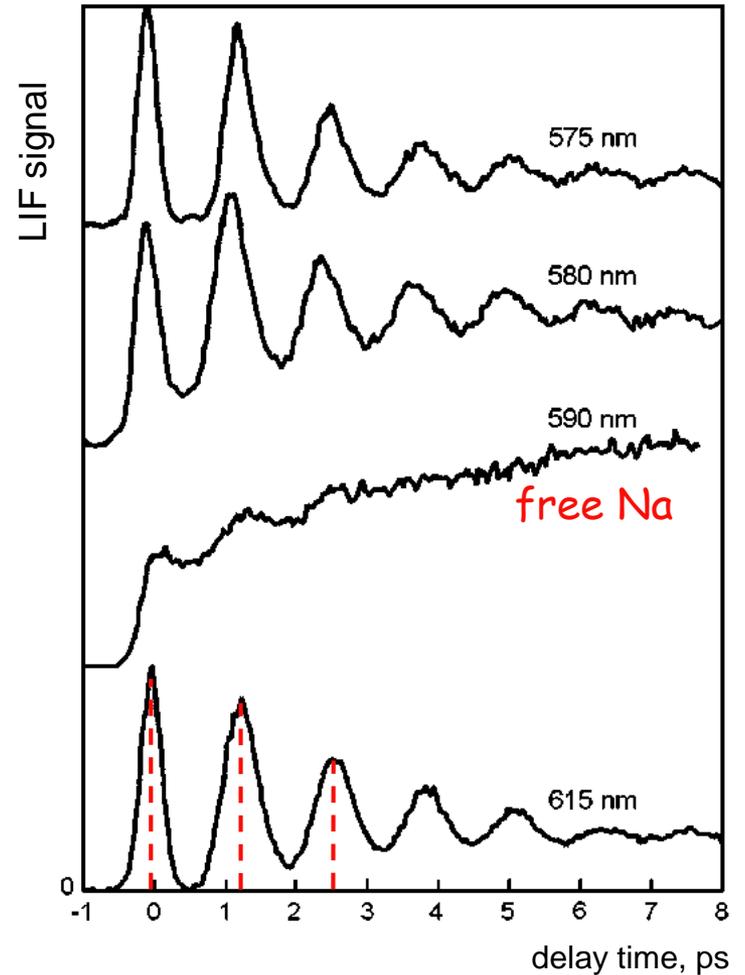
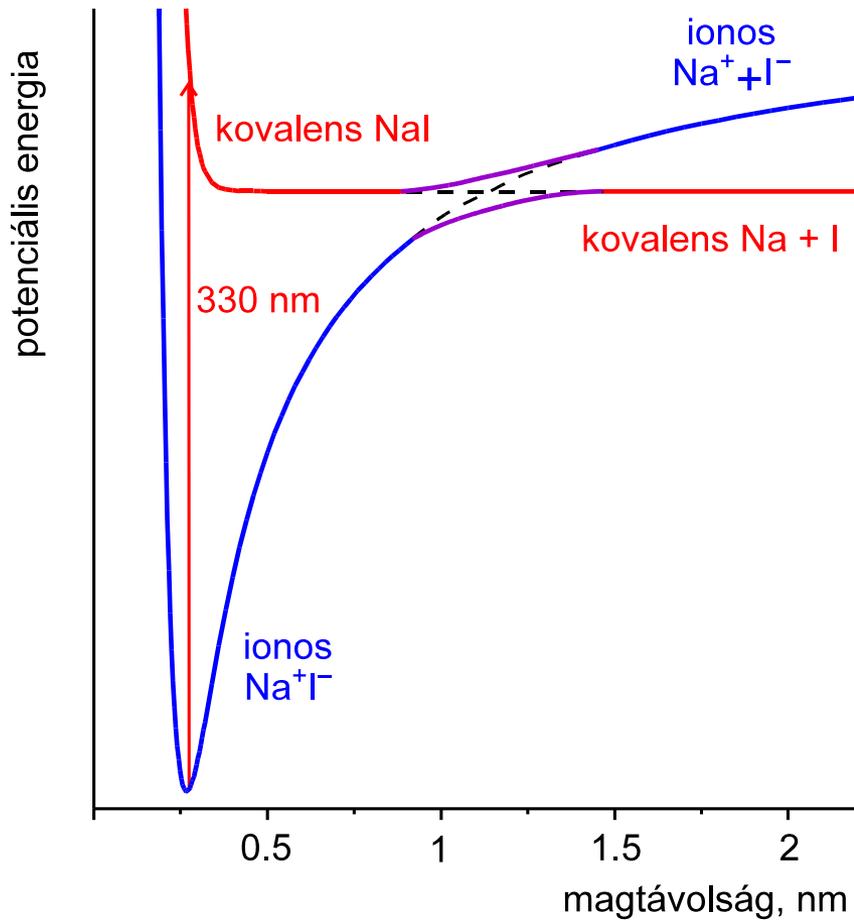


A. H. Zewail  
1997 Nobel prize  
in Chemistry

# The classical femtosecond ICN discovery

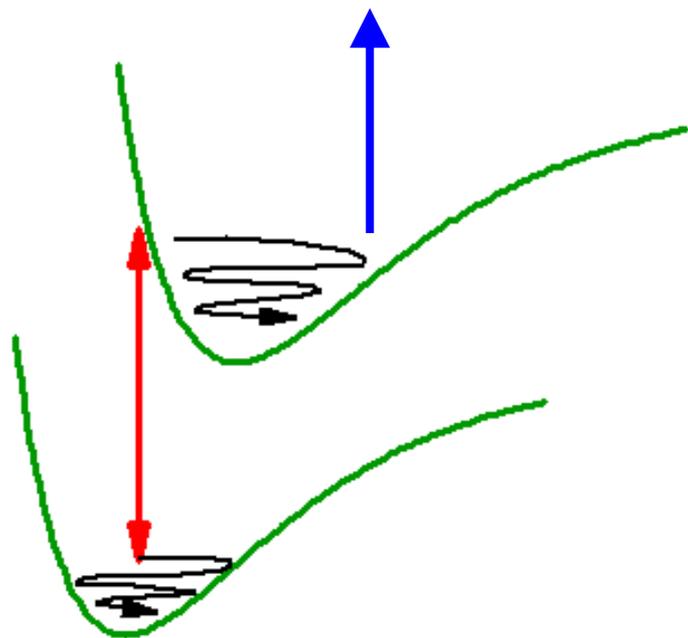


# Example 2:

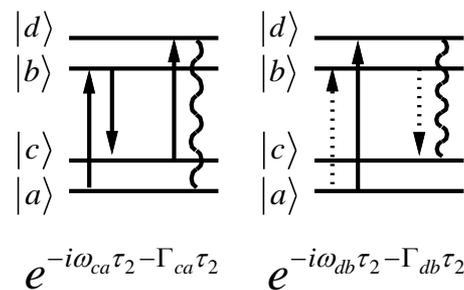
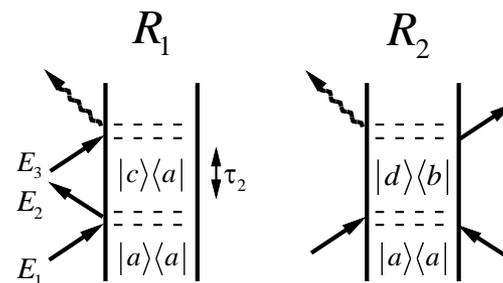


