《高等物理化学II》

第13章-知识点

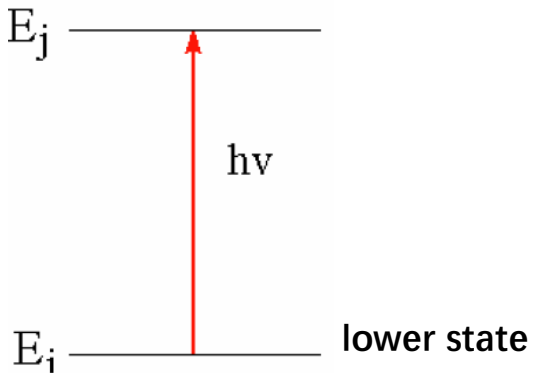
Chapter 13 Molecular Spectroscopy

2019.9

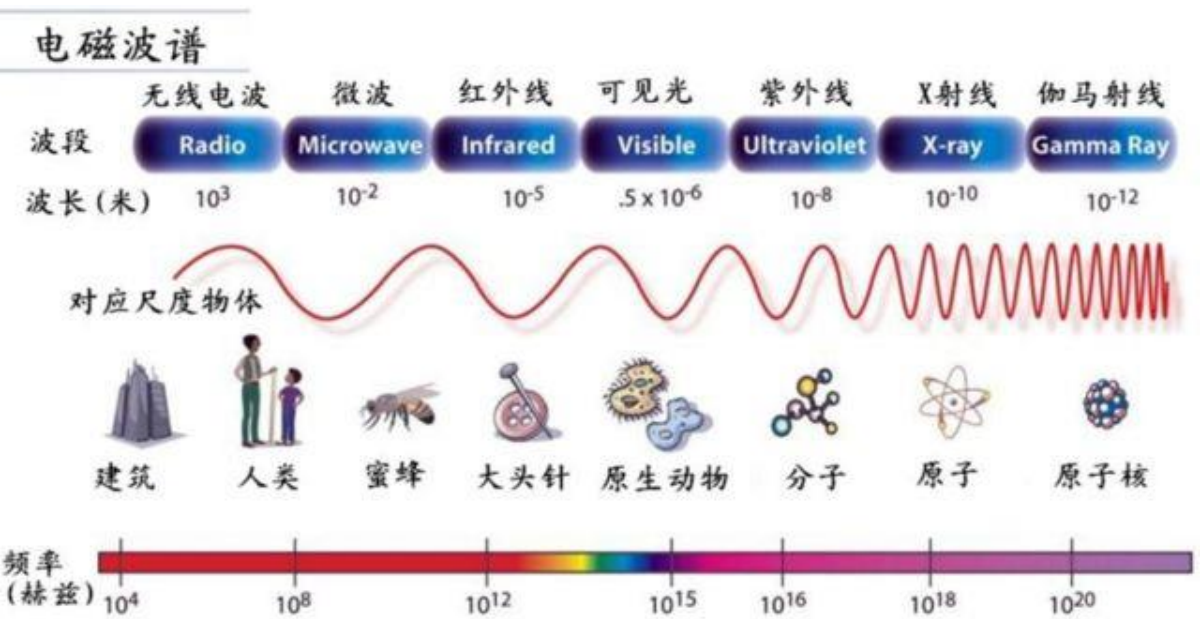
13.1 电磁光谱不同的区域→不同分子过程

分子光谱：研究电磁辐射与分子的相互作用

$$\Delta E = E_u - E_l = h\nu$$



电磁波谱



13.2 振动跃迁中伴随着转动跃迁

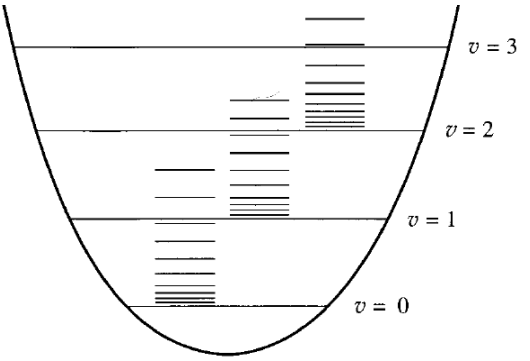
刚性转子-谐振子近似

双原子分子振转能(cm^{-1})

