振动光谱1. 双原子分子

- 双原子分子振动能级
- 振动光谱选择定则
- 振动非谐性
- 振-转跃迁

朱海明
hmzhu@zju.edu.cn
13429129488
海纳苑C419

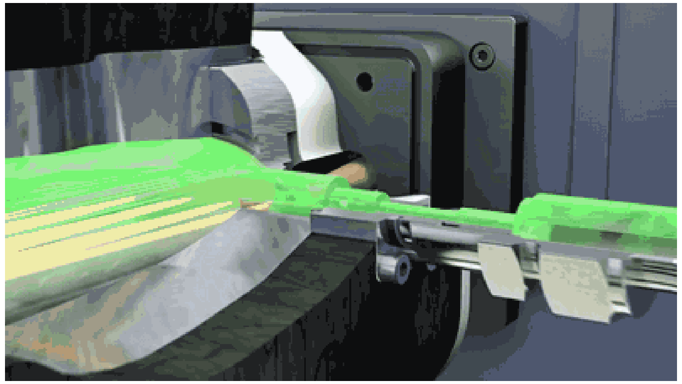
振动光谱

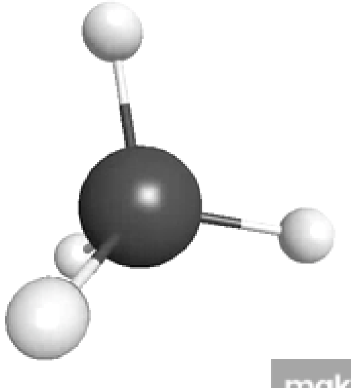
分子运动： 振动

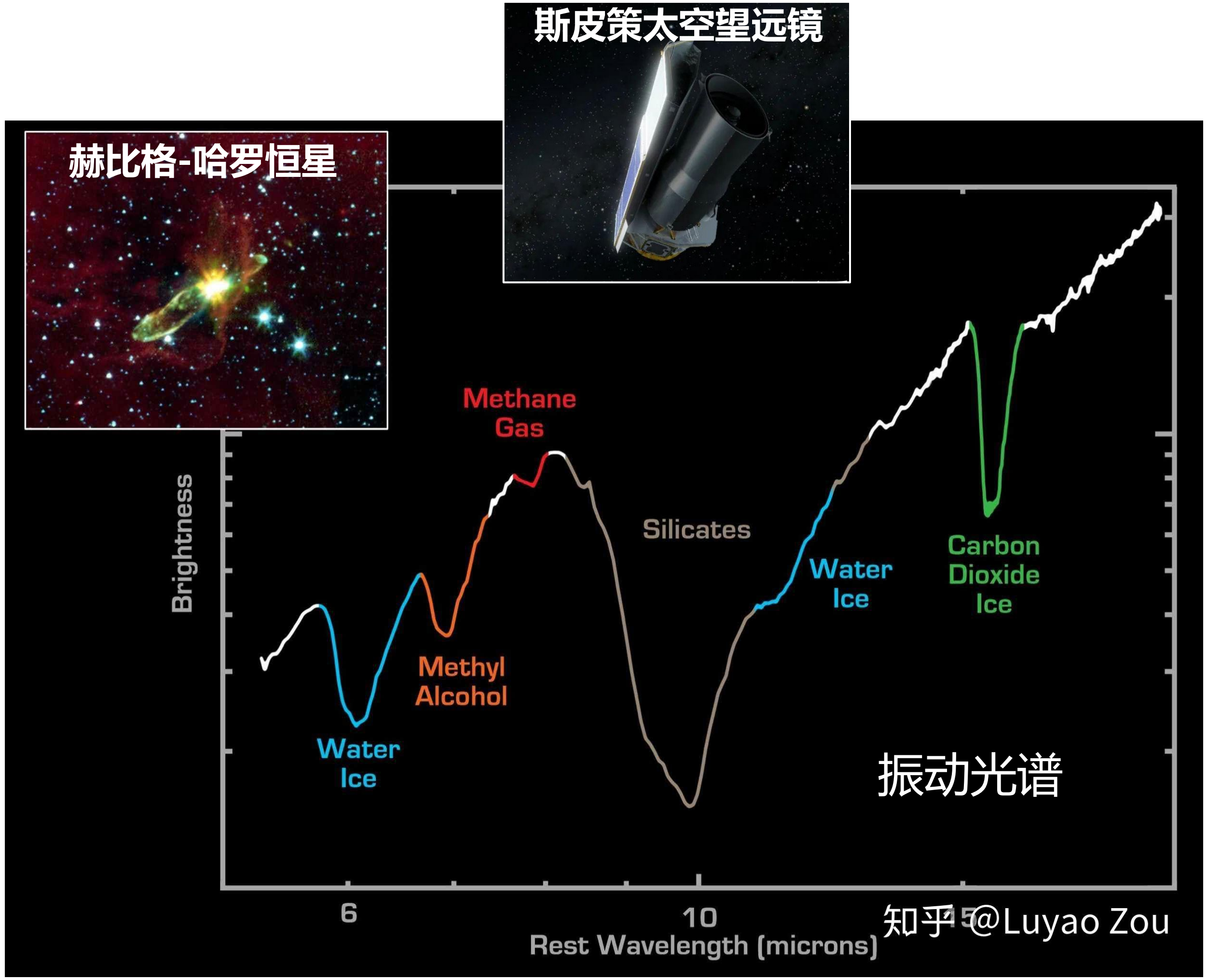
波段： 中红外，1-30 um

样品： 固体，液体，气体

转动光谱的不足：1. 必须为气态；2. 极性分子



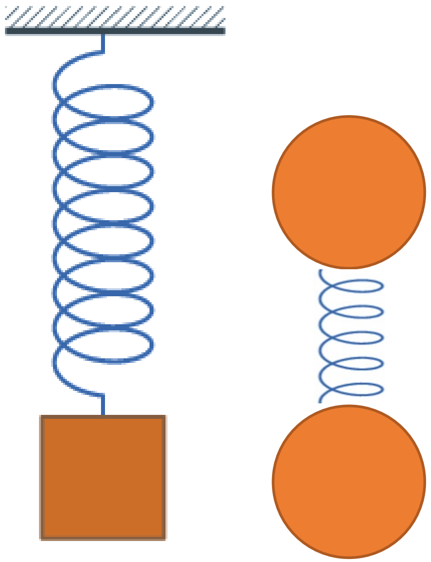




有机化合物分析，生物大分子研究，环境气体检测，食品分析，物质鉴定。。。

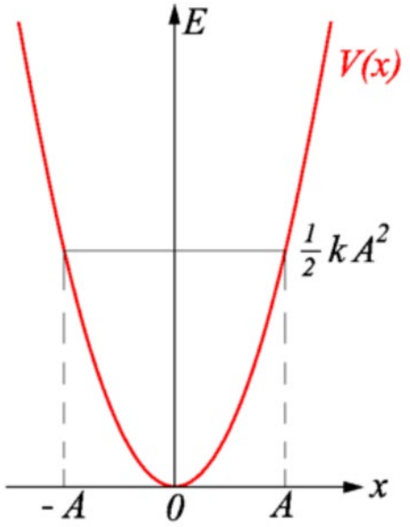
1. 双原子分子振动能级

简谐振动与胡克定理



胡克定理： $F = -k(r - r_e) = -kx$ 弹簧力常数 k

振动势能： $V(x) = \frac{1}{2}kx^2$

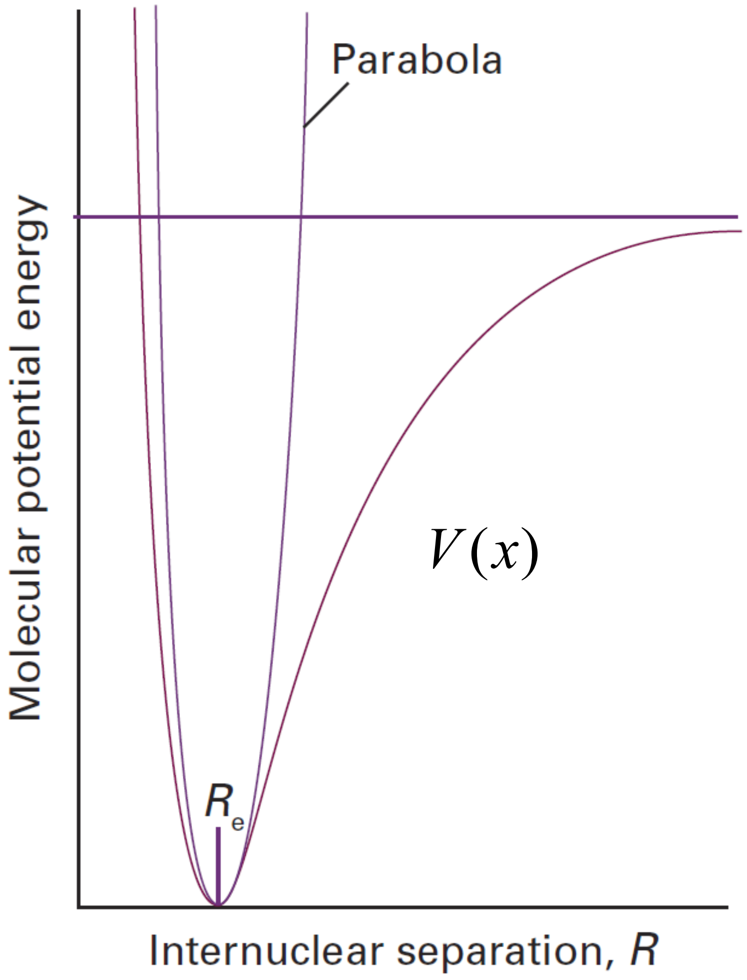


运动方程： $F = \mu \frac{d^2x}{dt^2} = -kx$ 约化质量 $\mu = \frac{m_1 m_2}{m_1 + m_2}$

简谐振子
Harmonic Oscillator

$x = A\sin(\omega t + \varphi)$ 振动频率 $\omega = \sqrt{k/\mu}$

1. 双原子分子振动能级



双原子势能曲线

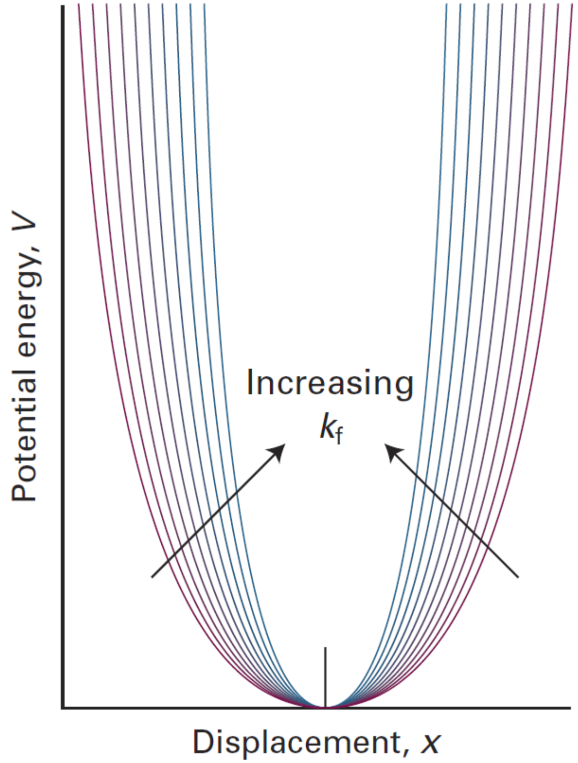
势能在最低点x=0的泰勒展开

$$V(x)=V(0)+\left(\frac{dV}{dx}\right)_0 x+\boxed{\frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2}+\ldots \qquad x=R-R_e$$

$V(0)\rightarrow 0$, $\left(\frac{dV}{dx}\right)_0\rightarrow 0$

谐振子近似

$$V(x)\approx\frac{1}{2}\boxed{\left(\frac{d^2V}{dx^2}\right)_0}x^2=\frac{1}{2}kx^2$$