# 量子拍频 (Quantum Beats)

时域解释



频域解释



$$e^{-i\omega_{ca}\tau_2 - \Gamma_{ca}\tau_2}$$

$$e^{-i\omega_{db}\tau_2 - \Gamma_{db}\tau_2}$$

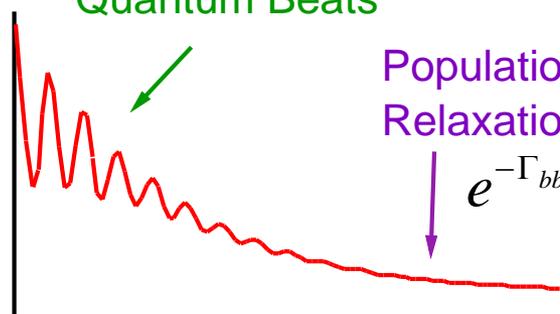
Quantum Beats

Population Relaxation

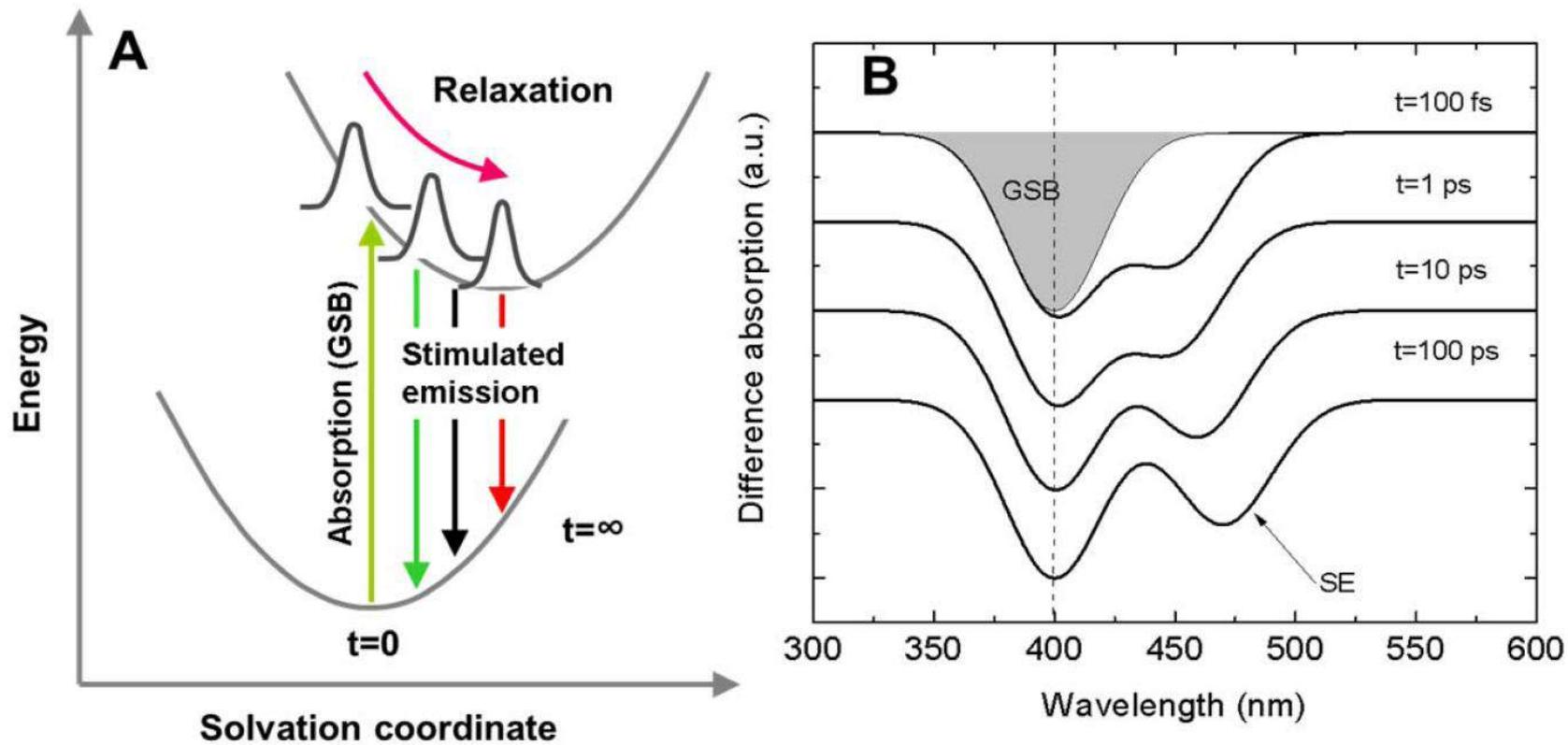
$\Delta I(\tau)$

$$e^{-\Gamma_{bb}\tau_2}$$

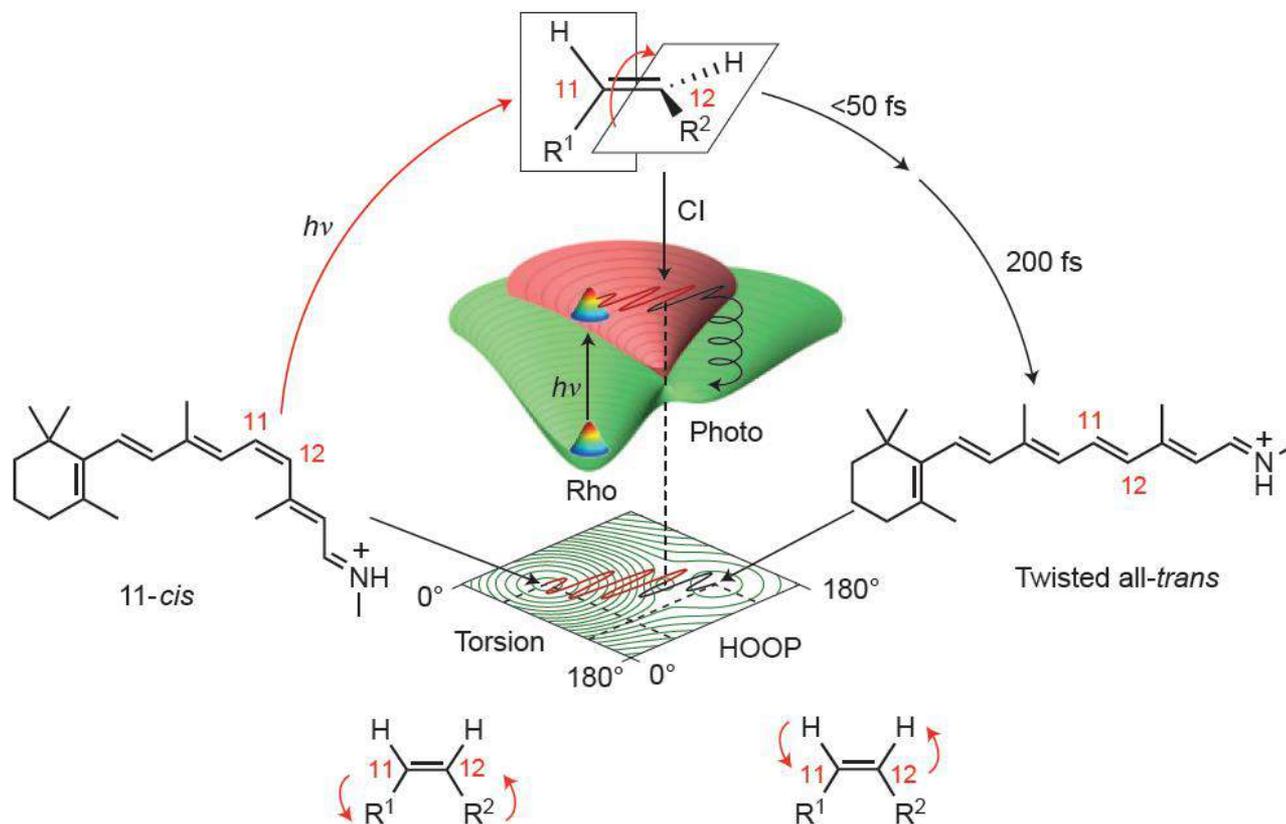
$\tau$



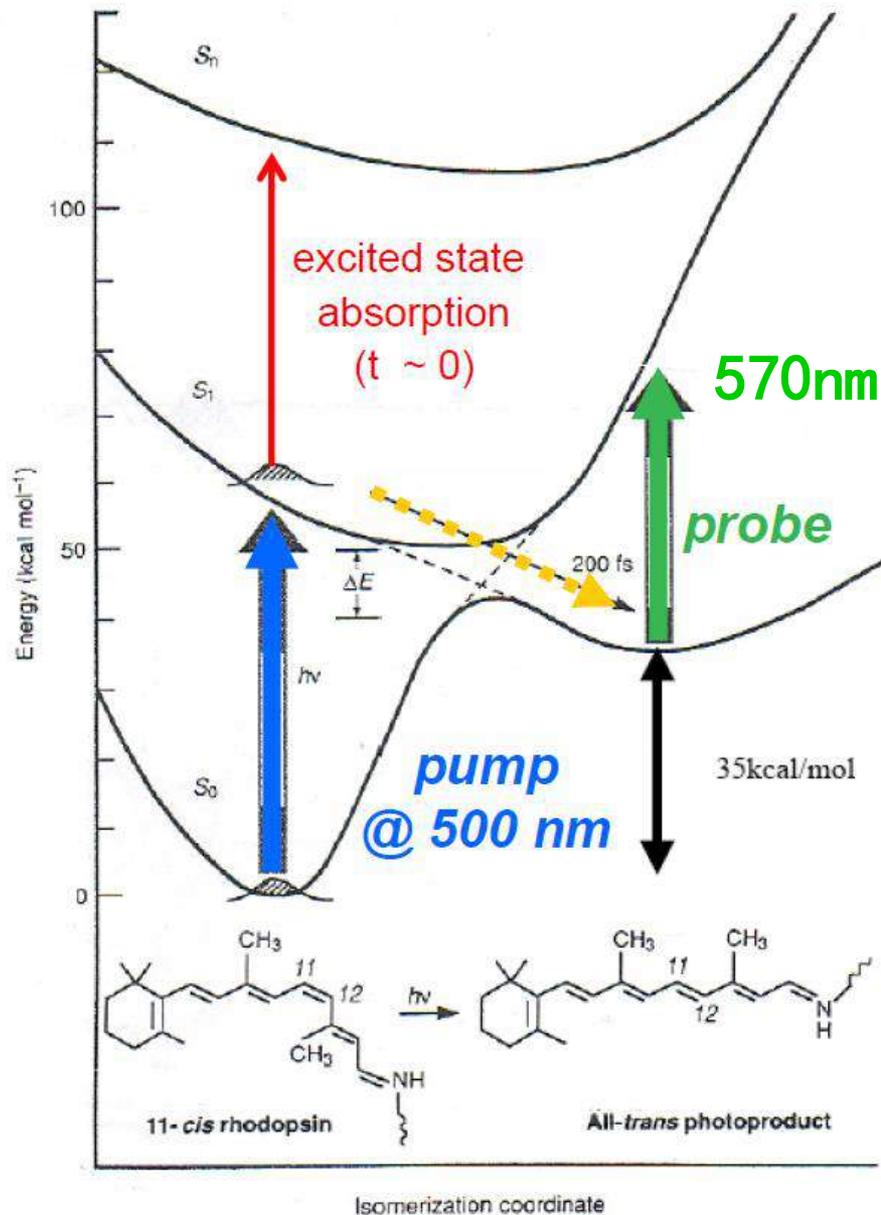
# Example 3 : 溶剂化动力学, solvation dynamics