$$\tilde{E}_{\upsilon,J} = G(\upsilon) + F(J)$$

$$= (\upsilon + \tfrac{1}{2})\tilde{\nu} + \tilde{B}J(J+1)$$

$$\upsilon = 0,\ 1,\ 2,\ \ldots \qquad J = 0,\ 1,\ 2,\ \ldots$$



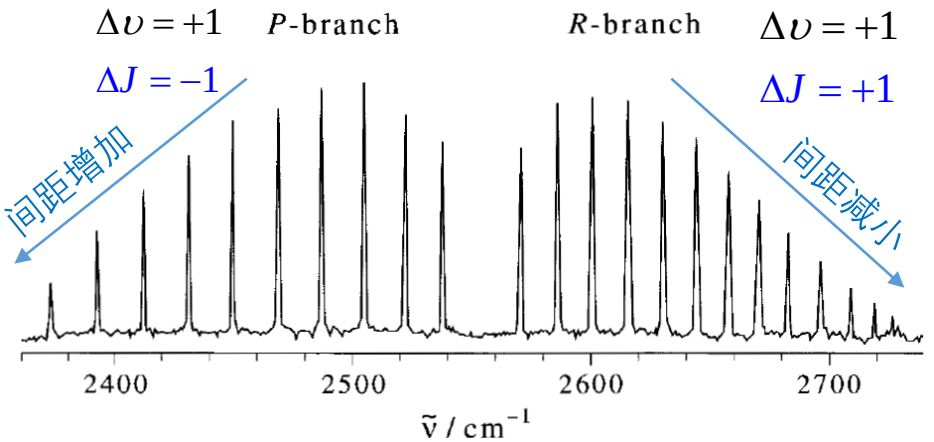
$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad \tilde{B} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R_e^2}$$

振转光谱

选择规则 (红外吸收谱)

$$\Delta\upsilon = +1 \qquad \Delta J = \pm 1 \Rightarrow \begin{cases} \Delta J = +1 & (R\text{支}) \\ \Delta J = -1 & (P\text{支}) \end{cases}$$

振动中偶极矩须变化



13.3 振转相互作用导致P支R支的不等间距

刚性转子-谐振子近似

双原子分子振转能(cm^{-1})

$$\tilde{E}_{\upsilon,J}=\tilde{\nu}(\upsilon+\tfrac{1}{2})+\tilde{B}J(J+1) \qquad \tilde{B}=\frac{h}{8\pi^2 cI}=\frac{h}{8\pi^2 c\mu R_e^2}$$

振转相互作用$\Rightarrow$ υ变大 $\rightarrow$ R_e 增加 $\rightarrow$ $\tilde{B}$ 减小

$$\tilde{E}_{\upsilon,J}=(\upsilon+\tfrac{1}{2})\tilde{\nu}+\tilde{B}_\upsilon J(J+1) \qquad \tilde{B}_0>\tilde{B}_1>\cdots$$

$$\tilde{B}_\upsilon=\tilde{B}_e-\tilde{\alpha}_e(\upsilon+\tfrac{1}{2}) \qquad \tilde{\alpha}_e:\ \text{振转耦合常数}$$

υ = 0→1跃迁中的P支和R支

P-branch

$$\tilde{\nu}_P(\Delta J=-1)=\tilde{E}_{1,J+1}-\tilde{E}_{0,J}$$
$$=\tilde{\nu}-(\tilde{B}_1+\tilde{B}_0)J+(\tilde{B}_1-\tilde{B}_0)J^2$$
$$J=1,\ 2,\ \ldots$$

R-branch

$$\tilde{\nu}_R(\Delta J=+1)=\tilde{E}_{1,J+1}-\tilde{E}_{0,J}$$
$$=\tilde{\nu}+2\tilde{B}_1+(3\tilde{B}_1-\tilde{B}_0)J+(\tilde{B}_1-\tilde{B}_0)J^2$$
$$J=0,\ 1,\ 2,\ \ldots$$

$$\tilde{\nu}_P(J+1)-\tilde{\nu}_P(J)$$
$$=-\left[(\tilde{B}_1+\tilde{B}_0)+2(\tilde{B}_0-\tilde{B}_1)J\right]$$
$$J=1,\ 2,\ \ldots$$

$$\tilde{\nu}_R(J+1)-\tilde{\nu}_R(J)$$
$$=2(2\tilde{B}_1-\tilde{B}_0)-2(\tilde{B}_0-\tilde{B}_1)J$$
$$J=0,\ 1,\ 2,\ \ldots$$