量子简谐振子
Quantum Harmonic Oscillator

1. 双原子分子振动能级

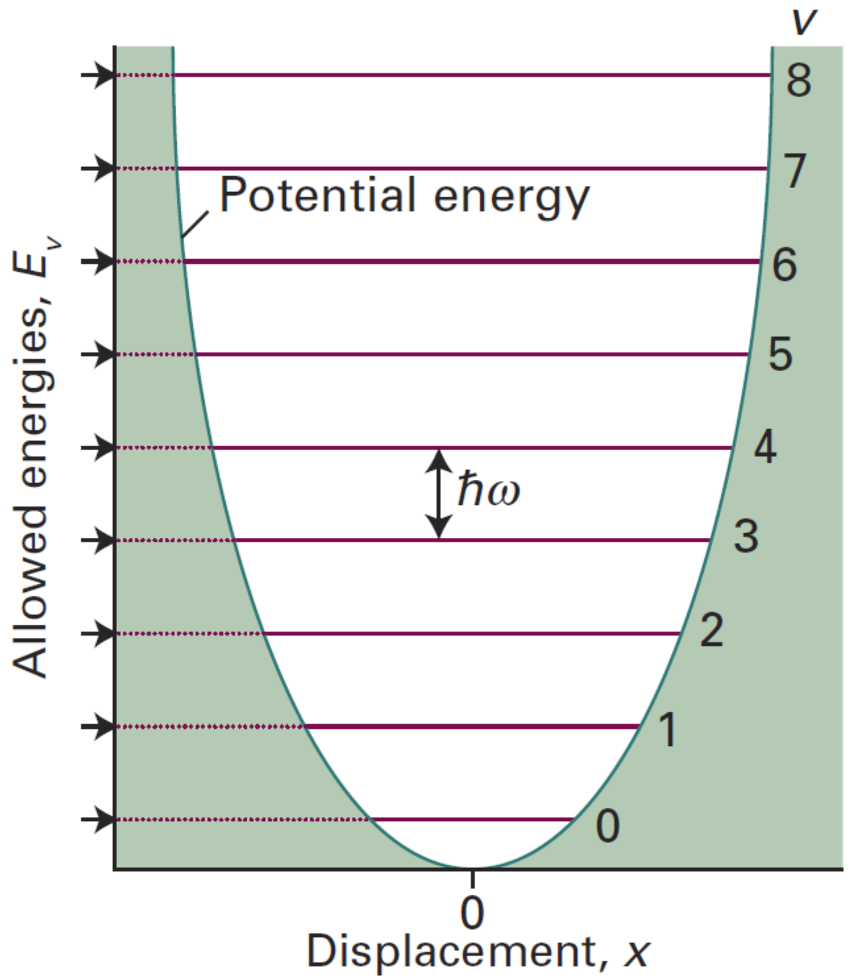
薛定谔方程（谐振势能下两个原子间的相对运动）

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}+\frac{1}{2}kx^2\right)\Psi = E\Psi \qquad \mu=\frac{m_1 m_2}{m_1+m_2}$$

振动能级： $E_v=(v+\frac{1}{2})\hbar\omega$ （单位J） $\omega=\sqrt{\frac{k}{\mu}}$

振动量子数 $v=0,\ 1,\ 2\ldots$

$$\tilde{G}_v=(v+\tfrac{1}{2})\tilde{\nu} \quad (\text{单位}cm^{-1}) \qquad \tilde{\nu}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$



- 振动零点能，在绝对零度也有振动（不确定原理）
- 振动能级等间隔

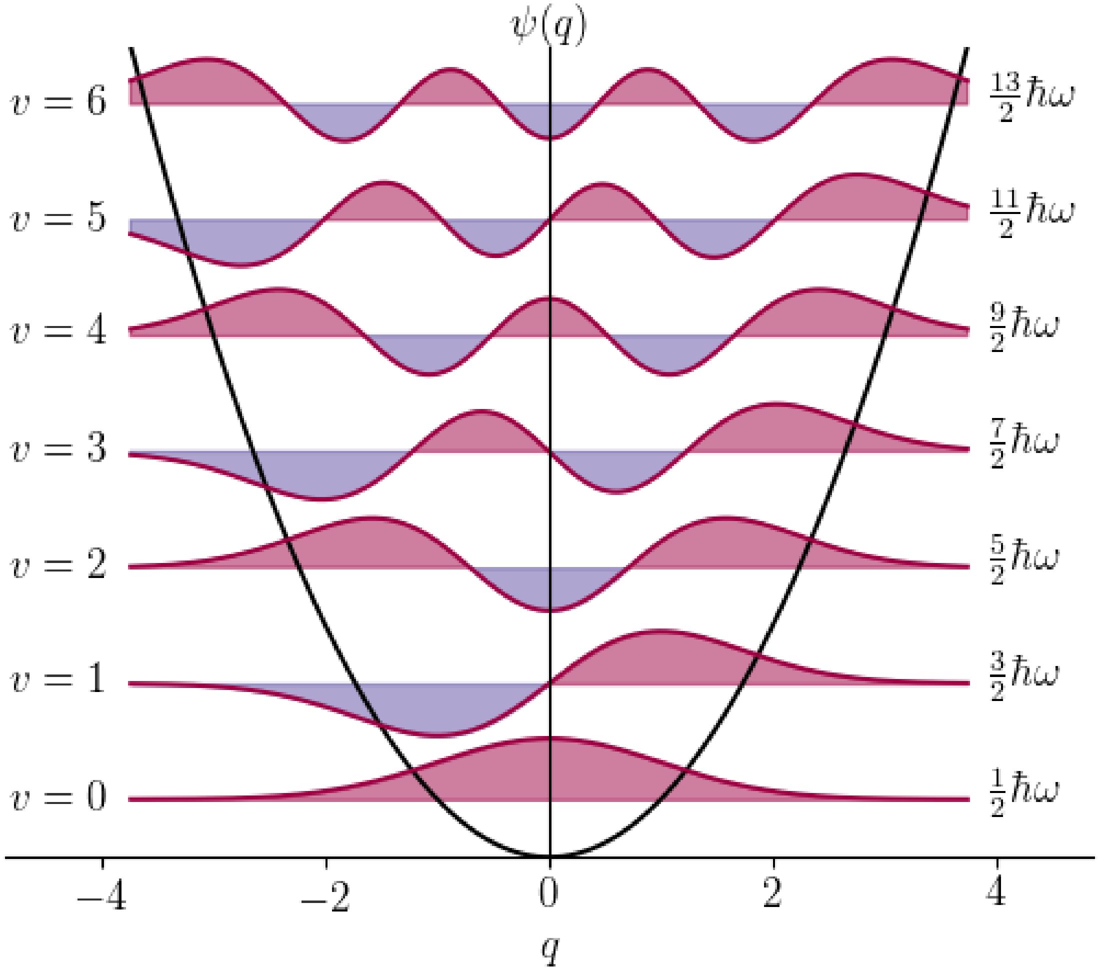
1. 双原子分子振动能级

波函数： $\psi_v(x) = N_v H_v(y) e^{-y^2/2}$

$$y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk_f}\right)^{1/4}$$

Table 8.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

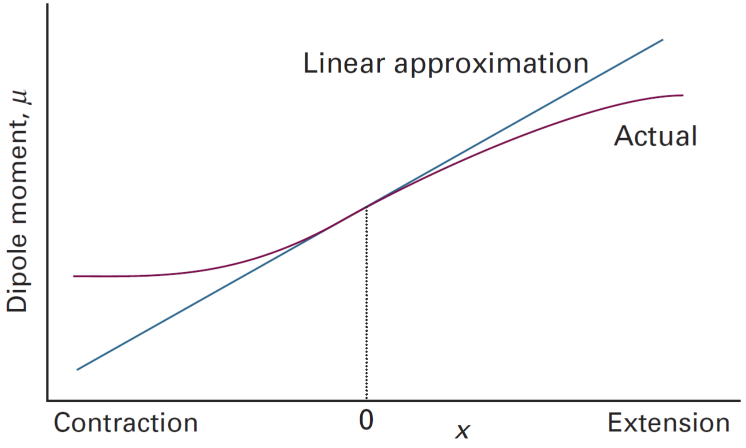


偶
奇
偶
奇
偶
奇
偶

2. 选择定则

振动能级跃迁偶极

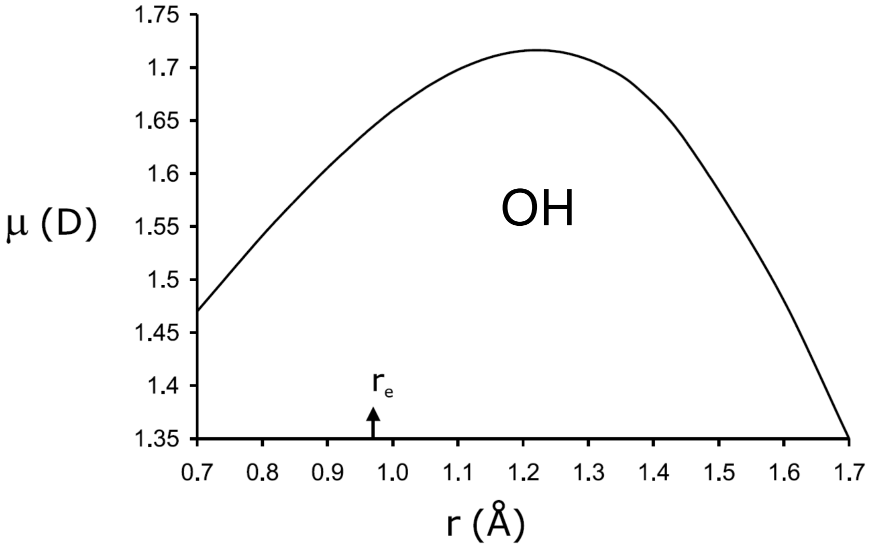
$$\mu_{if} = \left\langle \psi_v'(x) \middle| \vec{\mu}(x) \middle| \psi_v(x) \right\rangle$$



电偶极$\vec{\mu}$也是x的函数，在平衡位置0附近做泰勒展开

$$\mu(x) = \mu_{x=0} + \left(\frac{\partial \mu}{\partial x}\right)_0 x + \boxed{\frac{1}{2}\left(\frac{\partial^2 \mu}{\partial x^2}\right)_0 x^2 + \ldots}$$

忽略高阶项



认为电偶极矩在平衡位置附近是x的线性函数

$$\mu_{if} = \left\langle \psi_v'(x) \middle| \mu_0 + \left(\frac{\partial \mu}{\partial x}\right)_0 x \middle| \psi_v(x) \right\rangle$$

$$= \boxed{\left\langle \psi_v'(x) \middle| \mu_0 \middle| \psi_v(x) \right\rangle} + \boxed{\left(\frac{\partial \mu}{\partial x}\right)_0 \left\langle \psi_v'(x) \middle| x \middle| \psi_v(x) \right\rangle}$$

谐振近似下，振动波函数正交→0

必须≠0

2. 选择定则

$$\mu_{if} = \underbrace{\boxed{\left(\frac{\partial\mu}{\partial x}\right)_0}}_{①}\underbrace{\boxed{\langle\psi'(x)|x|\psi(x)\rangle}}_{②} \neq 0$$