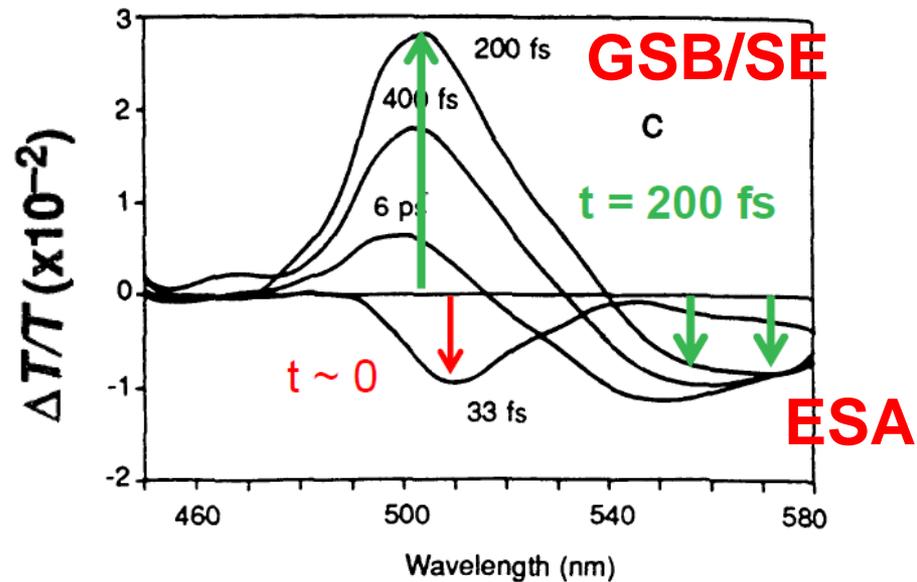
# Example 4: 视觉产生的光激发过程



Rhodopsin 视紫红质

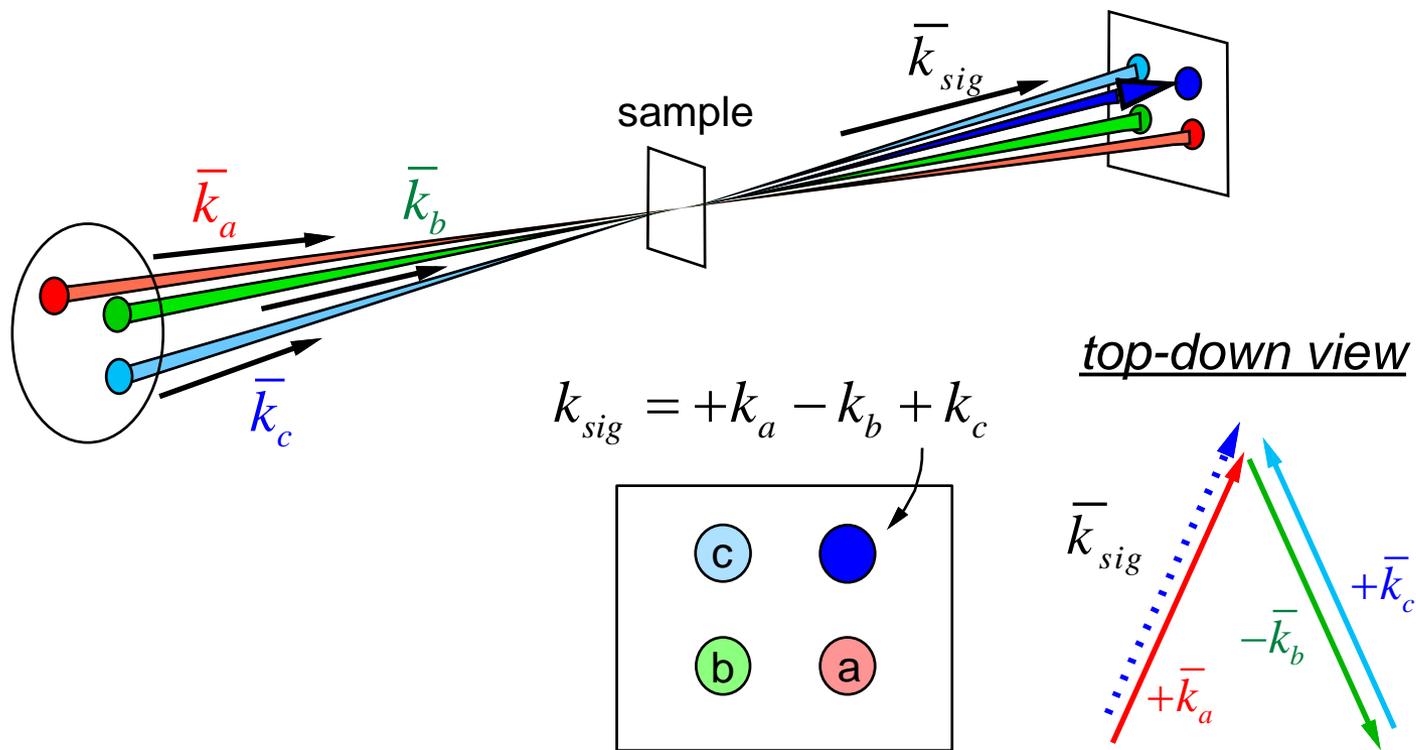


## Spectral changes after excitation



Primary step (*cis-trans* isomerization) of Retinal must occur within 200 fs !

# 5. 一般的三阶光谱现象： Four wave mixing 四波混频



四波混频属于相干光谱，需要相位匹配  
原则上可以有 $2^3 = 8$ 个不同的方向

# (非常简化的) 理论描述

第n个脉冲:

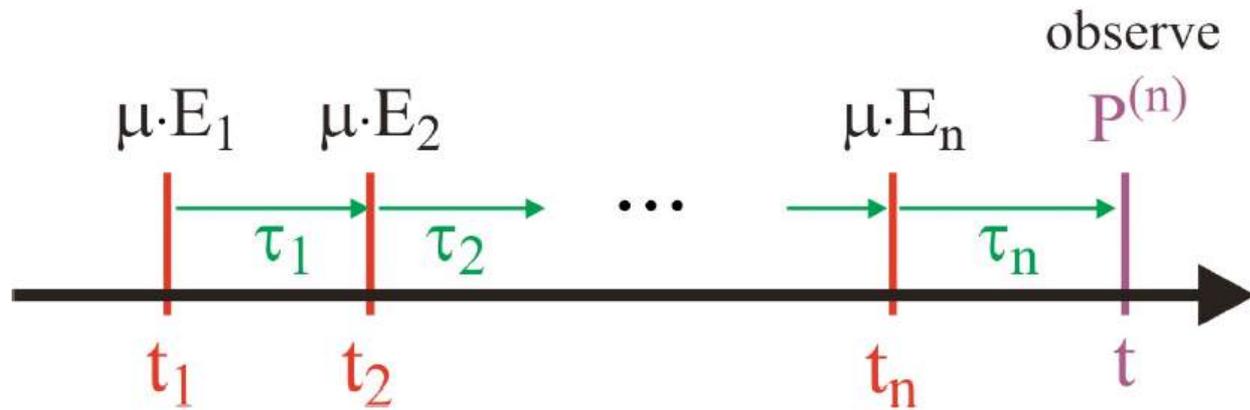
$$\bar{E}_n(t) = E_{n,0} \exp(i\bar{k}_n \cdot \bar{r} - i\omega_n t) + c.c.$$

$$\bar{P}(\bar{r}, t) = P(t) \exp\left(i\bar{k}'_{sig} \cdot \bar{r} - i\omega_{sig} t\right) + c.c.$$

$$P^{(n)}(t) = \int_0^\infty d\tau_n \cdots \int_0^\infty d\tau_1 R^{(n)}(\tau_1, \tau_2, \dots, \tau_n) \bar{E}_1(t - \tau_n - \dots - \tau_1) \cdots \bar{E}_n(t - \tau_n)$$

**微扰理论: 非常类似我们推导吸收光谱, 但是要繁琐很多**

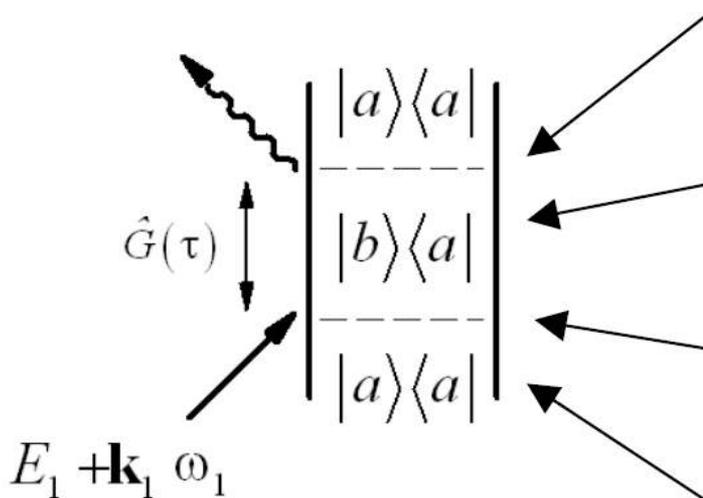
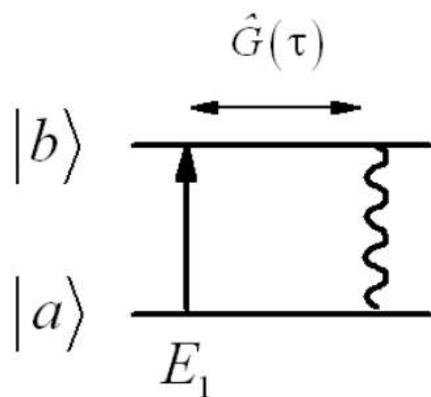
$$R^{(n)}(\tau_1, \tau_2, \dots, \tau_n) = \left(\frac{i}{\hbar}\right)^n \theta(\tau_1)\theta(\tau_2)\dots\theta(\tau_n) \\ \times Tr \left\{ \left[ \left[ \dots \left[ \mu_I(\tau_n + \tau_{n-1} + \dots + \tau_1), \mu_I(\tau_{n-1} + \tau_n + \dots + \tau_1) \right], \dots \right] \mu_I(0) \right] \rho_{eq} \right\}$$