$\tilde{B}_0>\tilde{B}_1\Rightarrow$ **J**变大 $\rightarrow$ **P**支间距增加，**R**支间距减小

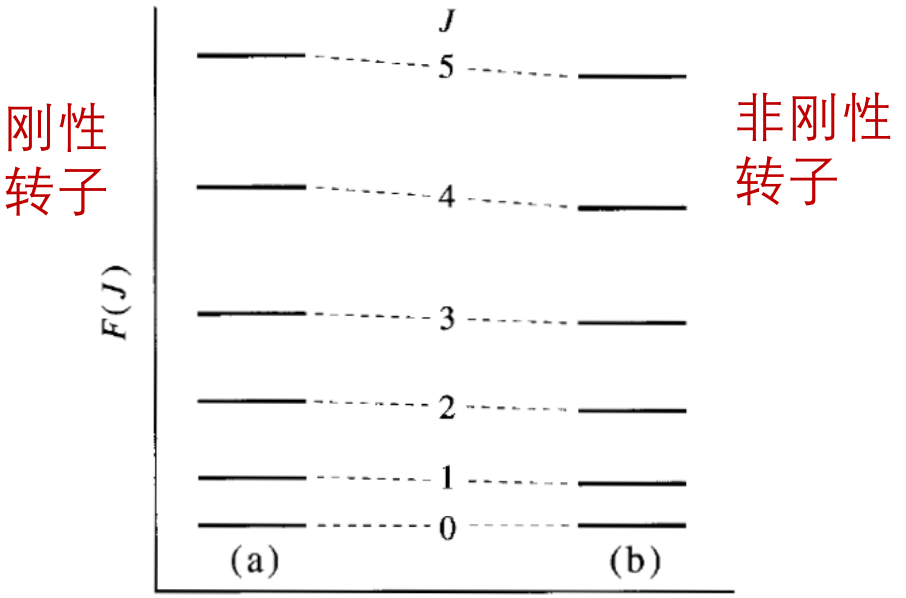
13.4 纯转动光谱也不等间距

双原子分子转动能(cm^{-1})

离心力 $\Rightarrow$ **J**变大 $\rightarrow$ $\boldsymbol{R_e}$ 增加 (非刚性)

$$F(J)=\tilde{B}J(J+1)-\tilde{D}J^2(J+1)^2$$

$\tilde{D}$:离心扭转常数



刚性转子

非刚性转子

非刚性转子转动光谱

$$\tilde{\nu}_{\text{obs}}=F(J+1)-F(J)$$

J $\rightarrow$ **J**+1跃迁

$$=2\tilde{B}(J+1)-4\tilde{D}(J+1)^3$$

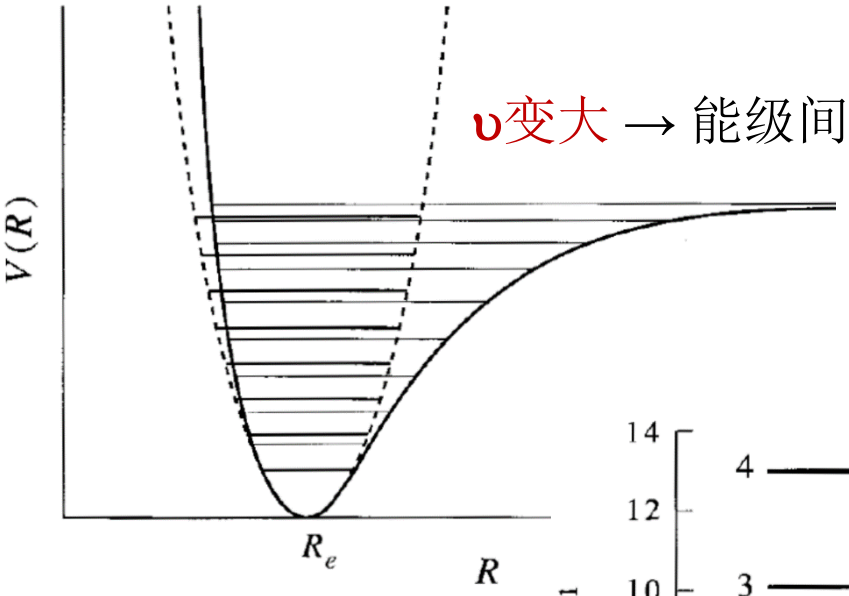
$$J=0,\ 1,\ 2,\ \ldots$$

13.5 振动光谱中能观测到倍频

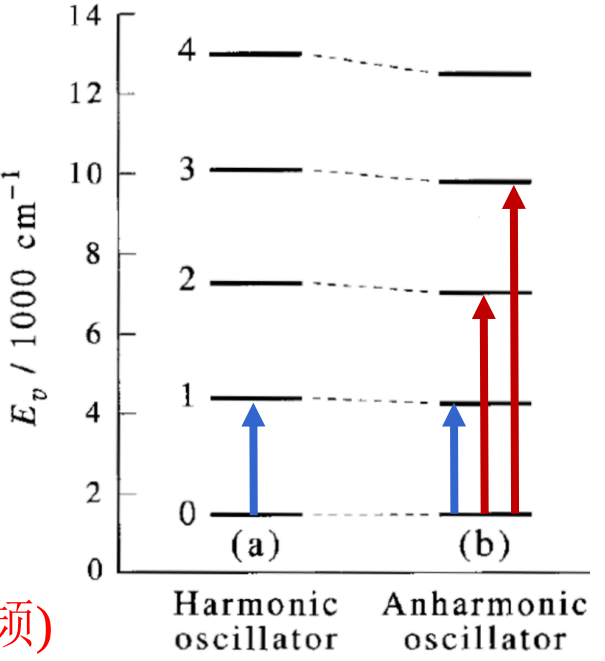
双原子分子的非谐振动

$$V(R)-V(R_e)=\frac{k}{2}x^2+\frac{\gamma_3}{6}x^3+\frac{\gamma_4}{24}x^4+\cdots$$