①→ $\left(\frac{\partial\mu}{\partial x}\right)_0 \neq 0$

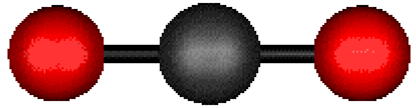
电偶极矩大小随振动发生改变

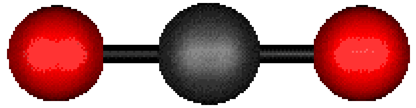
同核双原子分子： $\vec{\mu}_e = 0$

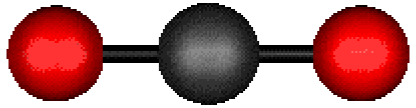
$d\vec{\mu}/dr = 0$

异核对称分子： $\vec{\mu}_e$可能 $= 0$

$d\vec{\mu}/dr$ 可能 $=\neq 0$

对称伸缩  **非红外活性**

非对称伸缩 

弯曲振动
xz和yz平面 

红外活性

2. 选择定则

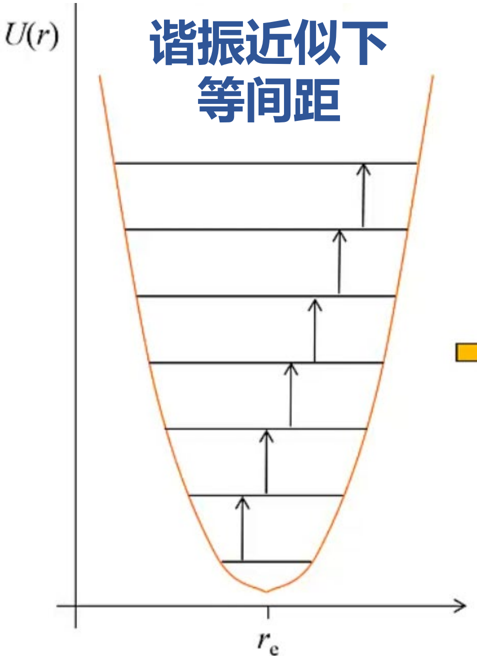
$$\mu_{if} = \boxed{\left(\frac{\partial \mu}{\partial x}\right)_0}\boxed{\left\langle \psi'(x) \middle| x \middle| \psi(x) \right\rangle} \neq 0$$

① ②

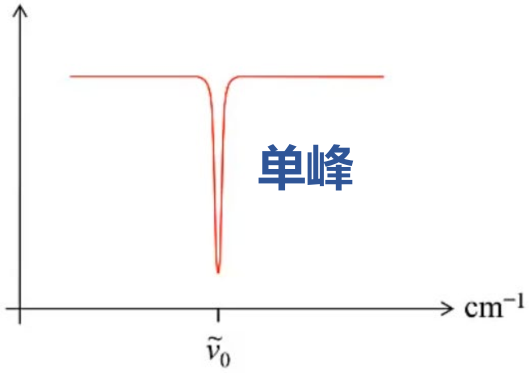
②→ $$\langle v'|x|v\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(\sqrt{v+1}\,\delta_{v',v+1} + \sqrt{v}\,\delta_{v',v-1}\right)$$