1. 光场的相位是决定信号光出射方向的关键，所以可以确定第n束光对应的是吸收还是发射。

2. Mukamel 与合作者发展了图形记号来标记不同光谱技术对应的过程和计算方法

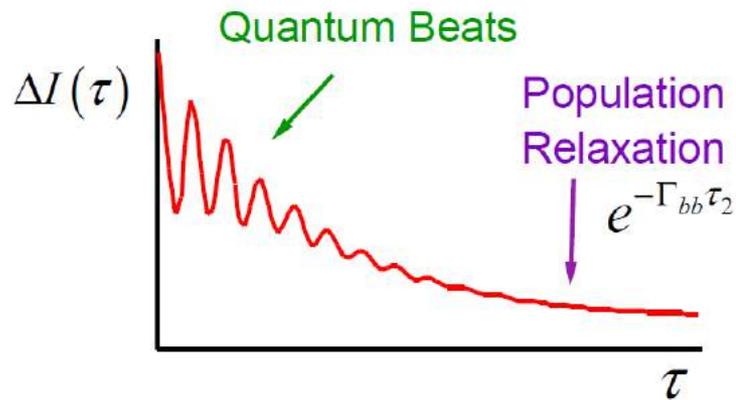
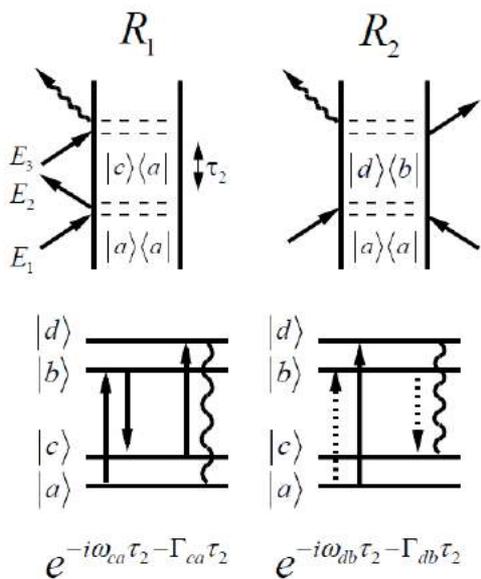
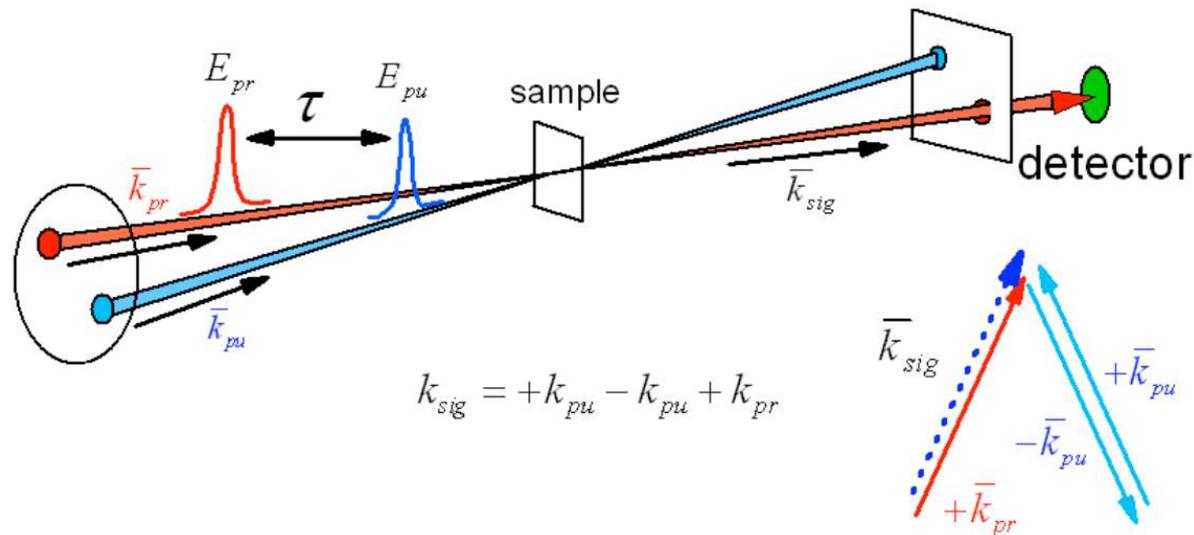
# 吸收光谱



- (1) Start in  $\rho_{aa}$  (add factor of  $p_a$  when reading).
- (2) Act on ket with  $\mu(0)$  to create  $\rho_{ba}$ .
- (3) Propagate under  $H_0$ :  

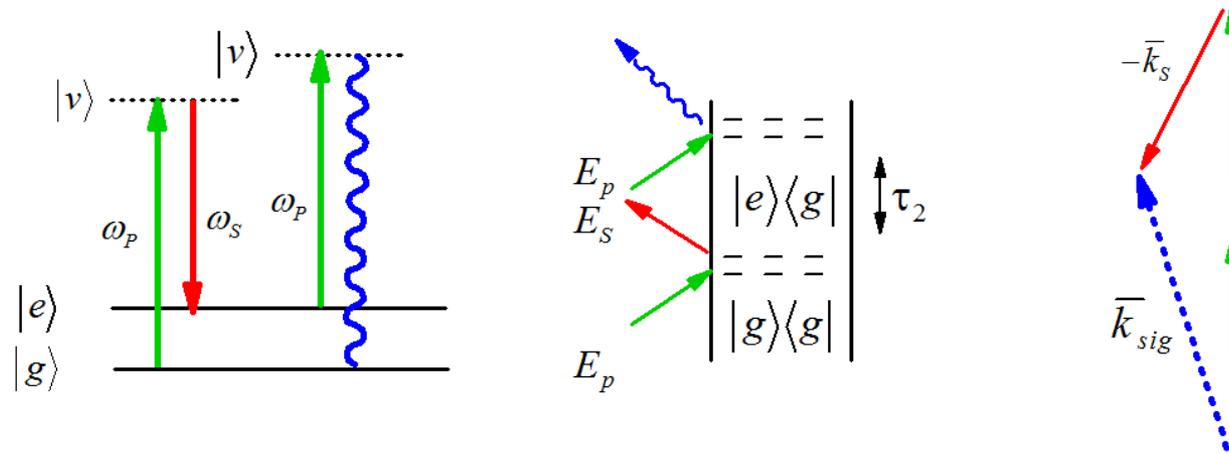
$$G_{ab}(\tau) = e^{-i\omega_{ba}\tau - \Gamma_{ba}\tau}$$
- (4) Act on ket with  $\mu$  and take trace.