$$G(\upsilon)=\tilde{\nu}_e(\upsilon+\tfrac{1}{2})-\tilde{x}_e\tilde{\nu}_e(\upsilon+\tfrac{1}{2})^2 \qquad \upsilon=0,\ 1,\ 2,\ \ldots$$



υ变大 → 能级间隔减小



选择规则

$\Delta\upsilon$ 可以是任何整数

$$\tilde{\nu}_{obs}=G(\upsilon)-G(0)$$

$$=\tilde{\nu}_e\upsilon-\tilde{x}_e\tilde{\nu}_e\upsilon(\upsilon+1)$$

$\upsilon=1$ (基频), 2,⋯ (倍频)

13.6 电子光谱包含振动和转动信息

双原子分子的总能量

$$\tilde{E}_{\text{total}} = \tilde{\nu}_{el} + \tilde{\nu}_e(\upsilon+\tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(\upsilon+\tfrac{1}{2})^2$$

$$+\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

转动能量非常小，最后两项可忽略

电振跃迁的选择规则

$\Delta\upsilon$ 可为任何整数，不必有永久偶极矩

$0 \rightarrow 0$ 电振跃迁:

$$\tilde{\nu}_{0,0} = \tilde{T}_e$$

$$+(\tfrac{1}{2}\tilde{\nu}'_e - \tfrac{1}{4}\tilde{x}'_e\tilde{\nu}'_e)$$

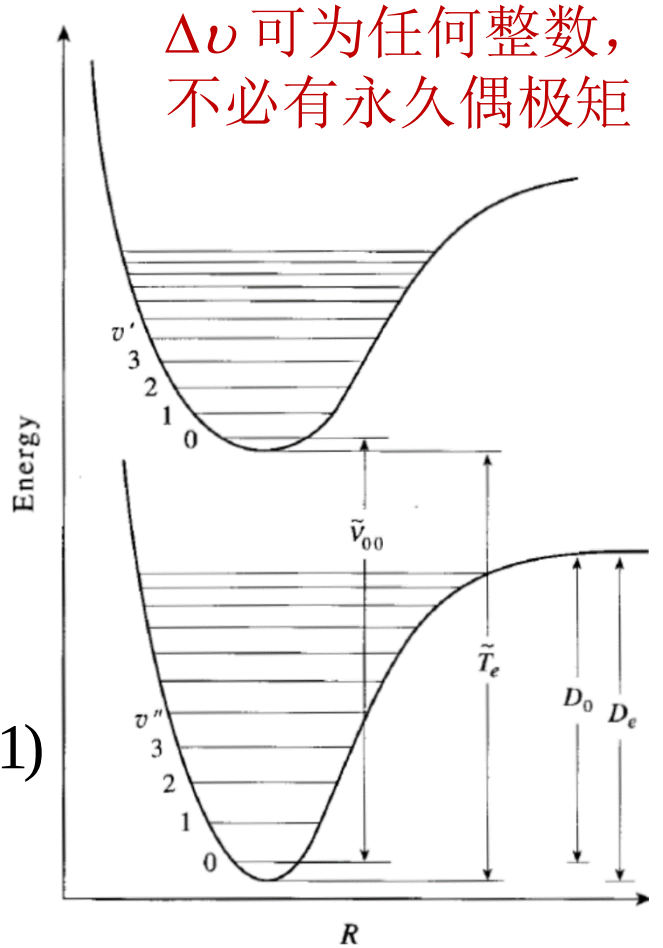
$$-(\tfrac{1}{2}\tilde{\nu}''_e - \tfrac{1}{4}\tilde{x}''_e\tilde{\nu}''_e)$$