$$\Delta v = \pm 1$$

相邻能级跃迁



$$\boxed{\tilde{G}(v) = (v+1/2)\tilde{\nu}_0}$$

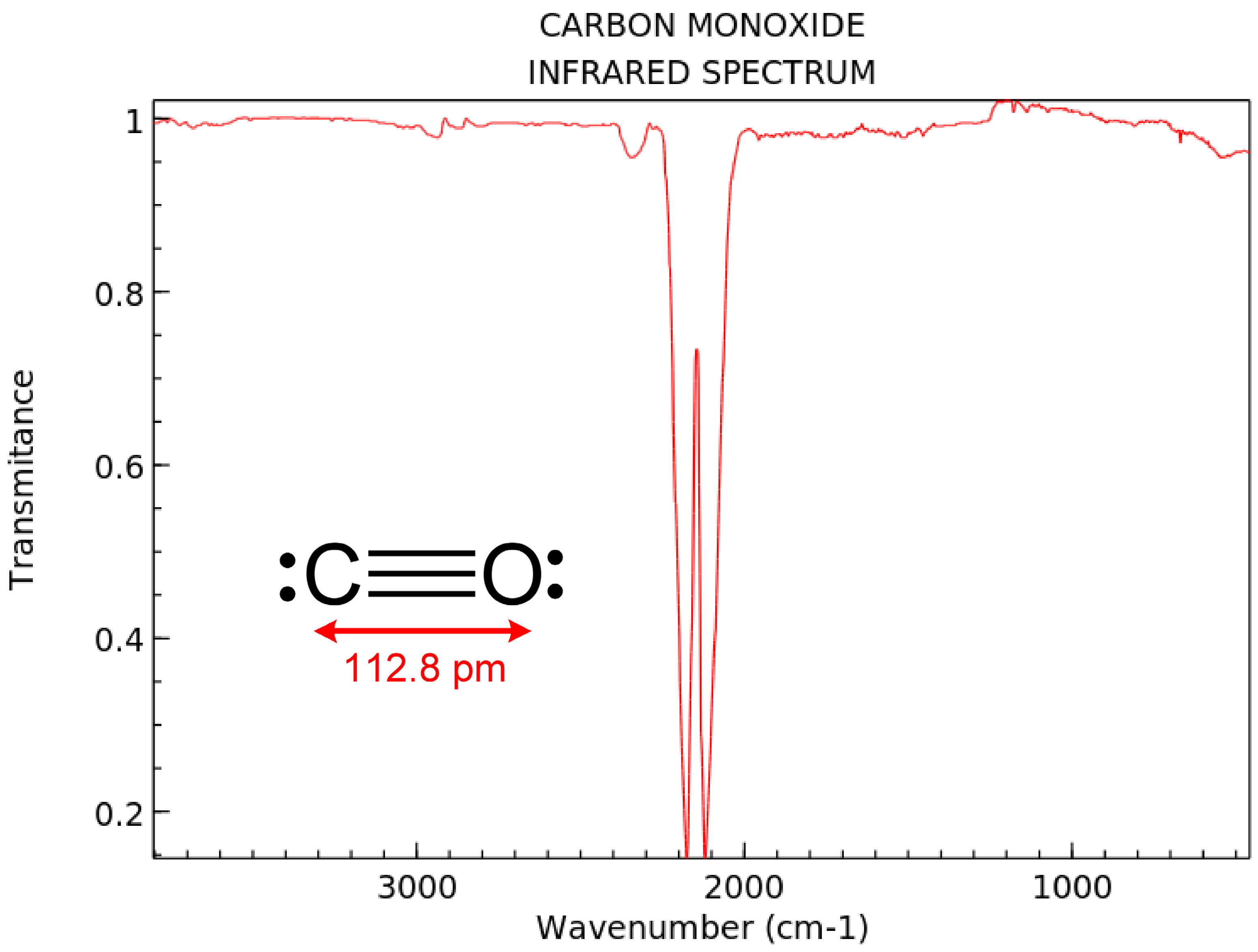


室温下，k_BT~200 cm^{-1}

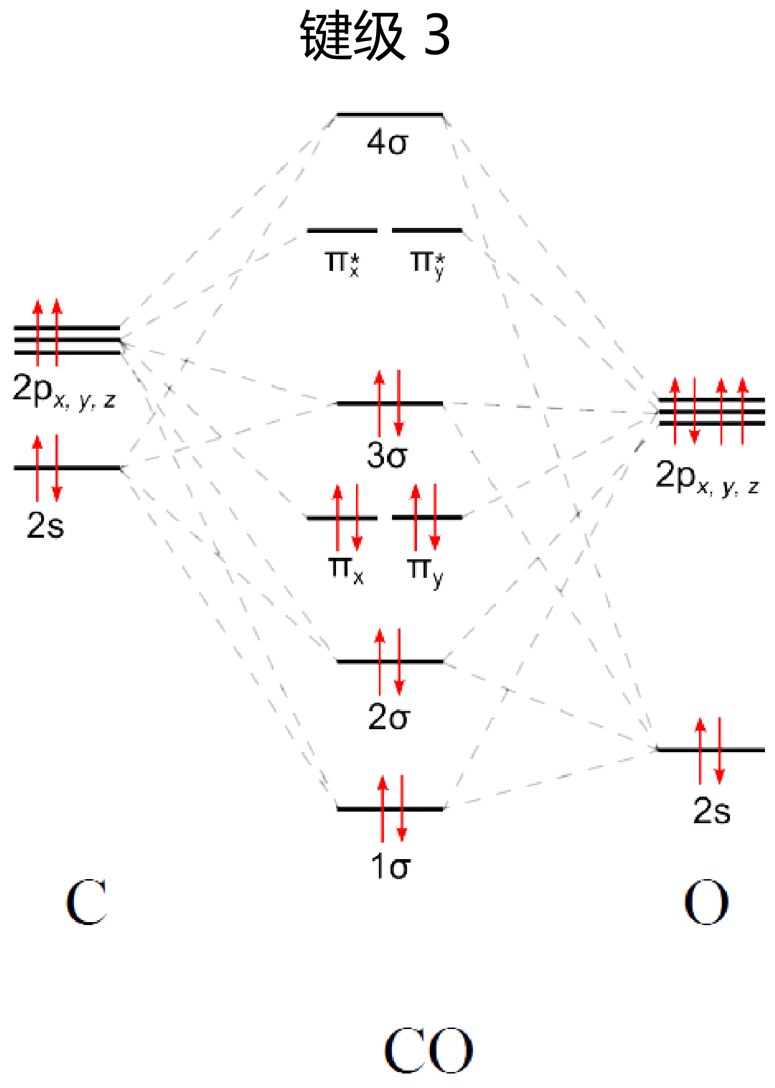
大部分分子都处于振动基态，v=0

主要的跃迁来自v=0→1，表现出单个跃迁谱线

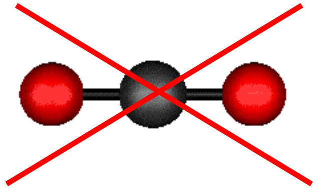
2. 选择定则

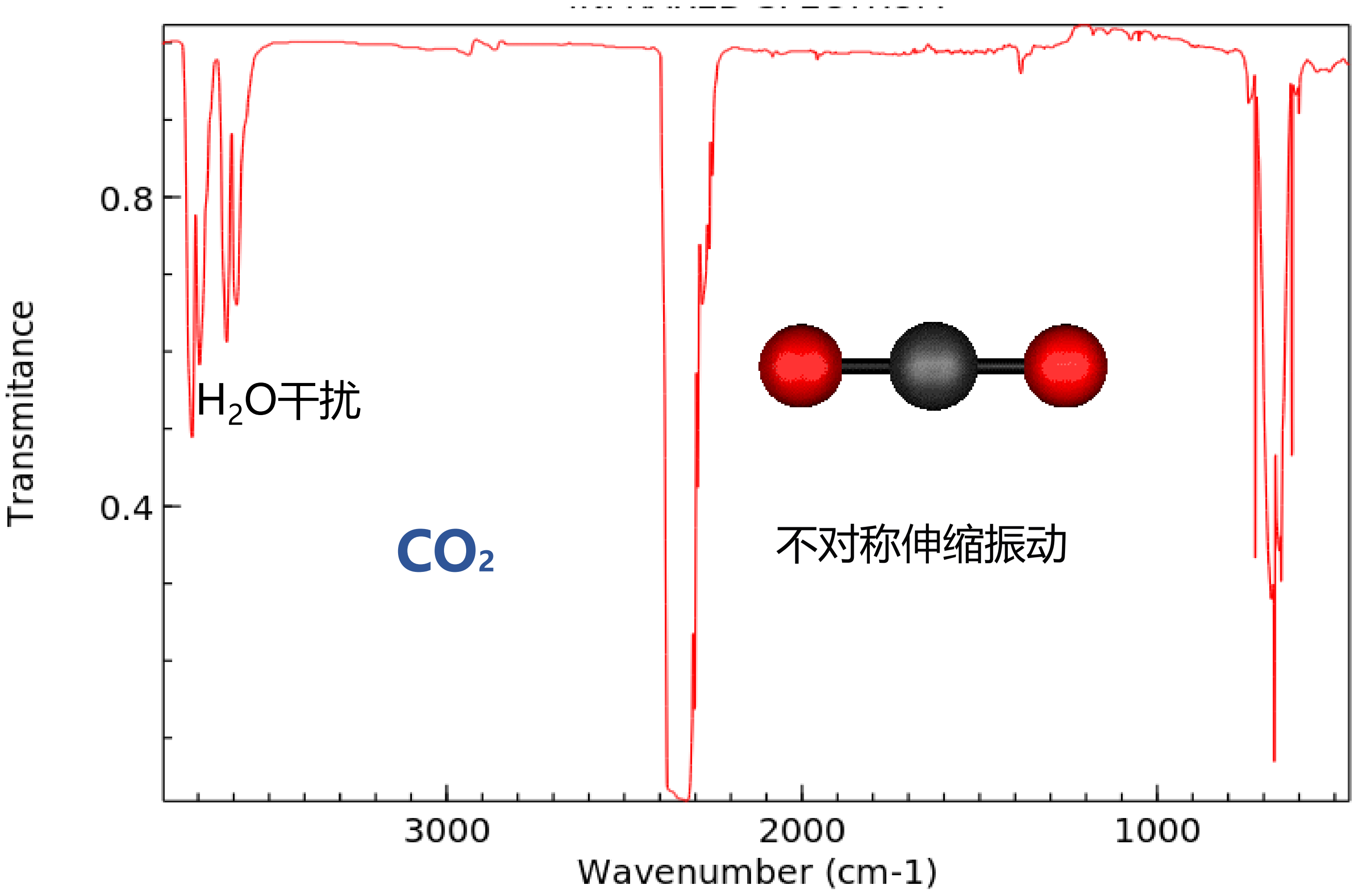


NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

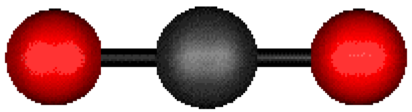


2. 选择定则



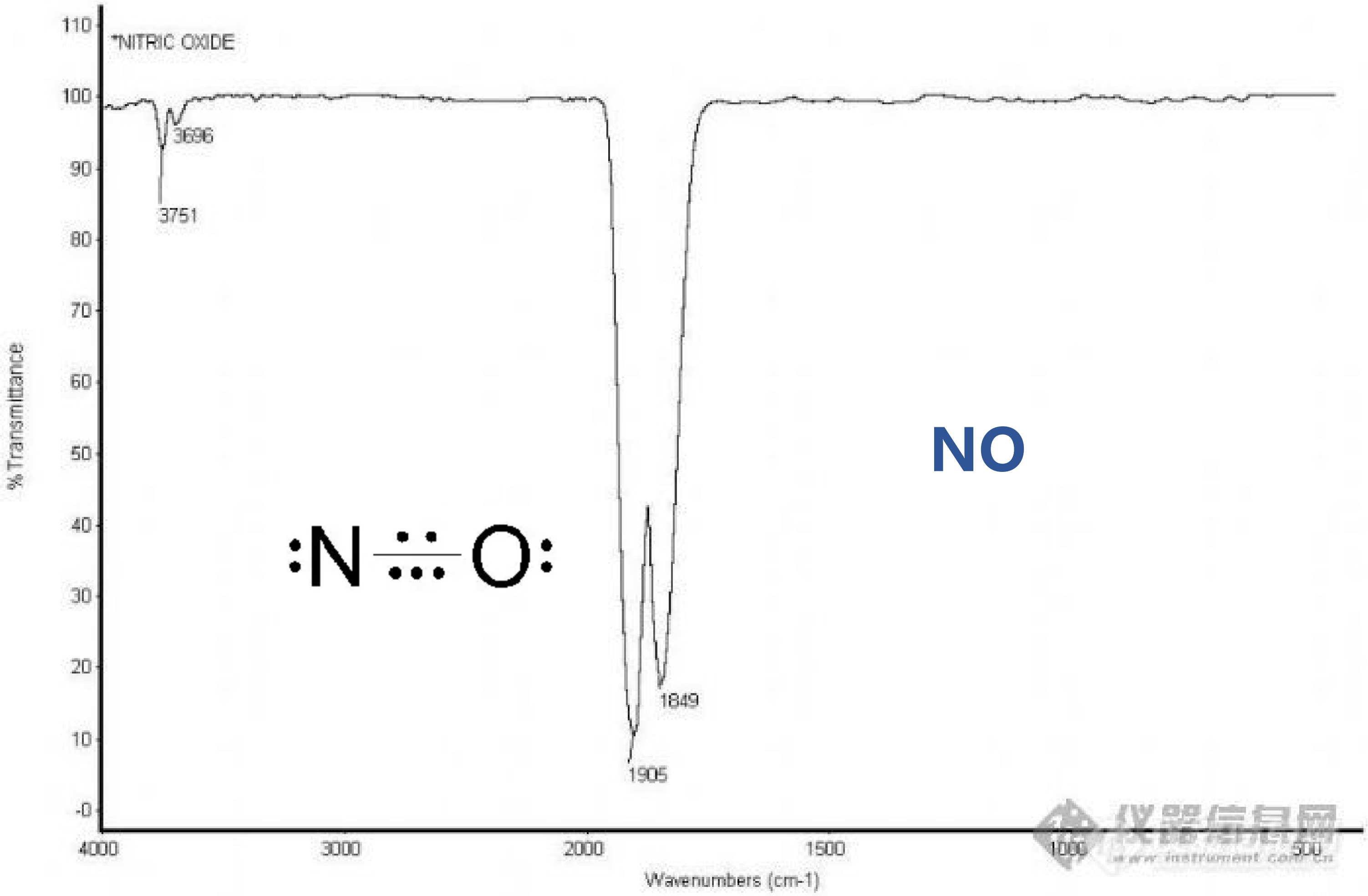


弯曲振动 (简并)



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

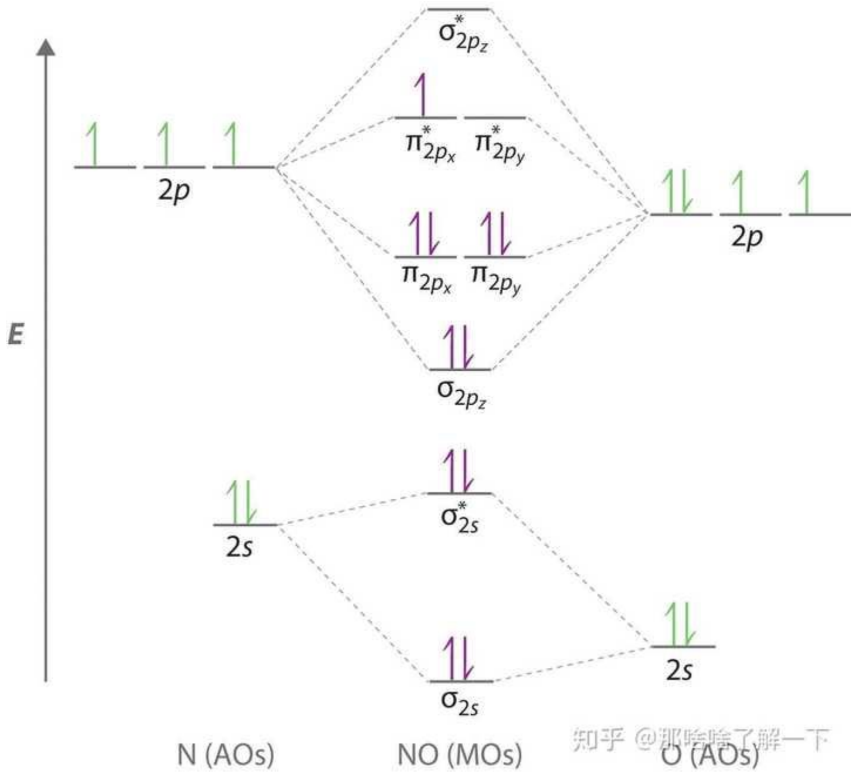
2. 选择定则



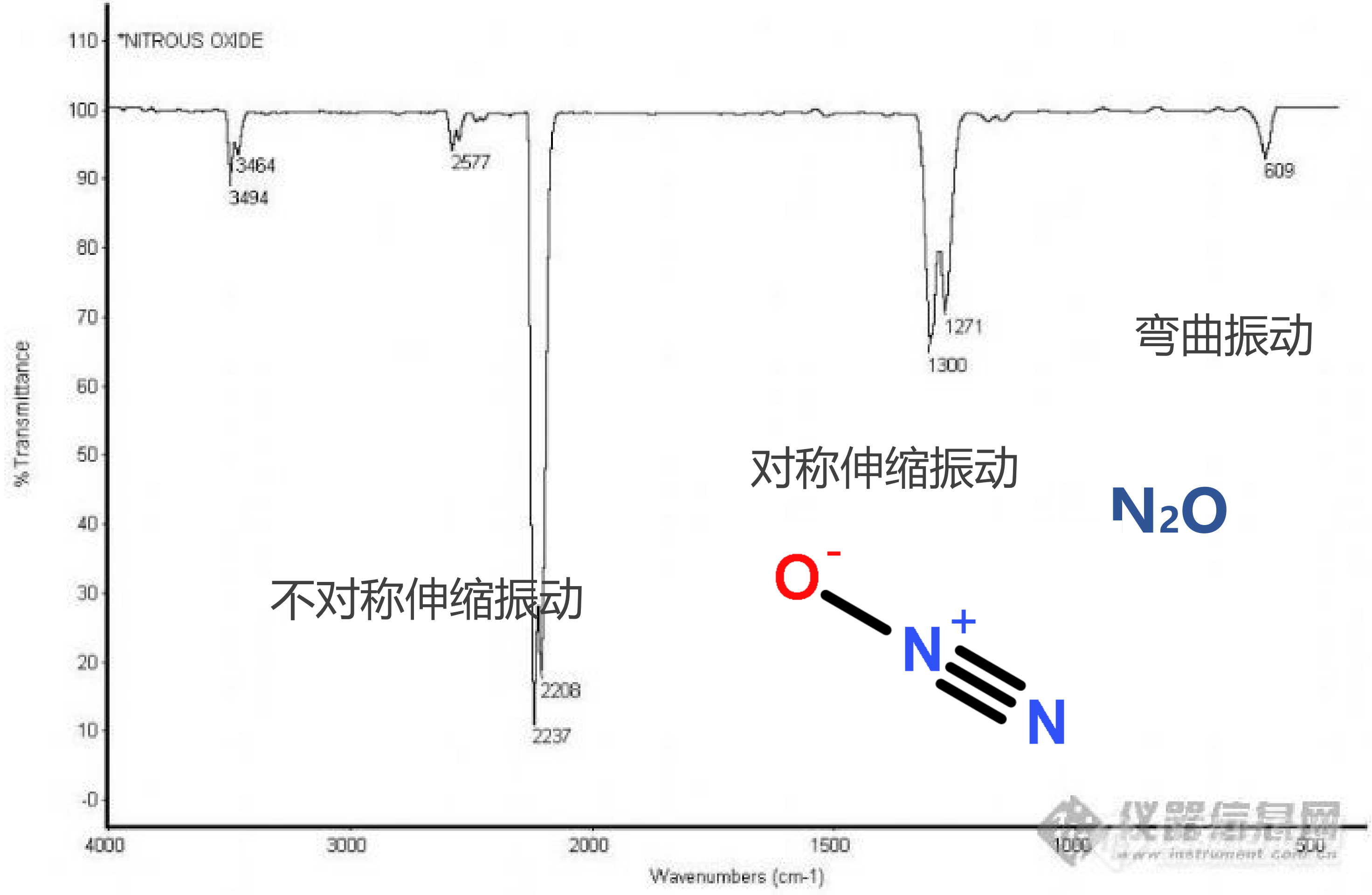
:N⋯O:

NO

键级 2.5



2. 选择定则

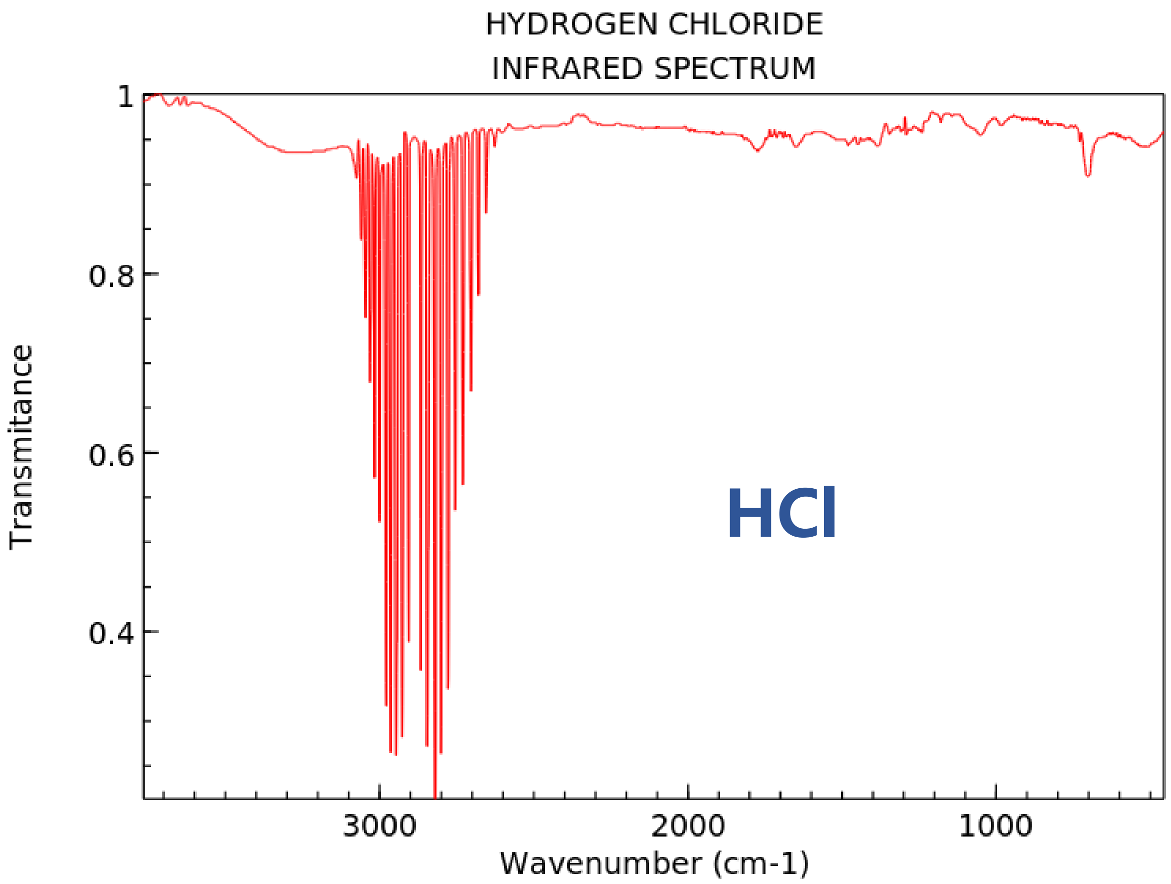


*NITROUS OXIDE
% Transmittance
Wavenumbers (cm-1)
3464
3494
2577
2208
2237
1271
1300
609
不对称伸缩振动
对称伸缩振动
弯曲振动
O-
N+
N
仪器信息网
www.instrument.com.cn

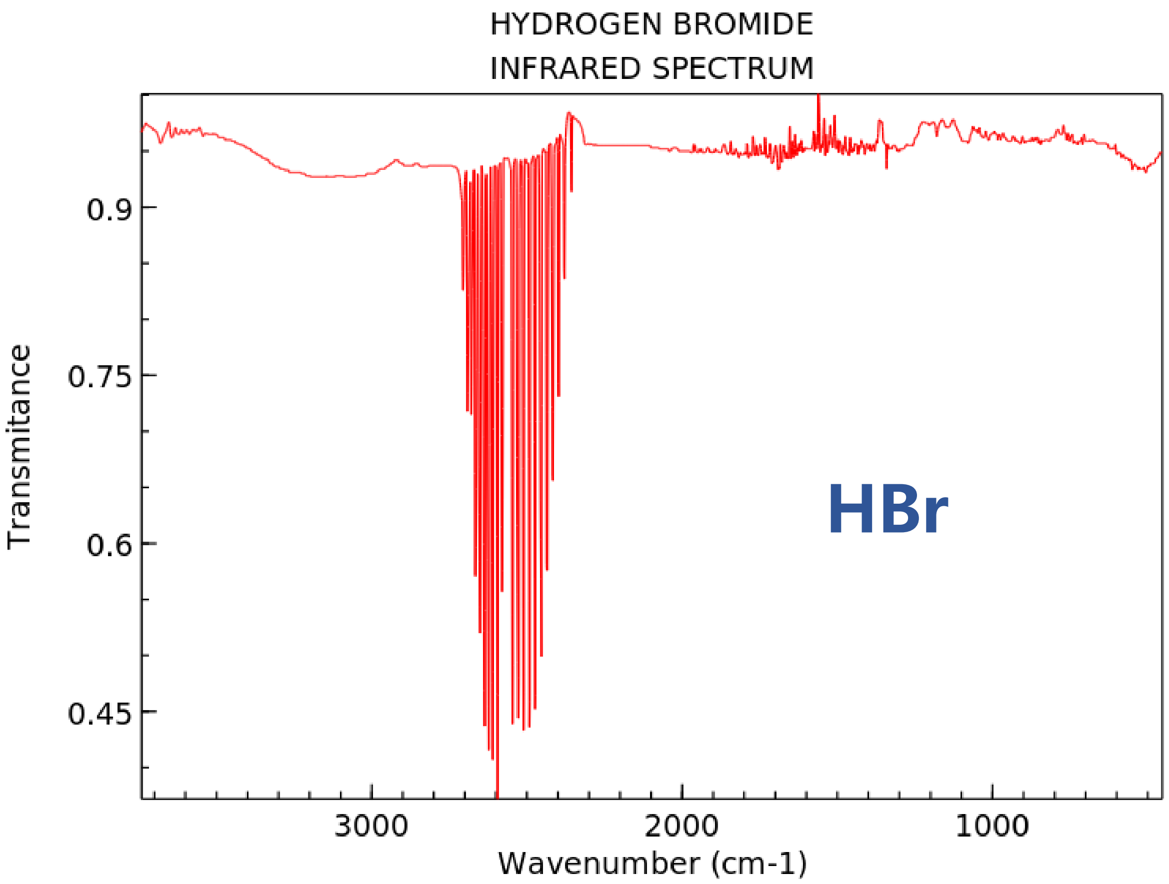
N_2O

“笑气”
致人上瘾、瘫痪、甚至死亡。

2. 选择定则



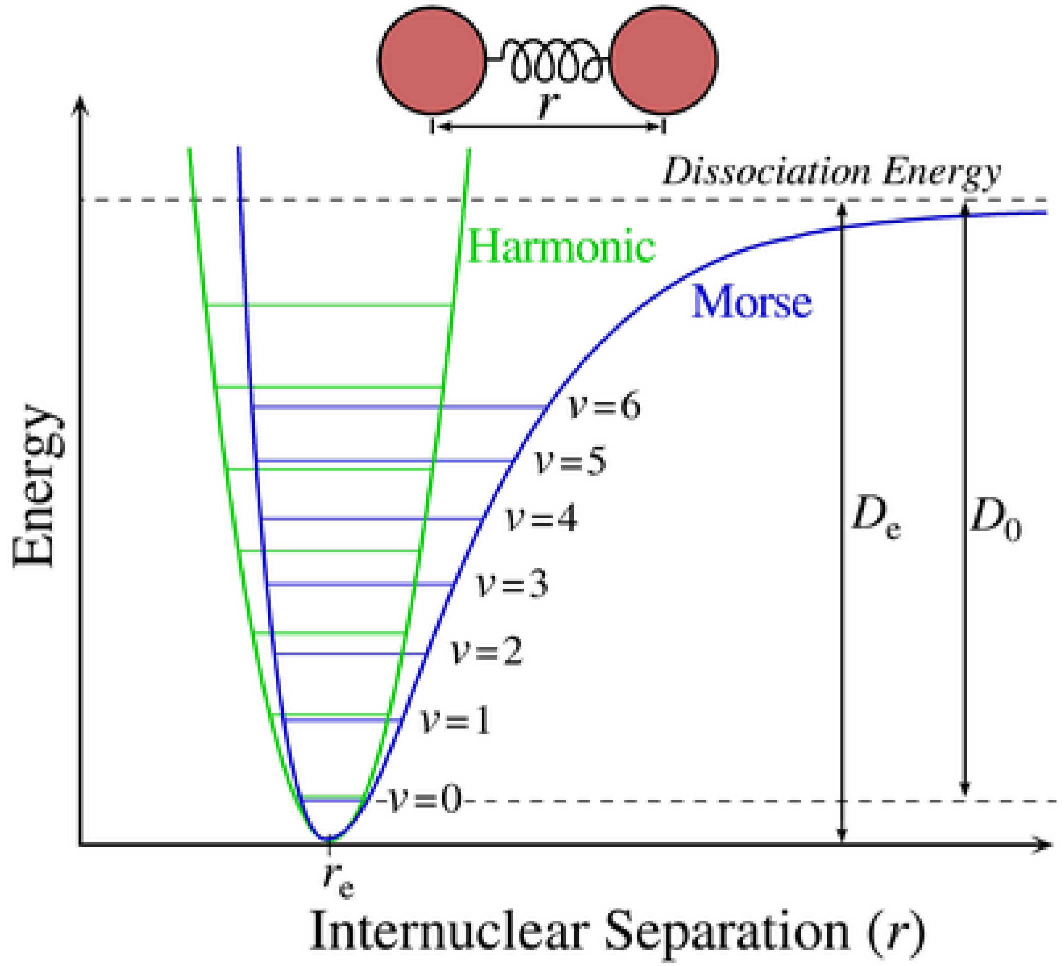
NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

3. 振动非谐性

摩尔斯（Morse）势：更接近真实势能曲线



只有在接近平衡位置的低能级振动满足简谐振子模型

$$V(q) = hcD_e(1-e^{-aq})^2 \qquad a = \left(\frac{k}{2hcD_e}\right)^{1/2}$$

D_e 势能曲线最小值对应的深度

求解薛定谔方程

非谐修正：在v大时产生影响

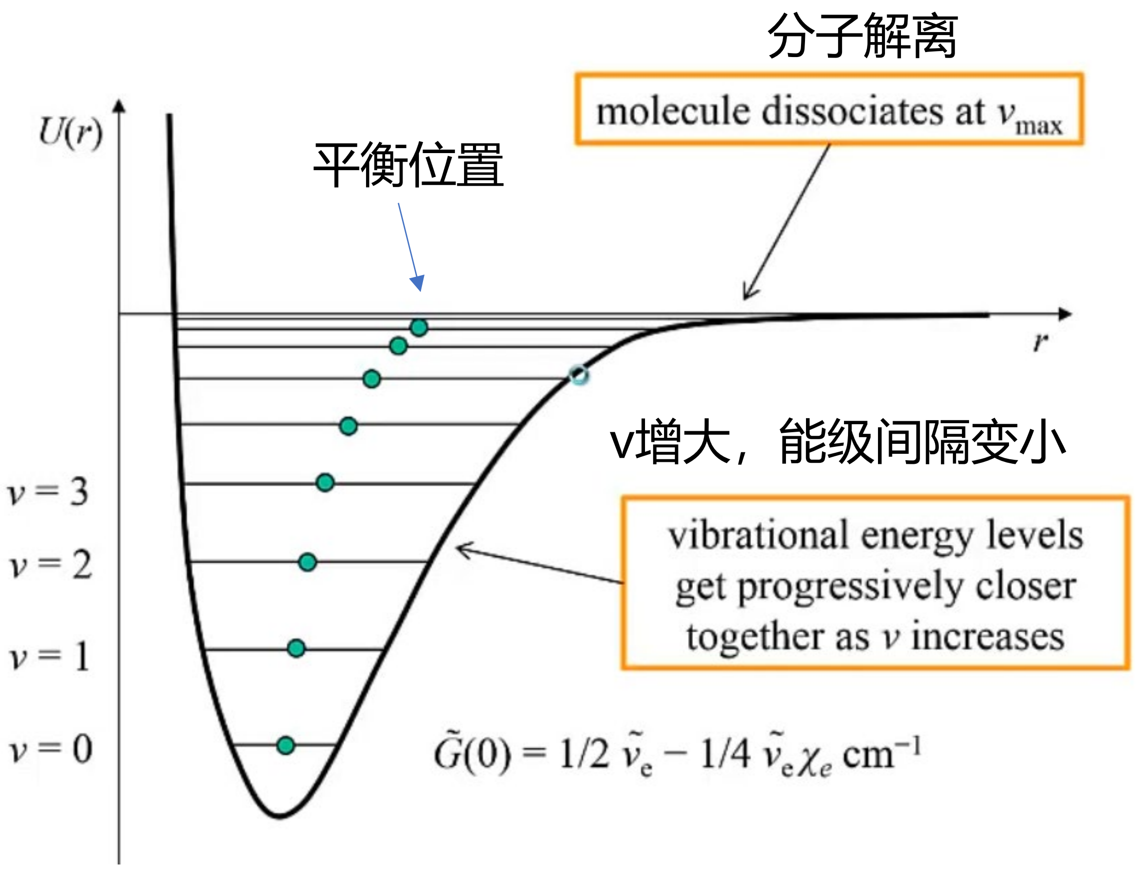
$$E_v = (v+\frac{1}{2})\hbar\omega_e \boxed{-(v+\frac{1}{2})^2\hbar\omega_e\chi_e} \quad [J]$$

$$\tilde{G}_v = (v+\tfrac{1}{2})\tilde{\nu}_e \boxed{-(v+\tfrac{1}{2})^2\tilde{\nu}_e\chi_e} \quad [\mathrm{cm}^{-1}]$$