# Pump-Probe的响应函数



# 其它三阶光谱方法

## CARS (anti-Stokes Raman scattering) 相干反斯托克斯拉曼散射



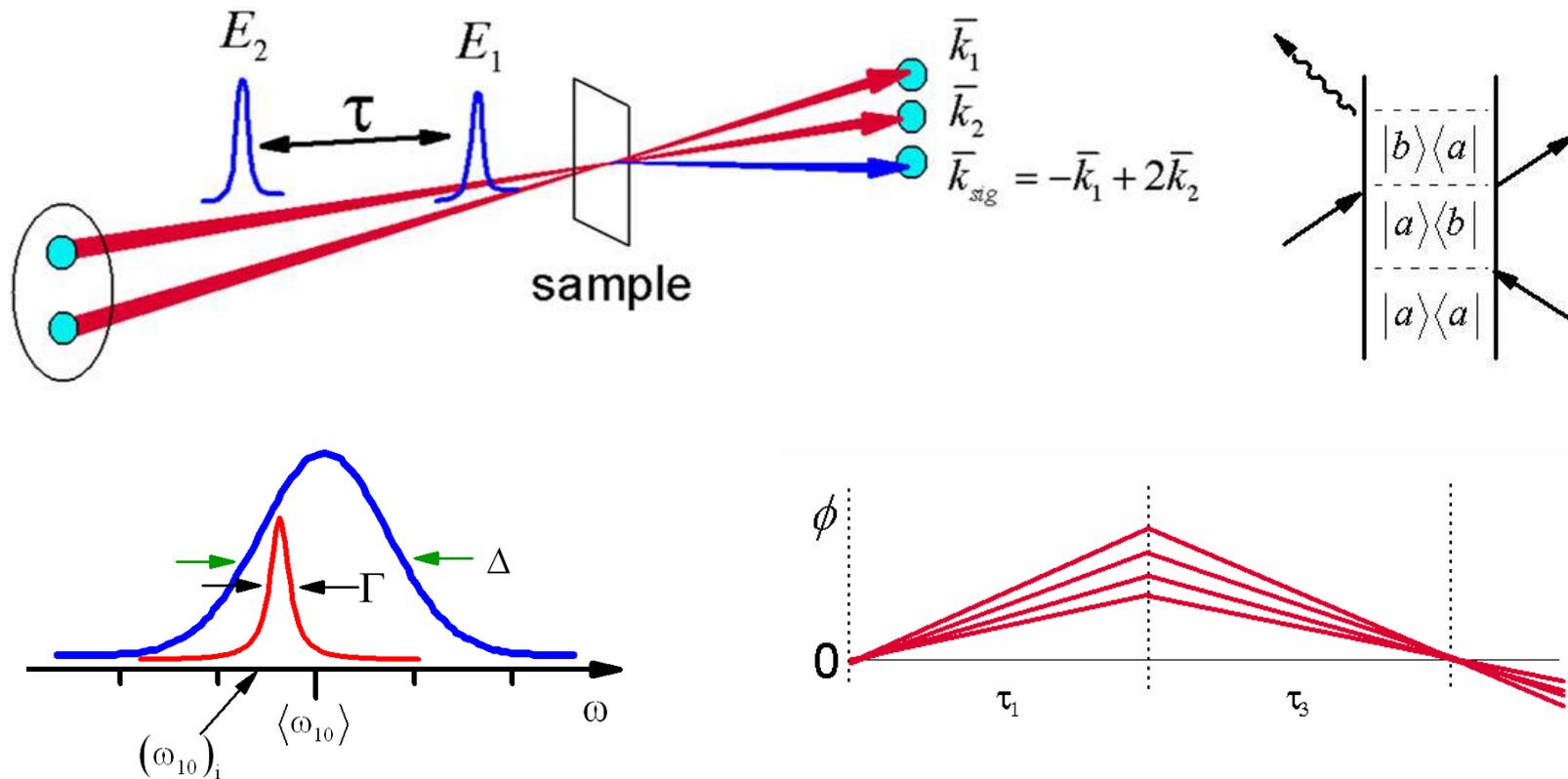
第一和第三束光一样

出射方向与入射方向不同, background Free

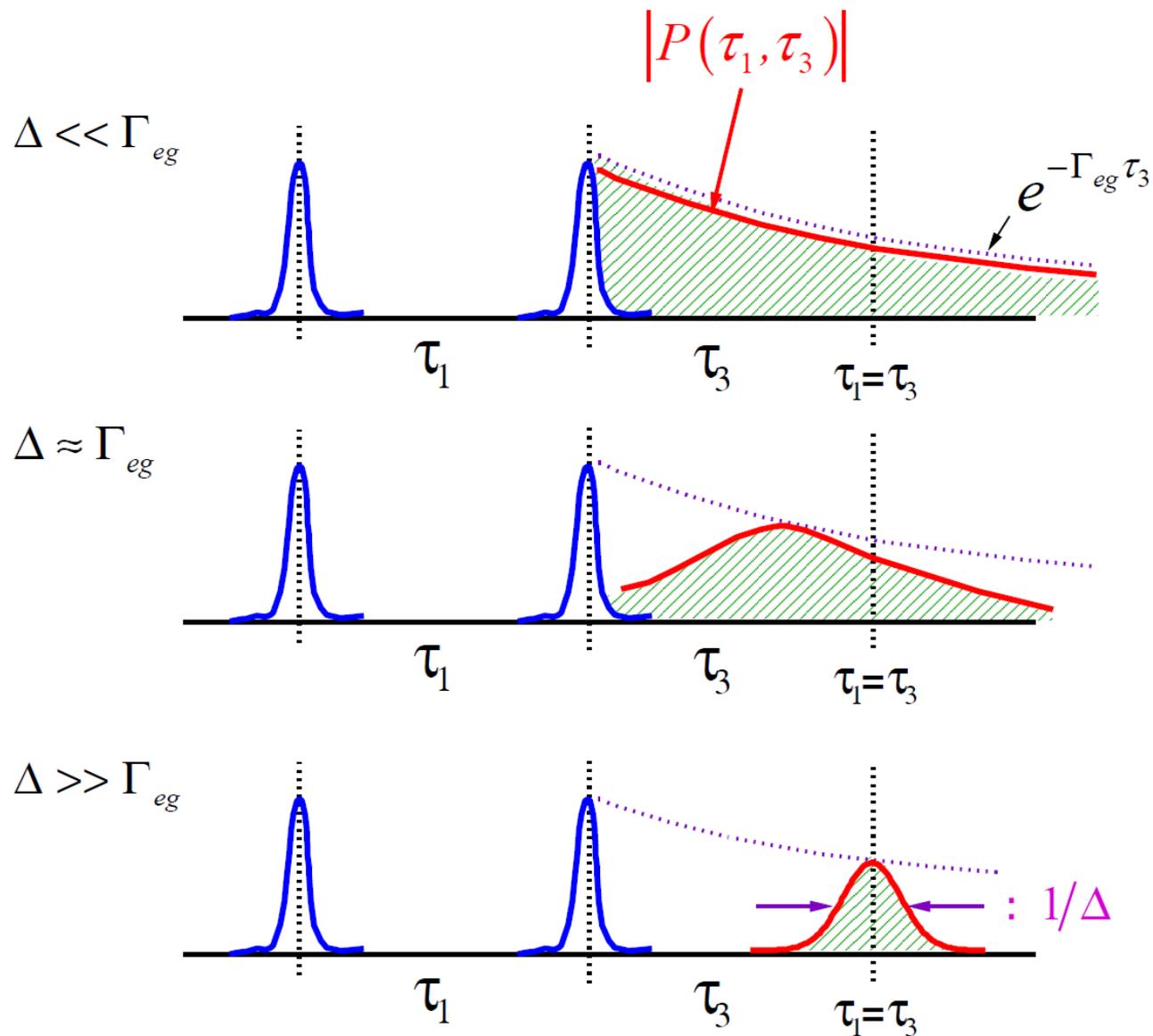
CARS 成像 (谢晓亮)

# 光子回声 (Photo-Echo)

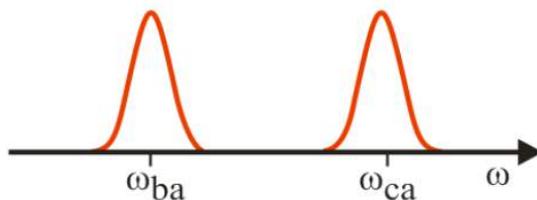
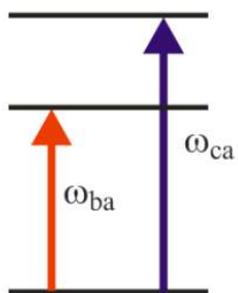
双脉冲PE,  $E_2 = E_3$



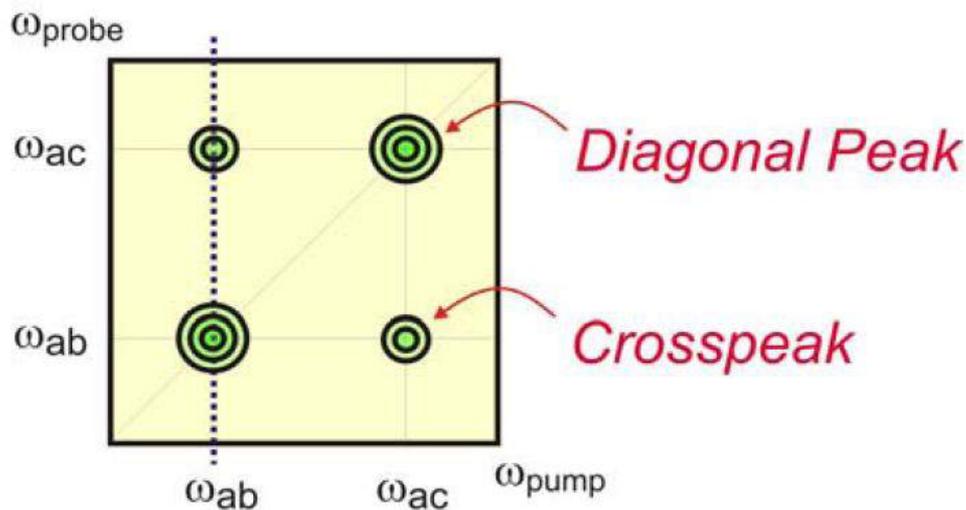
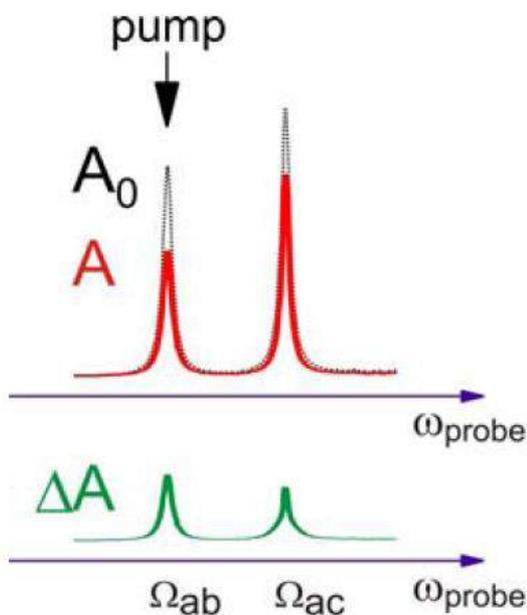
# 三阶信号可以区分均匀和非均匀加宽



# 二维光谱 (2D spectra)



- 激发一个波长改变另一个波长的发射
- 对角峰代表吸收
- 非对角峰代表能量转移、化学交换、...



# 相干二维光谱：四波混频方法

$$k_{\text{sig}} =$$

**Rephasing**

$$-k_1 + k_2 + k_3$$

**Non-rephasing**

$$+k_1 - k_2 + k_3$$

**pulse order:**

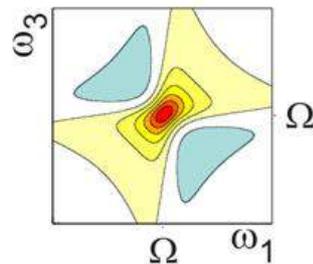
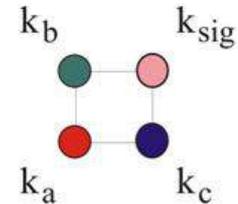
**a b c**

**b a c**

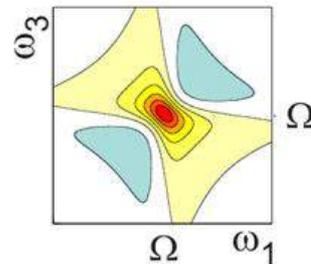
**vib. phase:**

$$e^{-i\Omega t_1} e^{+i\Omega t_3}$$

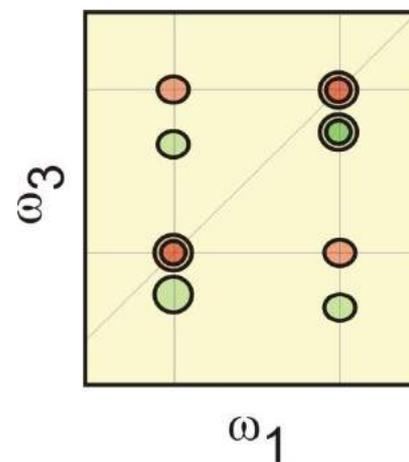
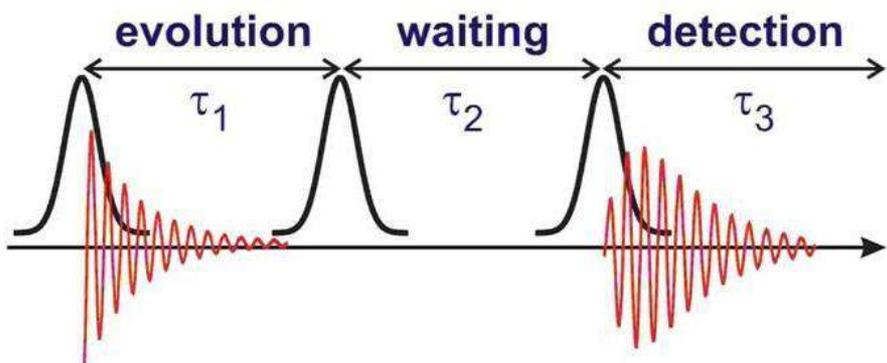
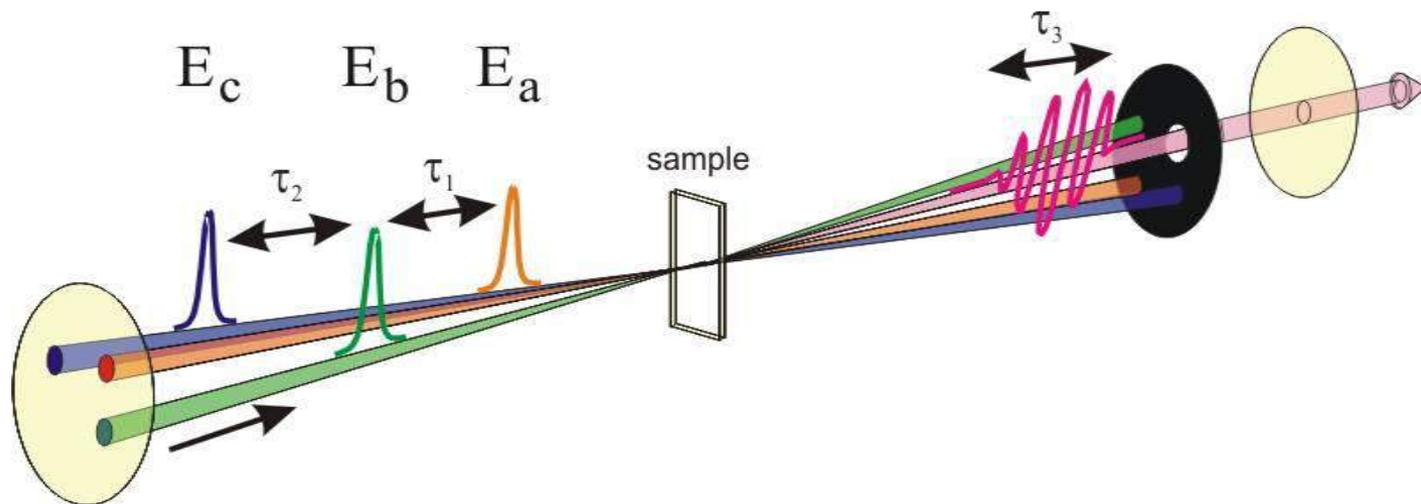
$$e^{+i\Omega t_1} e^{+i\Omega t_3}$$