$0 \rightarrow \upsilon'$ 电振跃迁:

$$\tilde{\nu}_{obs} = \tilde{\nu}_{0,0}$$

$$+\tilde{\nu}'_e\upsilon' - \tilde{x}'_e\tilde{\nu}'\upsilon'(\upsilon'+1)$$

$$\upsilon' = 0,\ 1,\ 2,\ \ldots$$



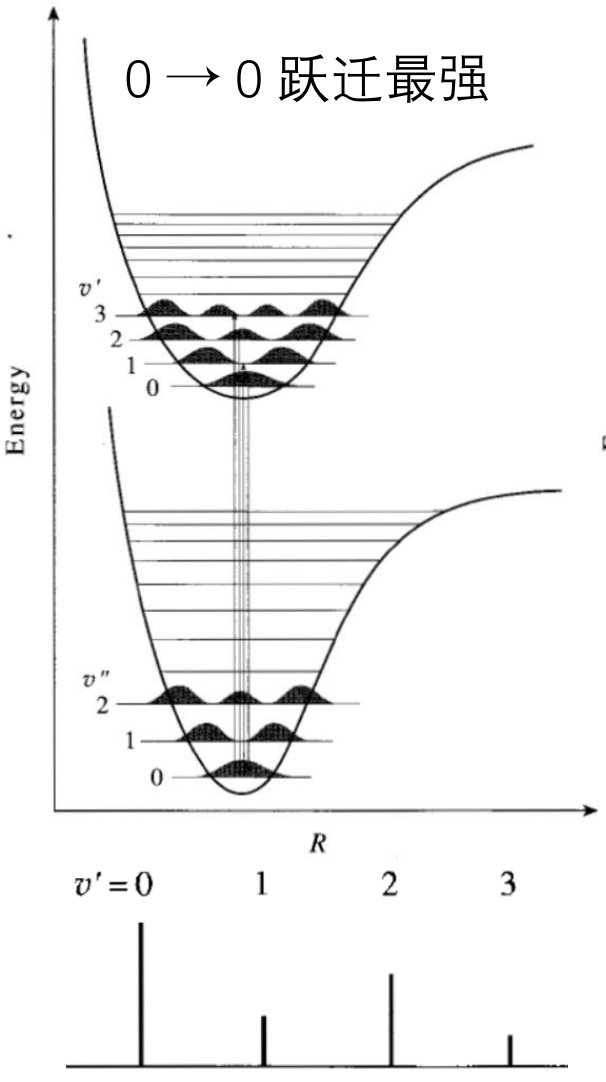
13.7 Franck-Condon原理预测电振跃迁强度

Franck-Condon原理

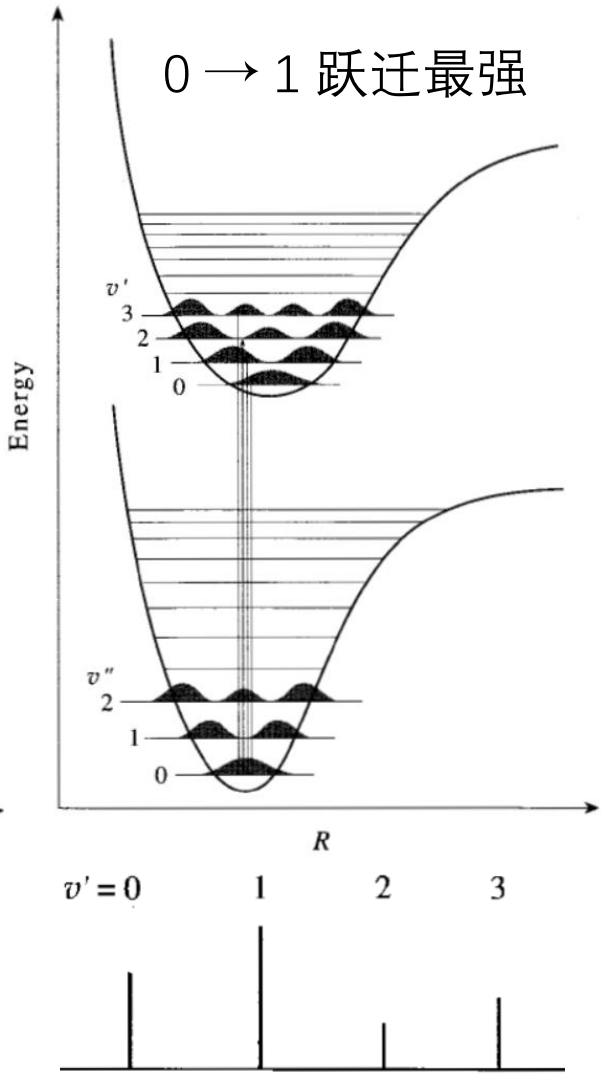
电子跃迁非常迅速，核的运动来不及跟上，基本保持原状。即电子跃迁是垂直的。

电振跃迁的强度

两电子态键长接近



高电子态键长增加



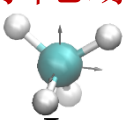
13.8 多原子分子的旋转光谱取决于主惯量

主惯量

变换坐标系，使惯量矩阵对角化，得到的I_A, I_B, I_C (通常取$I_A \le I_B \le I_C$) 称为**主惯量**，对应的旋转常数：$\tilde{A} \ge \tilde{B} \ge \tilde{C}$