非谐常数 $\chi_e = \dfrac{a^2\hbar}{2\mu\omega} = \dfrac{\tilde{\nu}}{4\tilde{D}_e}$

3. 振动非谐性

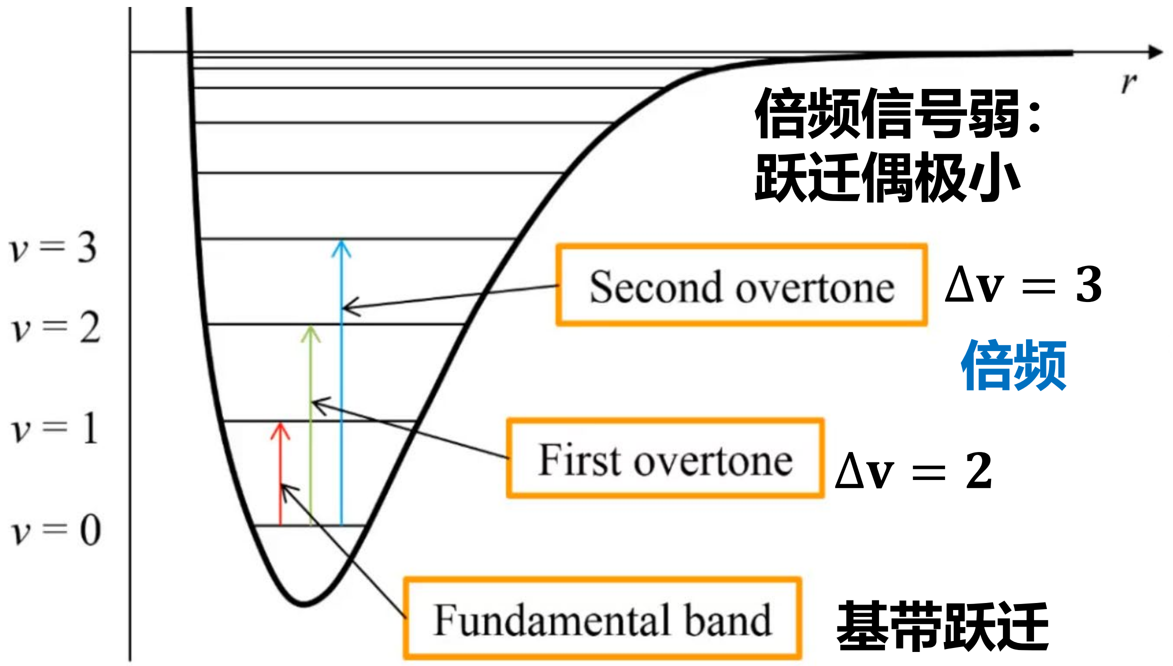
振动能级

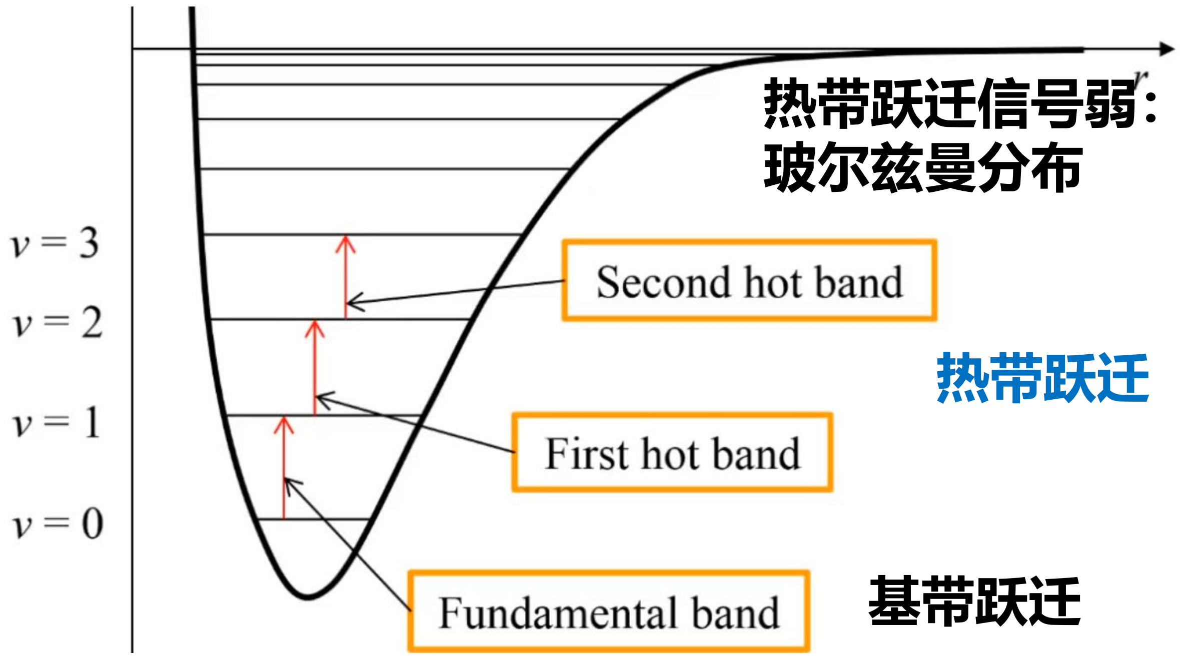


分子解离
molecule dissociates at v_{max}
$U(r)$
平衡位置
r
v增大，能级间隔变小
vibrational energy levels get progressively closer together as v increases
$v = 3$
$v = 2$
$v = 1$
$v = 0$
$\tilde{G}(0) = 1/2\ \tilde{\nu}_e - 1/4\ \tilde{\nu}_e \chi_e\ \mathrm{cm}^{-1}$

3. 振动非谐性

振动光谱跃迁





（怎么简单理解）

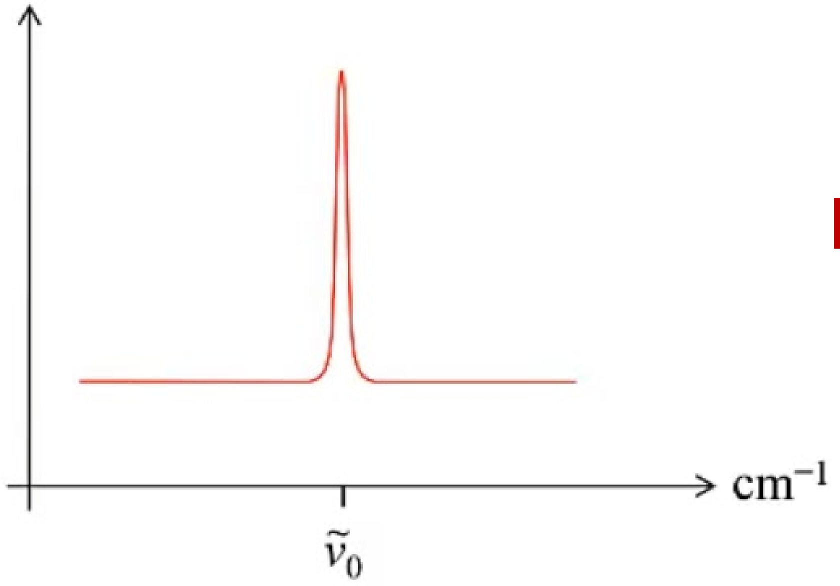
由于非谐性，跃迁定则可以不严格遵守$\Delta v = \pm 1$

$\Delta v = \pm 2, \pm 3 \ldots$ 可以，但信号弱很多（< 1/20）

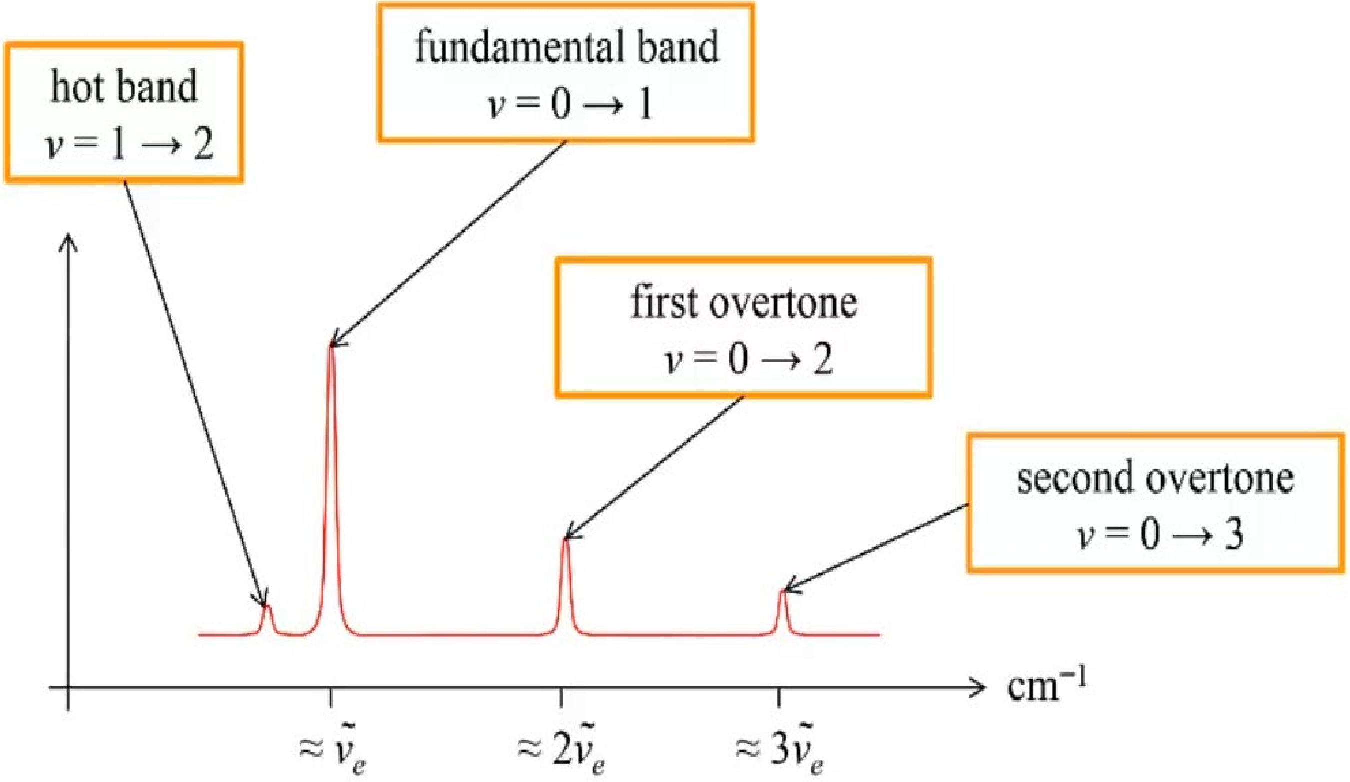
由于非谐性，热跃迁和基带跃迁谱线不再重合

3. 振动非谐性

谐振子模型



非谐



4. 双原子分子的振-转跃迁

刚性转子-谐振子

哈密顿量 $\hat{\mathcal{H}} = \hat{H}_{\text{vib}}(R) + \hat{H}_{\text{rot}}(\theta,\varphi)$