$S_I$

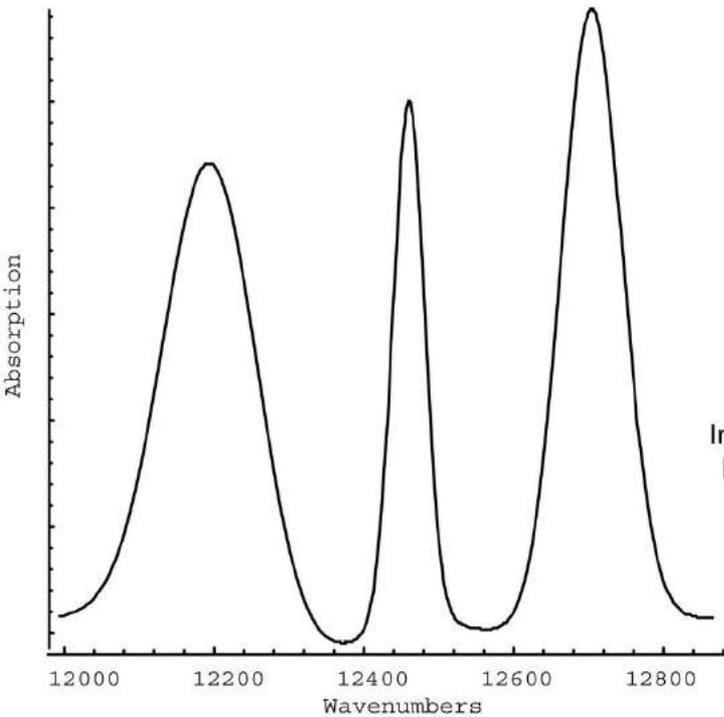


$S_{II}$

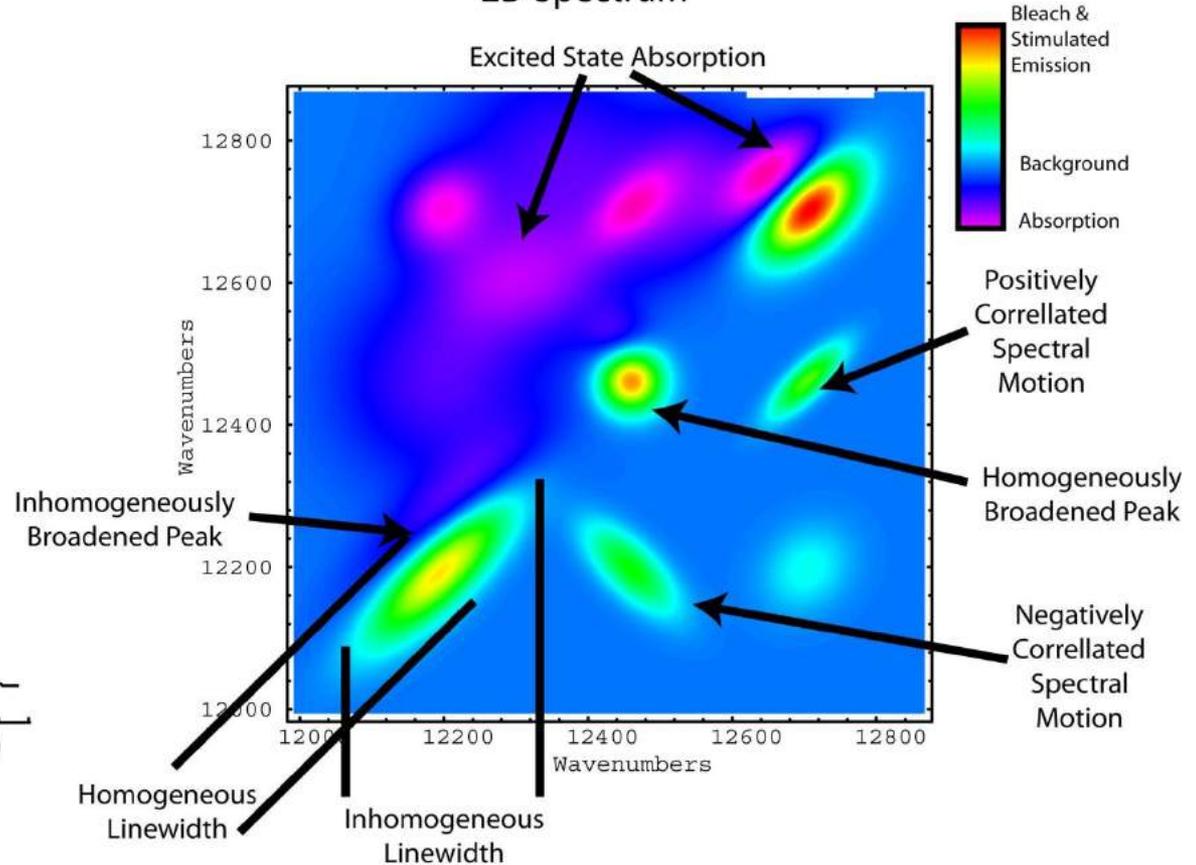


# 二维光谱包含的信息

Linear Spectrum



2D Spectrum

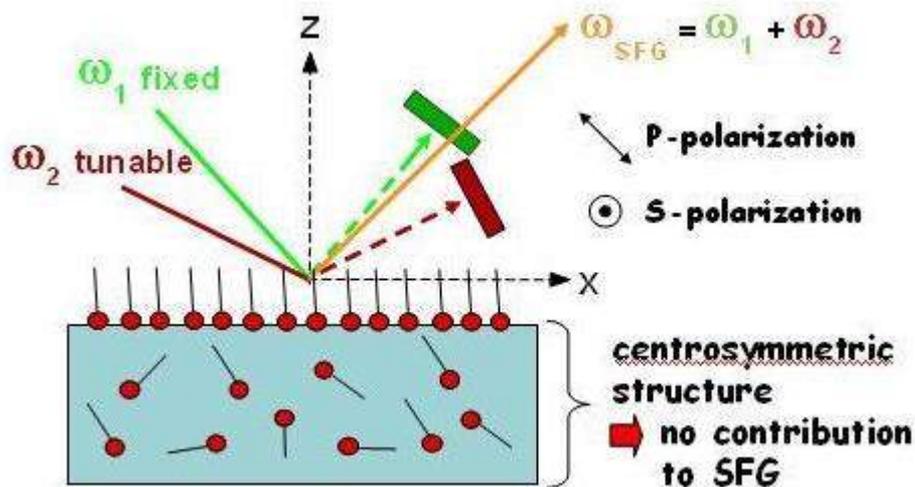
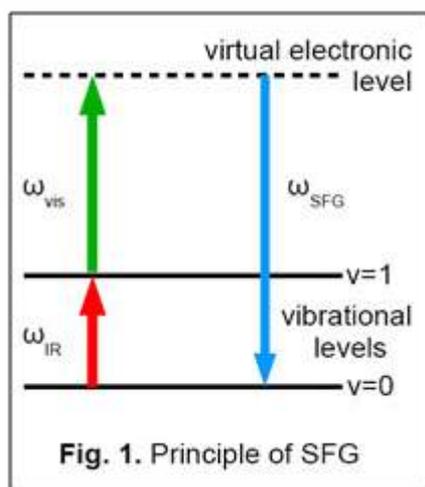


**对角峰：均匀加宽和非均匀加宽**

**非对角峰：能量转移、化学交换、激发态吸收、频率相关等等**

# 6. 本次课程内容小结

## 1. 表面和频光谱（二阶极化率）



### 1. 表面和界面的结构、取向和动力学

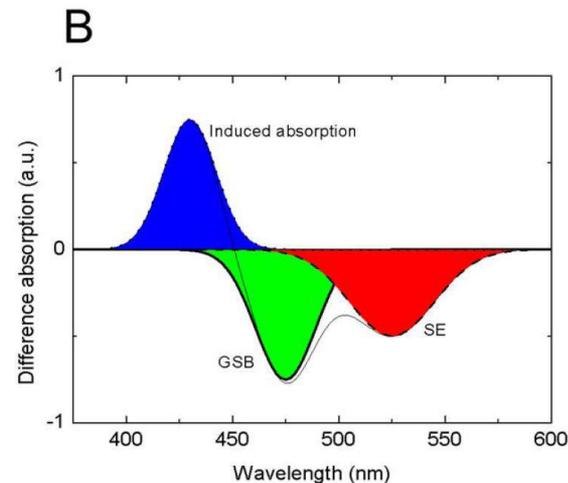
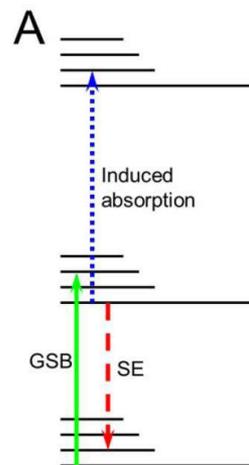
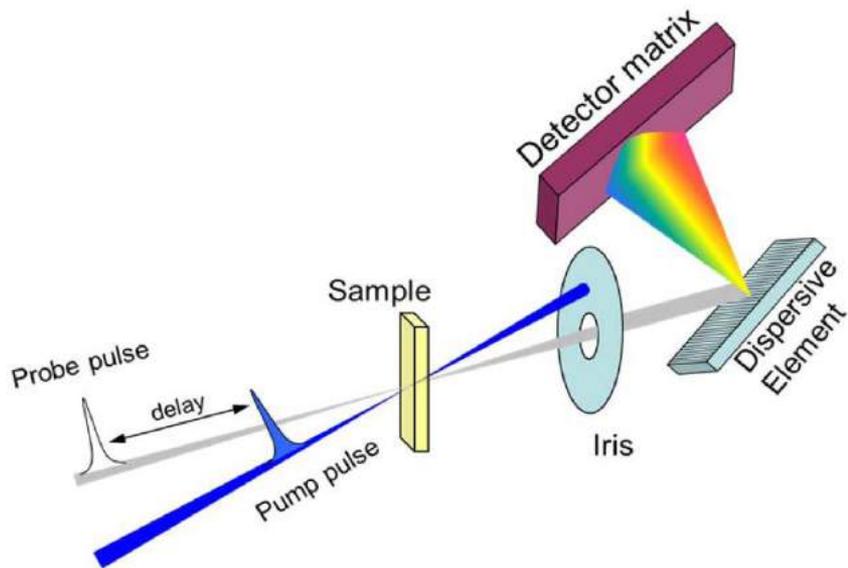
2. 和频光谱是表面敏感的技术，中心对称体系二阶极化率为0