刚体类型及能级

球陀螺



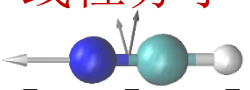
$I_C = I_B = I_A$

$F(J) = \tilde{B}J(J+1)$

$g_J = (2J+1)^2$

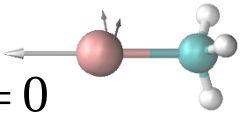
$J = 0,\ 1,\ 2,\ \ldots$

线性分子



$I_C = I_B > I_A = 0$

长对称陀螺



$I_C = I_B > I_A$

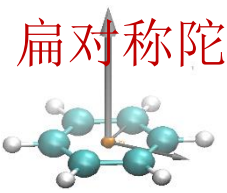
$F(J,K) = \tilde{B}J(J+1) + (\tilde{X} - \tilde{B})K^2$

$g_{JK} = 2J+1 \quad J = 0,\ 1,\ 2,\ \cdots$

$K = 0,\ \pm 1,\ \pm 2,\ \cdots,\ \pm J$

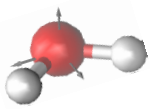
$\tilde{X} = \tilde{A}$(长对称) $\quad \tilde{X} = \tilde{C}$(扁对称)

扁对称陀螺



$I_C > I_B = I_A$

不对称陀螺



$I_C \ne I_B \ne I_A$

对称陀螺转动光谱的选择规则

$\Delta J = 0, \pm 1 \quad \Delta K = 0 \quad \text{for } K \ne 0$

$\Delta J = \quad \pm 1 \quad \Delta K = 0 \quad \text{for } K = 0$

吸收光谱 $\tilde{\nu} = 2\tilde{B}(J+1) - 2\tilde{D}_{JK}K^2(J+1)$

$-4\tilde{D}_J(J+1)^3$ 包含K对应的高分辨谱线

13.9 多原子分子的振动由简正模表示

简正坐标/简正模

多维谐振子:

$$\hat{H}_{vib}=\sum_{j=1}^{N_{vib}}\hat{H}_{vib,j}=\sum_{j=1}^{N_{vib}}\left(-\frac{\hbar^2}{2\mu_j}\frac{d^2}{dQ_j^2}+\frac{1}{2}F_jQ_j^2\right)$$

$$\psi_{\text{vib}}(Q_1,\cdots,Q_{N\text{vib}})=\prod_{j=1}^{N_{\text{vib}}}\psi_{\text{vib,j}}(Q_j)$$

$$E_{\text{vib}}=\sum_{j=1}^{N_{\text{vib}}}h\nu_j\left(\upsilon_j+\frac{1}{2}\right)\quad \text{each } \upsilon'=0,\ 1,\ \cdots$$

选择规则

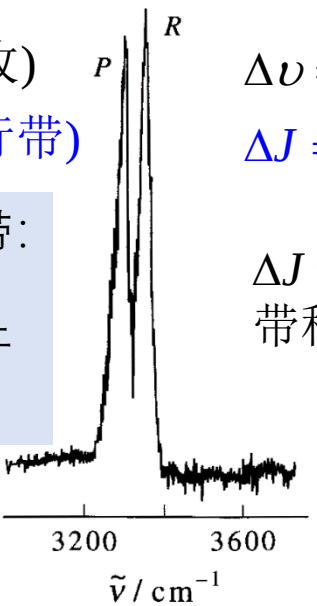
偶极矩发生变化的正则模具有红外活性

多原子线性分子的选择规则:

$\Delta\upsilon=+1$(吸收)

$\Delta J=\pm1$(平行带)

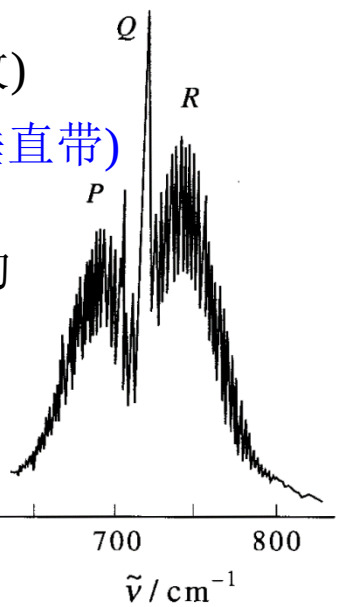
平行/垂直带:
偶极矩振动
平行/垂直于
分子轴



$\Delta\upsilon=+1$(吸收)