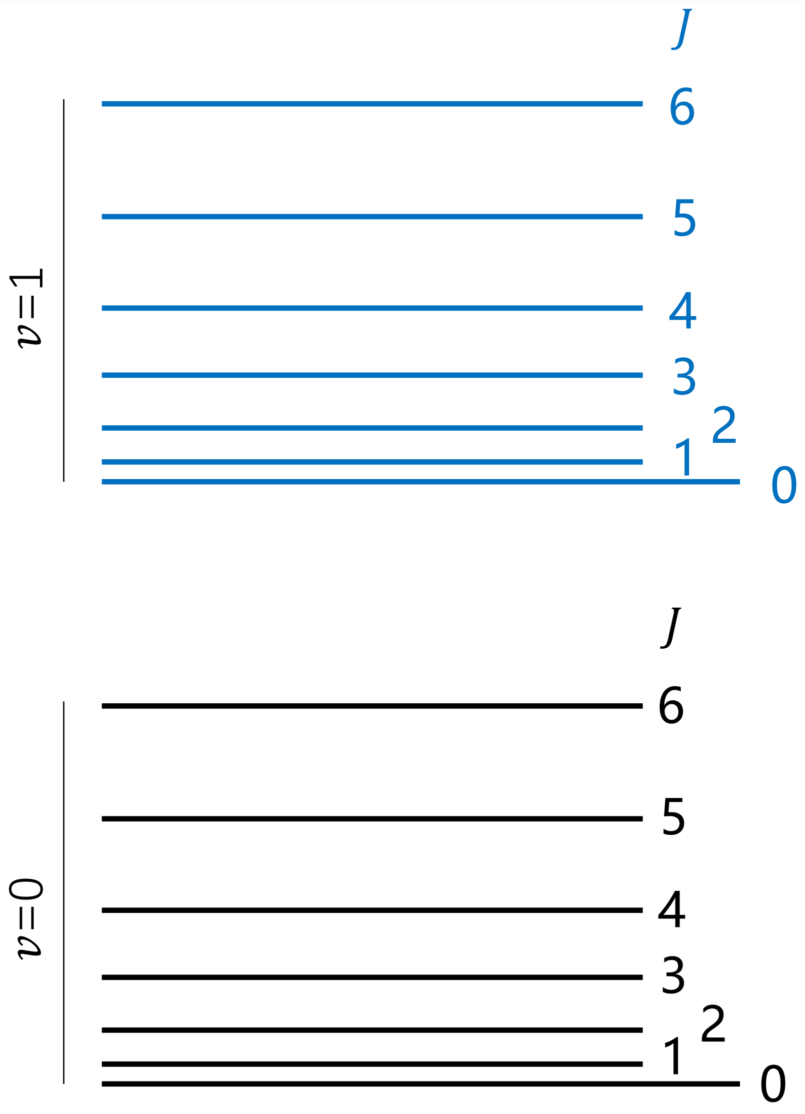
（忽略振动对转动的影响）

波函数 $\psi = \psi_{\text{vib}}(R)\psi_{\text{rot}}(\theta,\varphi)$

能量 $E_{vr} = (v+\frac{1}{2})\hbar\omega + hBJ(J+1)$ （J）

$$\tilde{S}_{\text{v},J} = \tilde{G}_{\text{v}} + \tilde{F}_J = \boxed{\left(v+\frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1)}$$ (cm^{-1})

（振动能级上叠加转动能级）



4. 双原子分子的振-转跃迁

跃迁选择定则

$$\left(\frac{\partial \mu}{\partial q}\right)_0 \neq 0 \qquad \Delta v = \pm 1 \qquad \Delta J = 0, \pm 1 \qquad \Delta M = 0, \pm 1$$

$\Delta J = 0$，非零角动量（非满壳层）分子，如NO

P 分支
$\Delta J = -1$

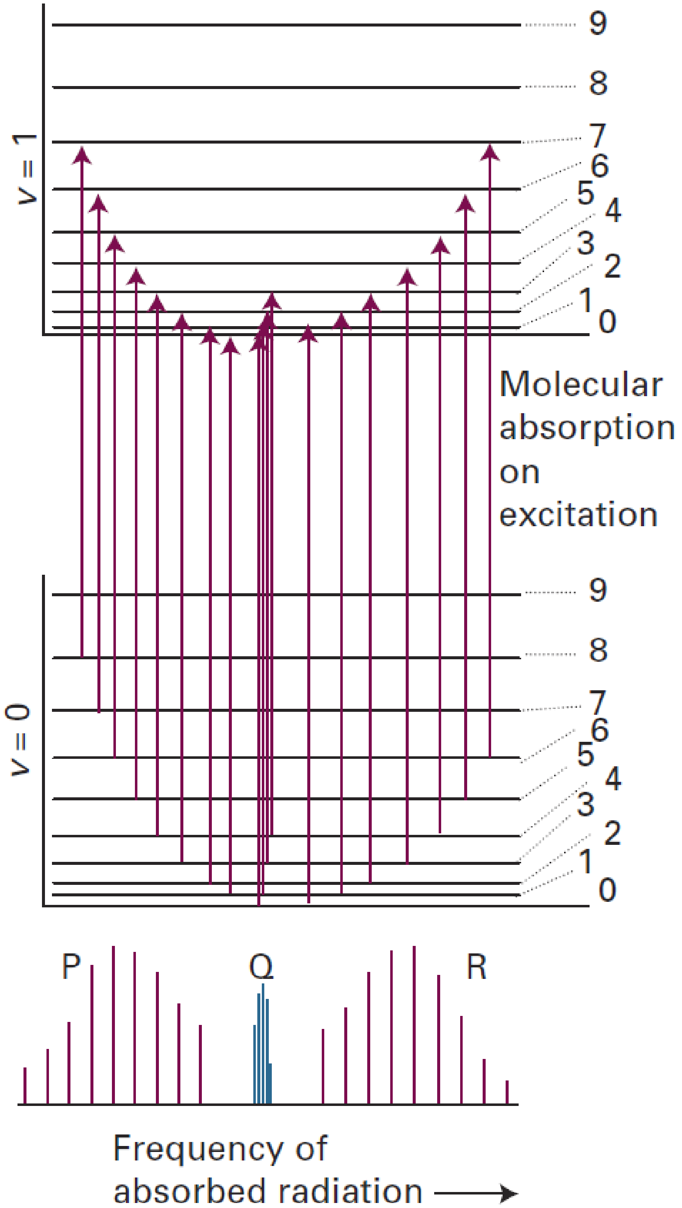
$$\tilde{\nu}_{\mathrm{P}}(J) = \tilde{S}(v+1, J-1) - \tilde{S}(v, J) = \tilde{\nu} \boxed{-} 2\tilde{B}J$$

Q 分支
$\Delta J = 0$

$$\tilde{\nu}_{\mathrm{Q}}(J) = \tilde{S}(v+1, J) - \tilde{S}(v, J) = \tilde{\nu}$$

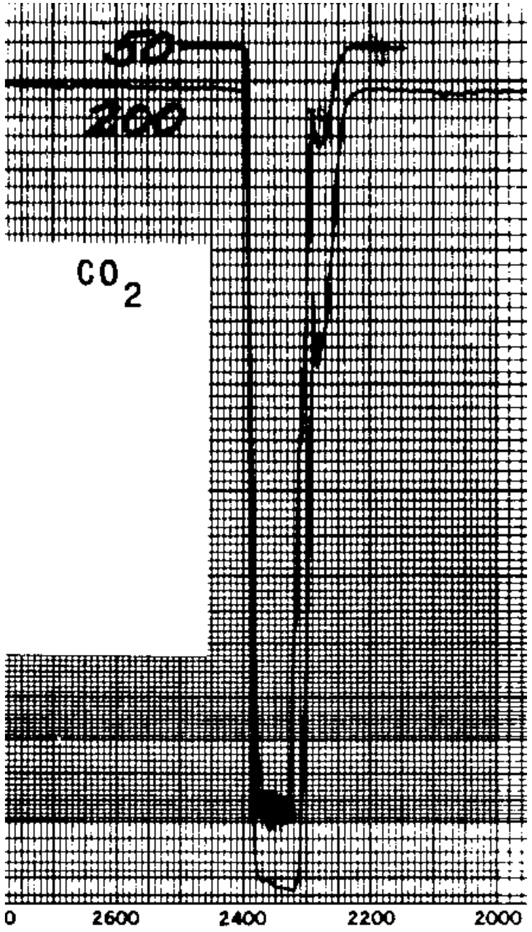
R 分支
$\Delta J = +1$

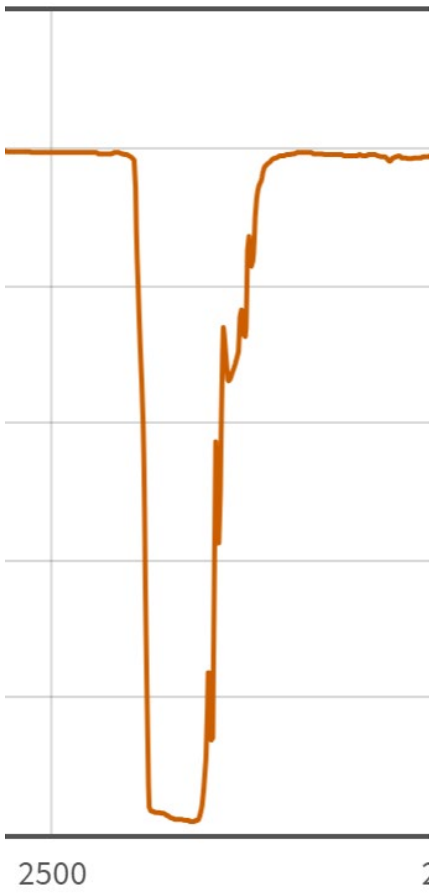
$$\tilde{\nu}_{\mathrm{R}}(J) = \tilde{S}(v+1, J+1) - \tilde{S}(v, J) = \tilde{\nu} \boxed{+} 2\tilde{B}(J+1)$$