3. SFG信号和三束光的偏振、分子取向有很大关系

4. 和时间分辨技术结合，研究表面动力学关系

# 2. Pump-Probe (泵浦-探测) 光谱

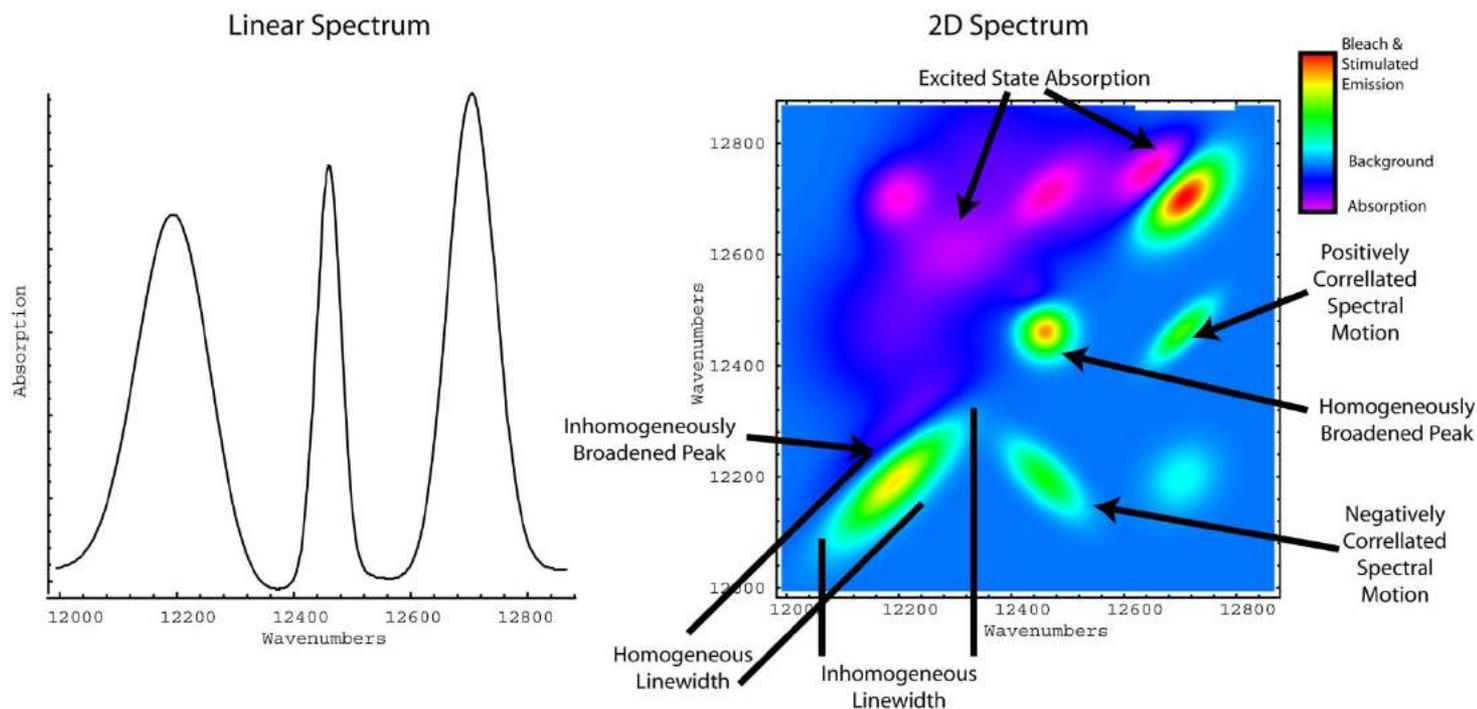
$$\Delta A \equiv A_{exc} - A_{noexc} = \lg \frac{I_{noexc}}{I_{exc}}$$



- Pump-Probe信号的3个来源
- 量子拍频现象的两种解释

### 3. 光学响应函数、其它三阶光谱

$$P^{(n)}(t) = \int_0^\infty d\tau_n \cdots \int_0^\infty d\tau_1 R^{(n)}(\tau_1, \tau_2, \dots, \tau_n) \bar{E}_1(t - \tau_n - \dots - \tau_1) \cdots \bar{E}_n(t - \tau_n)$$



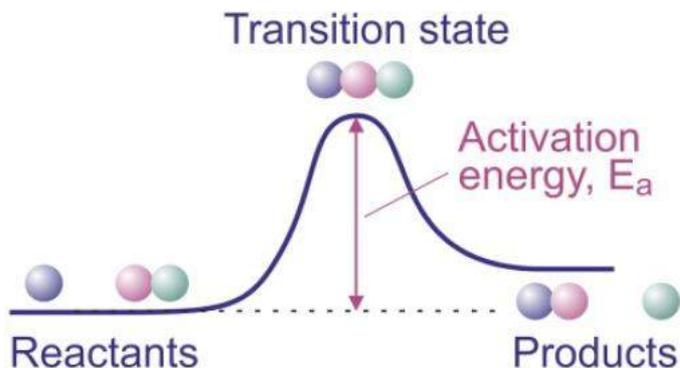
例子：二维光谱技术

# 化学动力学部分总结

分子体系随时间的演化、能量转移转换、光和物质相互作用

1. 化学反应的理论（单个势能面上的反应速率）
2. 分子在多个势能面上的运动：非绝热动力学，B0近似  
电子转移反应、激发态能量转移
3. 凝聚相分子光谱：电子态吸收和发射光谱、红外和拉曼光谱
4. 时间分辨光谱

# 1. 单个势能面上反应：过渡态理论



$$k_{TST} = A \cdot e^{-E_a/RT}$$

$$k = \alpha_{tunnuling} K_{recrossing} K_{ZPE} k_{TST}^{classical}$$

隧穿修正

反复穿越  
交叉面修正

零点能修正

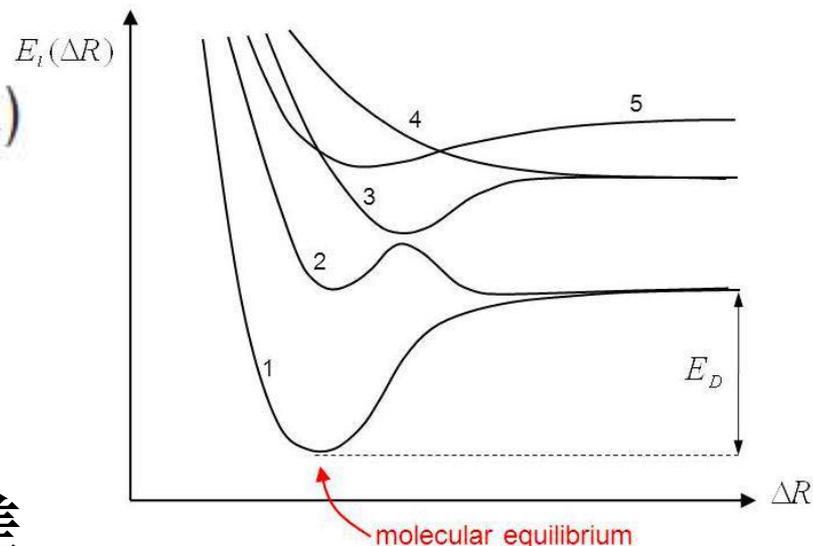
## 2. 玻恩-奥本海默近似、非绝热动力学

$$H_{el}(R)\phi_a(r; R) = E_a(R)\phi_a(r; R)$$

- 求解电子薛定谔方程得到一组势能面，势能面间距大时-BO近似成立

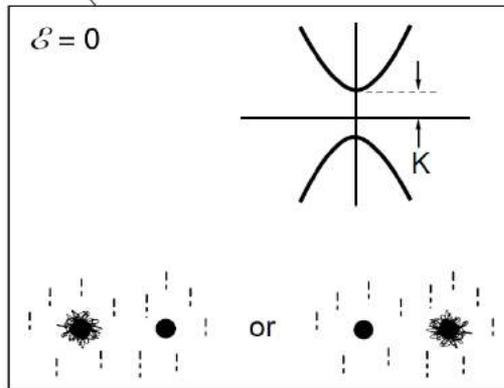
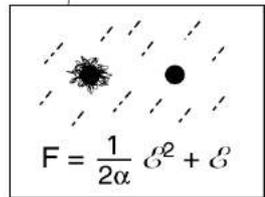
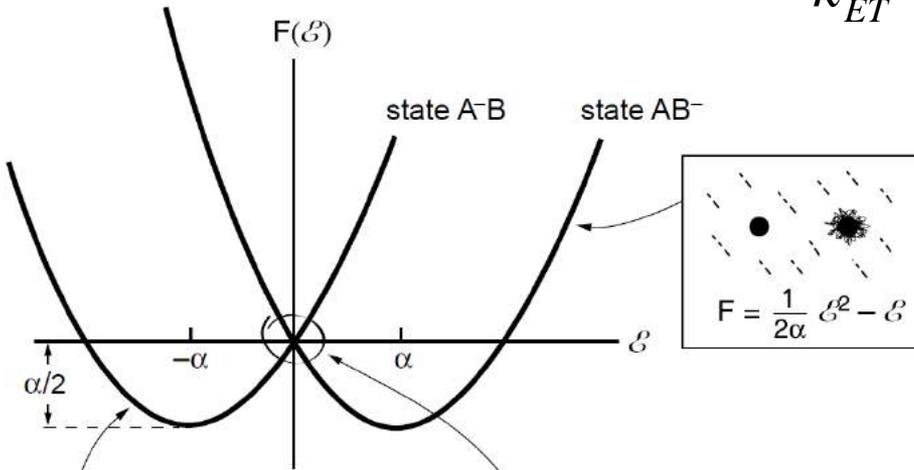
平衡位置，基态到激发态能级差 2-3eV；振动能级差，10-400meV