$\Delta J=0,\pm1$ (垂直带)

$\Delta J=0$对应的
带称为Q支



13.10 简正坐标属于分子点群的不可约表示

判断简正坐标的不可约表示

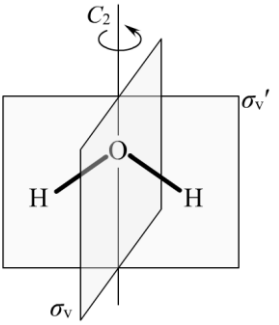
仅需考虑对称操作下未移动的原子，每个未移动的原子对3N维表示的特征标贡献为：

$\hat{E}$	3
$\hat{\sigma}$	1
$\hat{i}$	−3
$\hat{C}_2$	−1
$\hat{C}_3, \hat{C}_3^2$	0
$\hat{C}_4, \hat{C}_4^3$	1
$\hat{C}_6, \hat{C}_6^5$	2
$\hat{S}_2$	−3
$\hat{S}_3, \hat{S}_3^2$	−2
$\hat{S}_4, \hat{S}_4^3$	−1
$\hat{S}_6, \hat{S}_6^5$	0

对得到3N维可约表示利用群论约化分解，根据群的特征标表，找到平动和转动对应的不可约表示（x, y, z, R_x, R_y, R_z），剩余的即为振动对应的不可约表示。

以水分子为例：

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
Γ_{3N}	9	−1	1	3



$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$$

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	R_z
B_1	1	−1	1	−1	x, R_y
B_2	1	−1	−1	1	y, R_x

平动：A_1, B_1, B_2

转动：A_2, B_1, B_2

振动：

$$\Gamma_{vib} = 2A_1 + B_2$$

13.11 选择规则可通过含时微扰理论得到

$$\hat{H}^{(1)} = -\boldsymbol{\mu}\mathbf{E} = -\boldsymbol{\mu}\mathbf{E}_0 \cos 2\pi\nu t$$

电场处于z方向

$$= -\mu_z \mathrm{E}_{0z} \cos 2\pi\nu t = \frac{-\mu_z \mathrm{E}_{0z}}{2}(e^{i2\pi\nu t} + e^{-i2\pi\nu t})$$

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad \hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \qquad \hat{H}^{(0)}\psi = E_n\psi$$

仅考虑两态系统

$$\Psi(t) = a_1(t)\Psi_1(t) + a_2(t)\Psi_2(t) \qquad \Psi_k(t) = \psi_k e^{-iE_k t/\hbar}$$

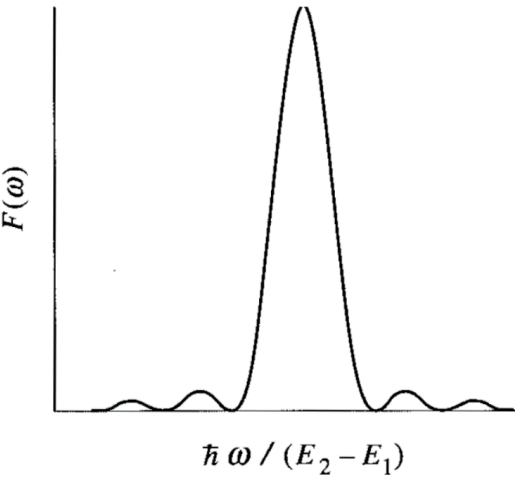
$$i\hbar\frac{da_2}{dt} = \exp\left[\frac{-i(E_1 - E_2)t}{\hbar}\right]\int \psi_2^* \hat{H}^{(1)}\psi_1 d\tau$$

$$\frac{da_2}{dt} \propto (\mu_z)_{12}\,\mathrm{E}_{0z}\left\{\exp\left[\frac{i(\Delta E + h\nu)t}{\hbar}\right] + \exp\left[\frac{i(\Delta E - h\nu)t}{\hbar}\right]\right\}$$

$$\Delta E = E_2 - E_1 \qquad (\mu_z)_{12} = \int \psi_2^* \mu_z \psi_1 d\tau$$ 跃迁偶极矩须非零

$$a_2^*(t)a_2(t) \propto F(\omega)$$

$$= \frac{\sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2}$$



态间跃迁，吸收/发射光子的能量等于能级差

$$h\nu = \hbar\omega \approx E_2 - E_1$$

13.12-13 刚性转子和谐振子的选择规则

刚性转子的跃迁偶极矩:

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi}\int_0^{\pi} Y_{J'}^{M'}(\theta,\phi)^* \mu_z Y_J^M(\theta,\phi)\sin\theta d\theta d\phi$$

$$= \mu N_{JM} N_{J'M'} \int_0^{2\pi} d\phi e^{i(M-M')\phi} \int_{-1}^{1} P_{J'}^{|M'|}(x) x P_J^{|M|}(x) dx$$

$$\Downarrow \quad M = M'$$

$$= \frac{2\pi\mu N_{JM} N_{J'M}}{2J+1} \int_{-1}^{1} dx P_{J'}^{|M|}(x)$$

$$\left[(J-|M|+1)P_{J+1}^{|M|}(x) + (J+|M|)P_{J-1}^{|M|}(x)\right]$$

选择规则: 永久偶极矩, $\Delta J = \pm 1$, $\Delta M = 0$

谐振子的跃迁偶极矩:

$$(\mu_z)_{\upsilon,\upsilon'}$$

$$= \int_{-\infty}^{\infty} N_\upsilon N_{\upsilon'} H_{\upsilon'}(\alpha^{1/2}q) e^{-\alpha q^2/2} \mu_z(q) H_\upsilon(\alpha^{1/2}q) e^{-\alpha q^2/2} dq$$

$$\Downarrow \quad \mu_z(q) = \mu_0 + \left(d\mu/dq\right)_0 q + \cdots$$

$$= \frac{N_\upsilon N_{\upsilon'}}{\alpha}\left(\frac{d\mu}{dq}\right)_0 \int_{-\infty}^{\infty} H_{\upsilon'}(\xi)\left[\upsilon H_{\upsilon-1}(\xi) + \tfrac{1}{2} H_{\upsilon+1}(\xi)\right] e^{-\xi^2} d\xi$$

选择规则: 偶极矩须变化, $\Delta\upsilon = \pm 1$

13.14 群论可以判断简正模的红外活性

简正模下的跃迁偶极矩

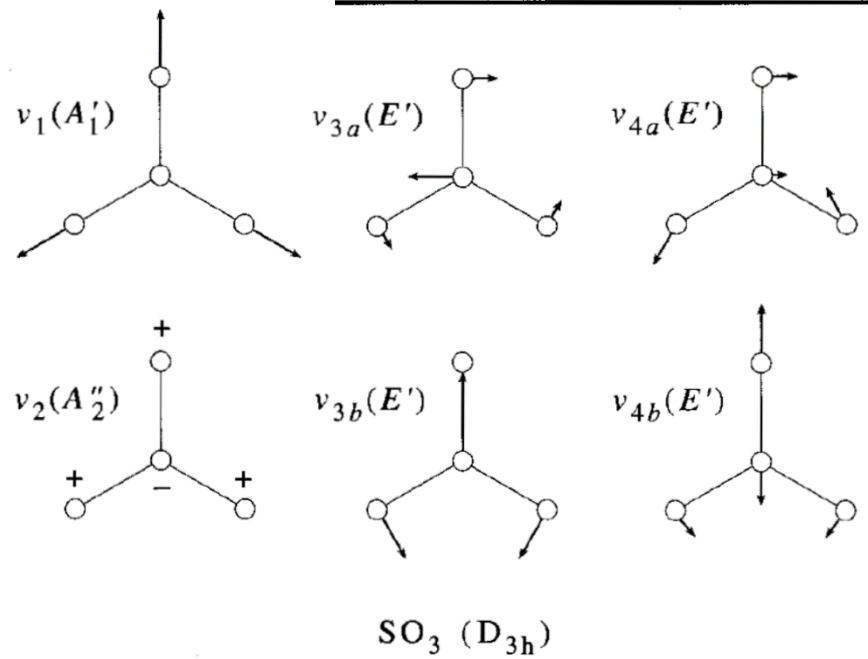
$$I_{0\to1} \propto \int \psi_0(Q_1,\cdots,Q_{N_{\text{vib}}}) \begin{Bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{Bmatrix} \psi_1(Q_1,\cdots,Q_{N_{vib}}) dQ_1,\cdots,Q_{N_{\text{vib}}}$$

$$\hat{R} I_{0\to1} = \chi_{\mu_x}(\hat{R})\chi_{Q_j}(\hat{R}) I_{0\to1} = I_{0\to1}$$

仅当Q_j与$x, y,$ 或z属于相同不可约表示时$I_{0\to1}$才非零.

例: 判断SO_3分子正则模的红外活性

$\mathbf{D}_{3h}$	$\hat{E}$	$2\hat{C}_3$	$3\hat{C}_2$	$\hat{\sigma}_h$	$2\hat{S}_3$	$3\hat{\sigma}_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	−1	1	1	−1	R_z
E'	2	−1	0	2	−1	0	(x, y)
A_1''	1	1	1	−1	−1	−1	
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	(R_x, R_y)



SO_3 (D_{3h})

这六个振动模中仅$\nu_1(A_1')$红外非活性，其余都是红外活性