- 势能面接近或交叉：非绝热动力学  
远离平衡构型、激发态（光/电激发）



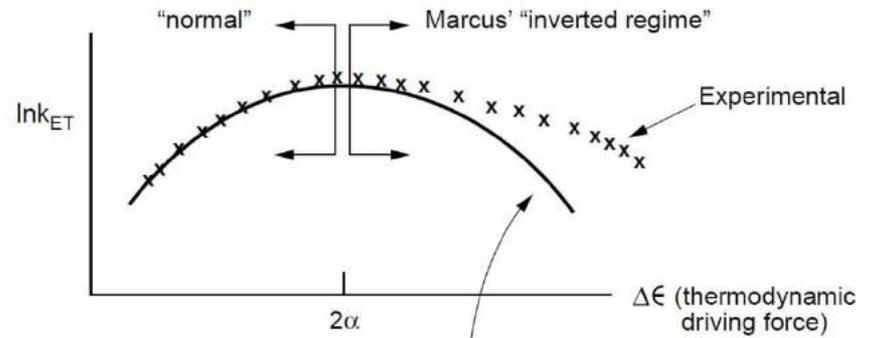
原因：电子质量远小于原子核质量

# 2. 电子转移的物理图像、Marcus公式



Energy gap,  $\Delta E = H_B - H_A = -2G$

$$k_{ET} = K^2 \sqrt{\frac{\pi}{\hbar^2 \lambda k_B T}} \exp\left\{-\frac{(\lambda - \Delta\varepsilon)^2}{4\lambda k_B T}\right\}$$



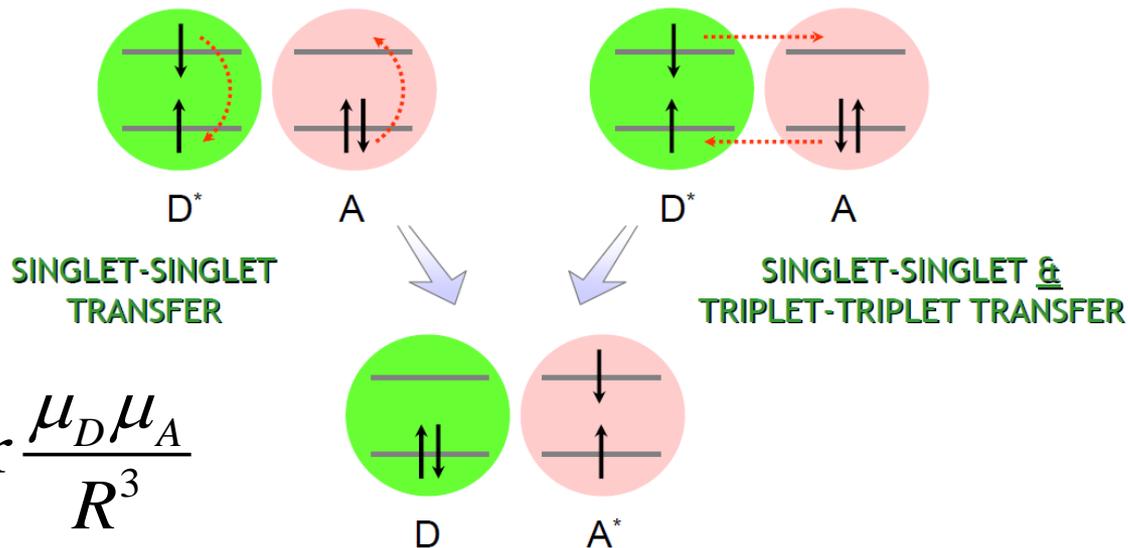
Landau-Zener: 随耦合增大从非绝热反应到绝热反应的转变

Bixon-Jortner: 高频振动模式，量子化部分自由度

# 3: 激发态能量转移、Förster公式

**Förster**, Coulombic  
(long range ~30-100 Å)

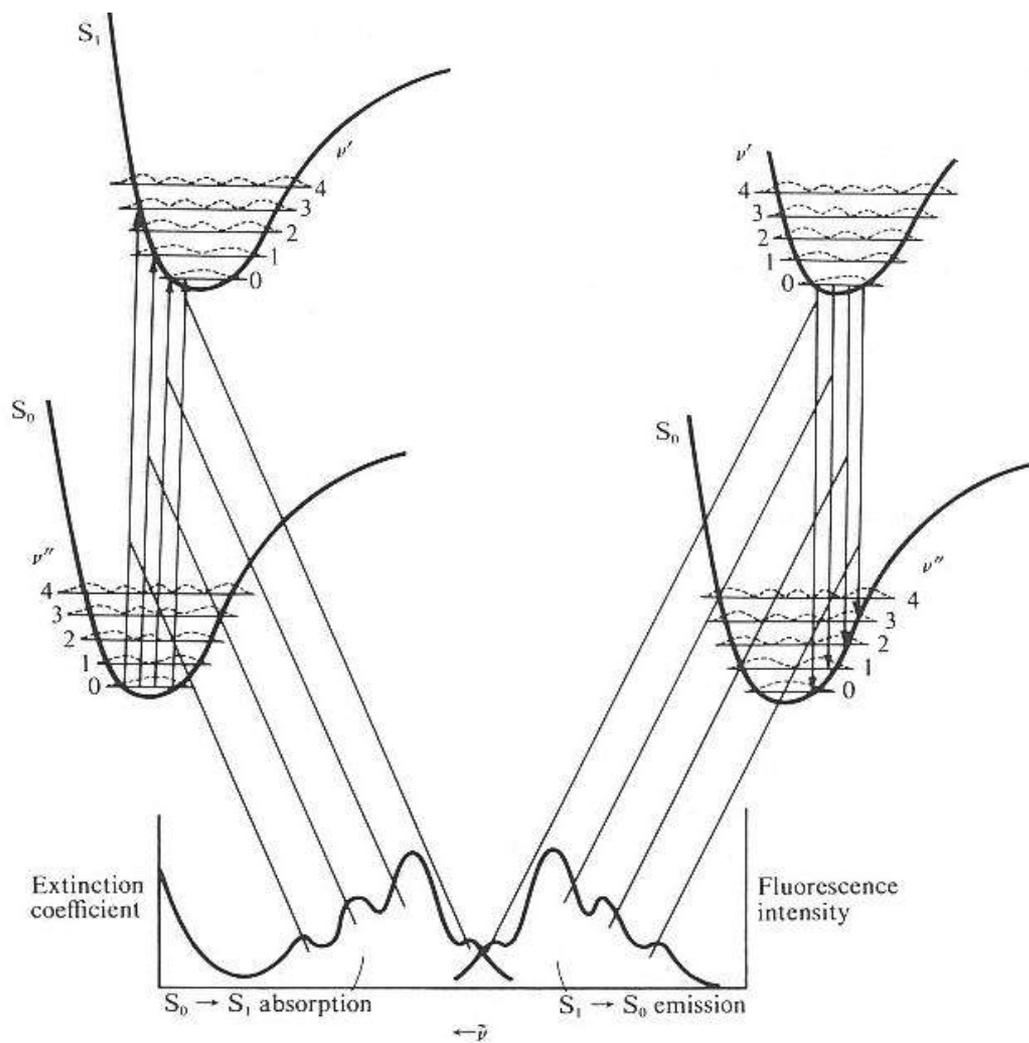
**Dexter**, e<sup>-</sup> exchange  
(short range ~6-20 Å)



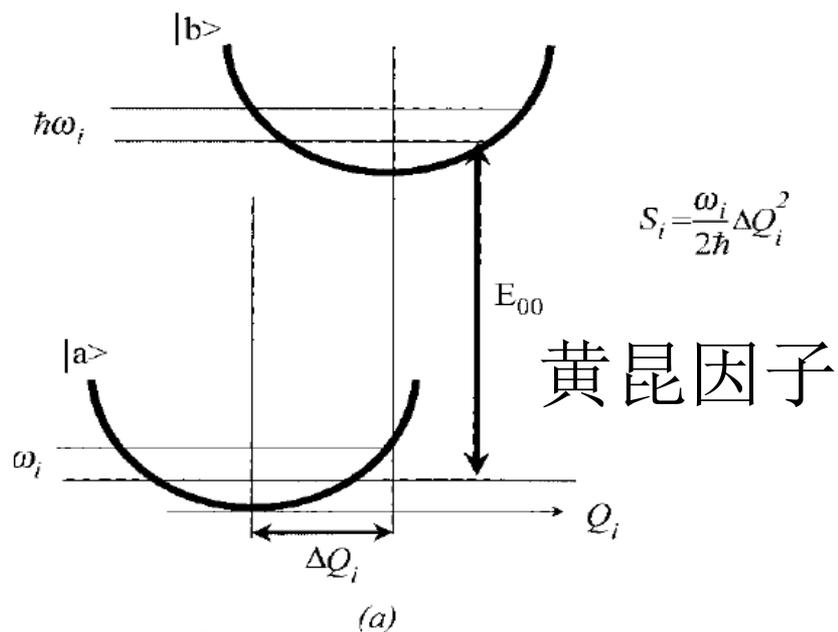
$$K_{coul} = K \frac{\mu_D \mu_A}{R^3}$$

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

# 4: 吸收和发射光谱



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



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

**谢谢大家！**

**祝元旦快乐！**