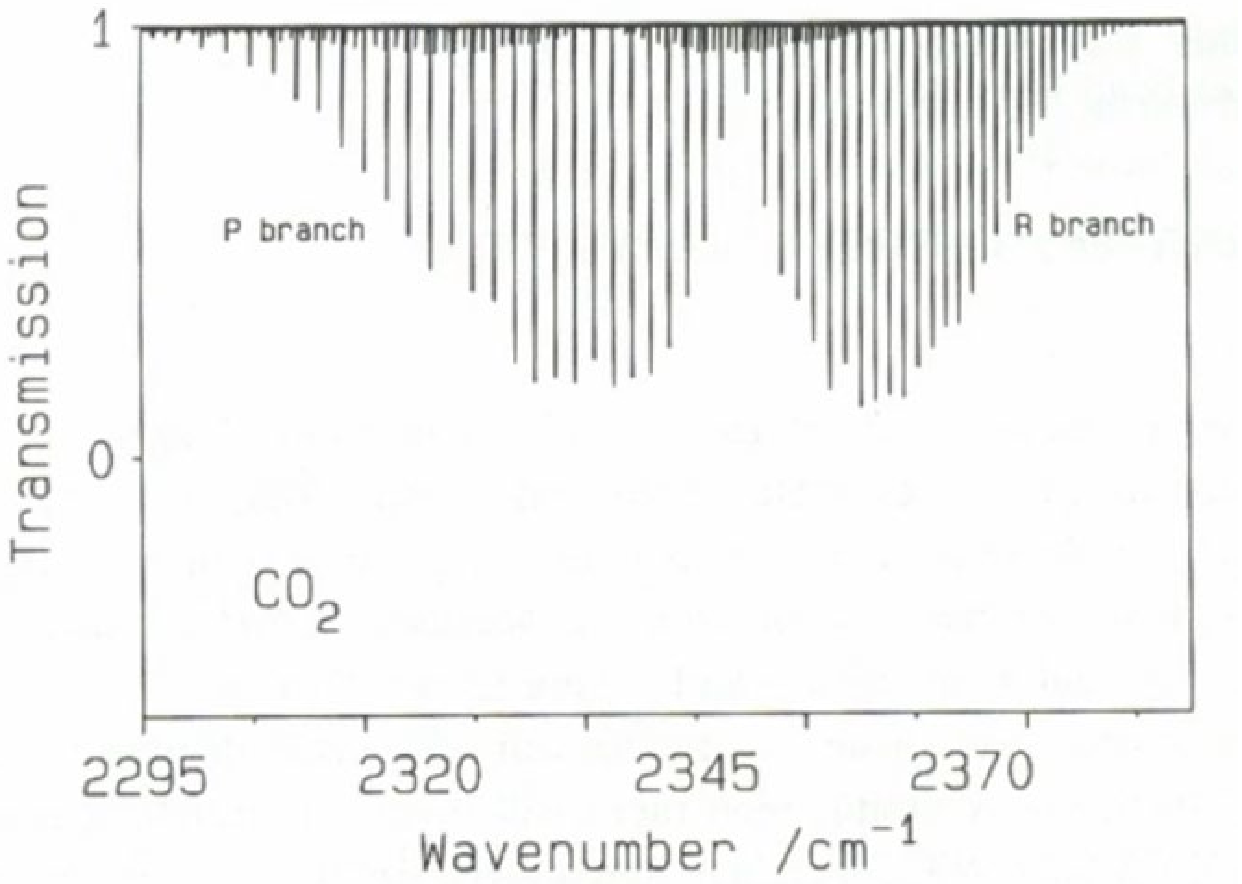
4. 双原子分子的振-转跃迁

振转光谱





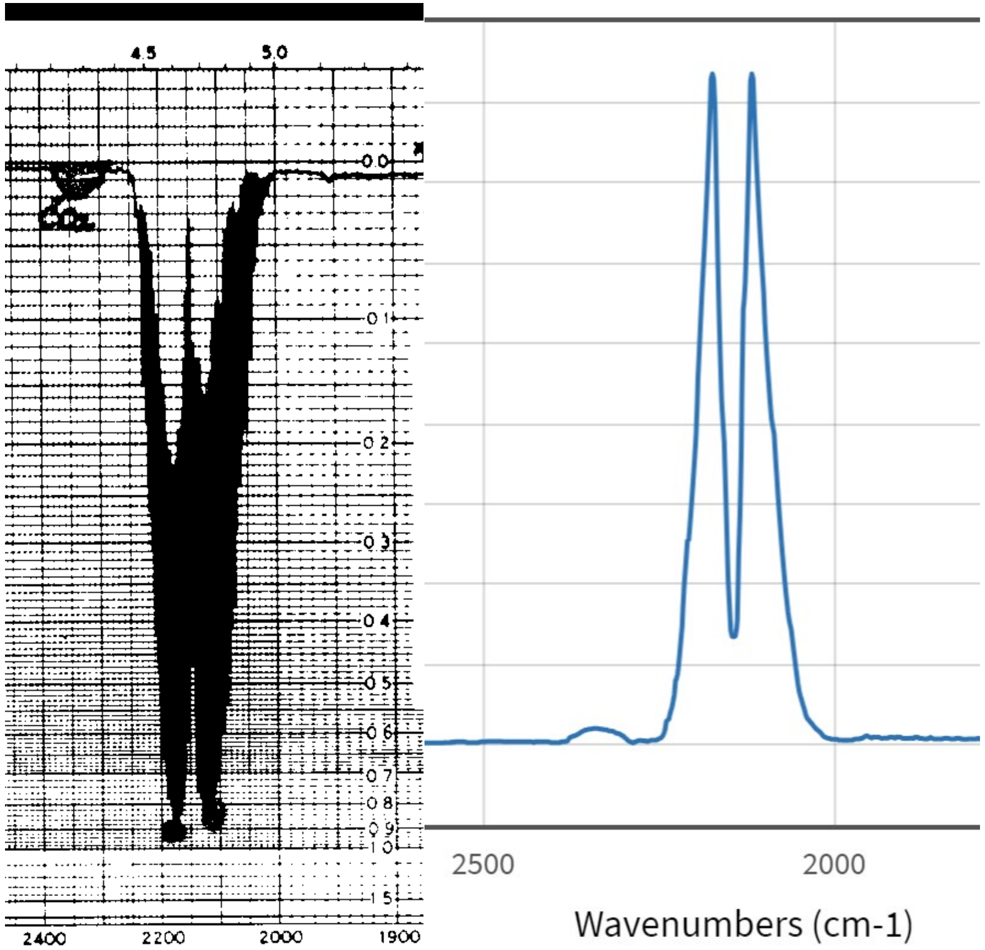
低分辨率（1964）



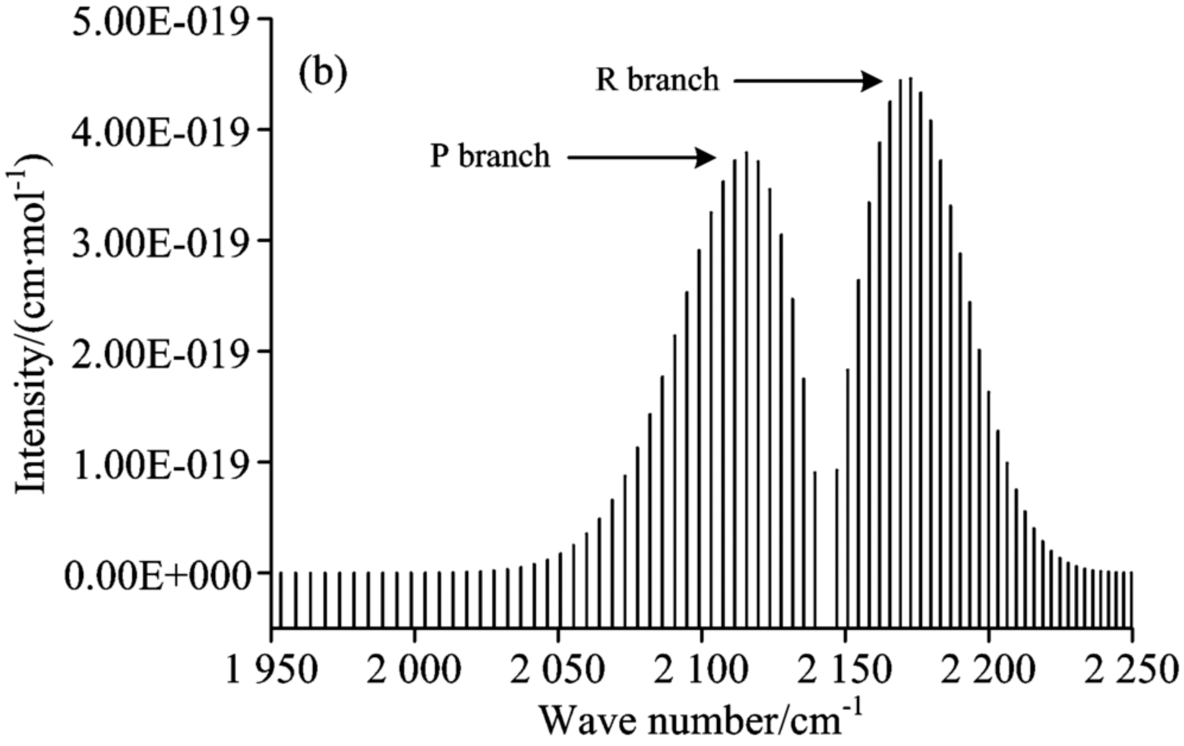
高分辨率

4. 双原子分子的振-转跃迁

振转光谱



低分辨率（1964）

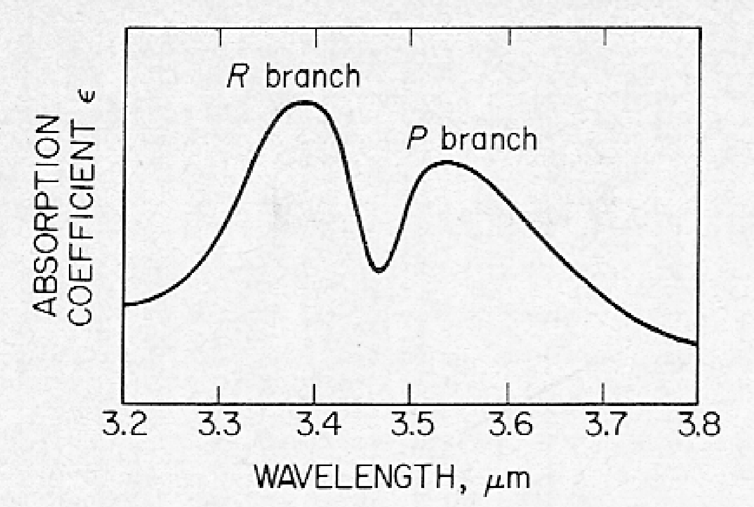


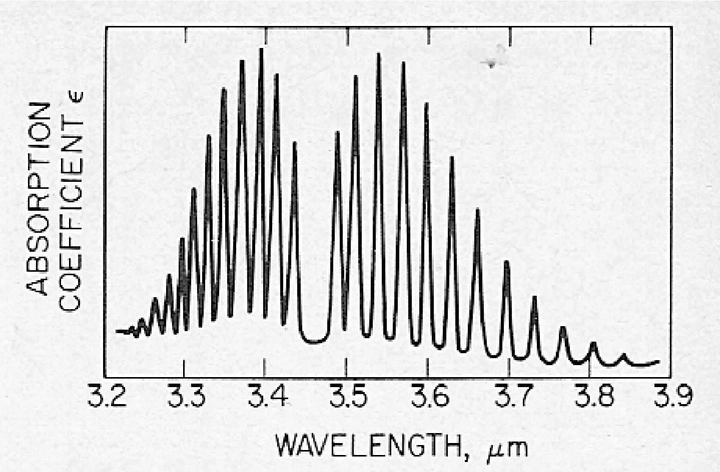
高分辨率

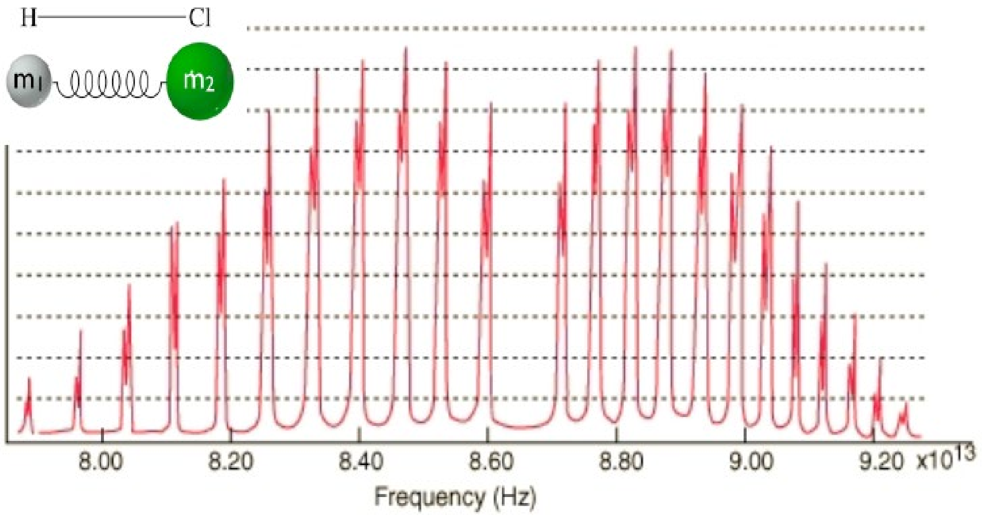
4. 双原子分子的振-转跃迁

振转光谱

IR spectrum of HCl in gas phase







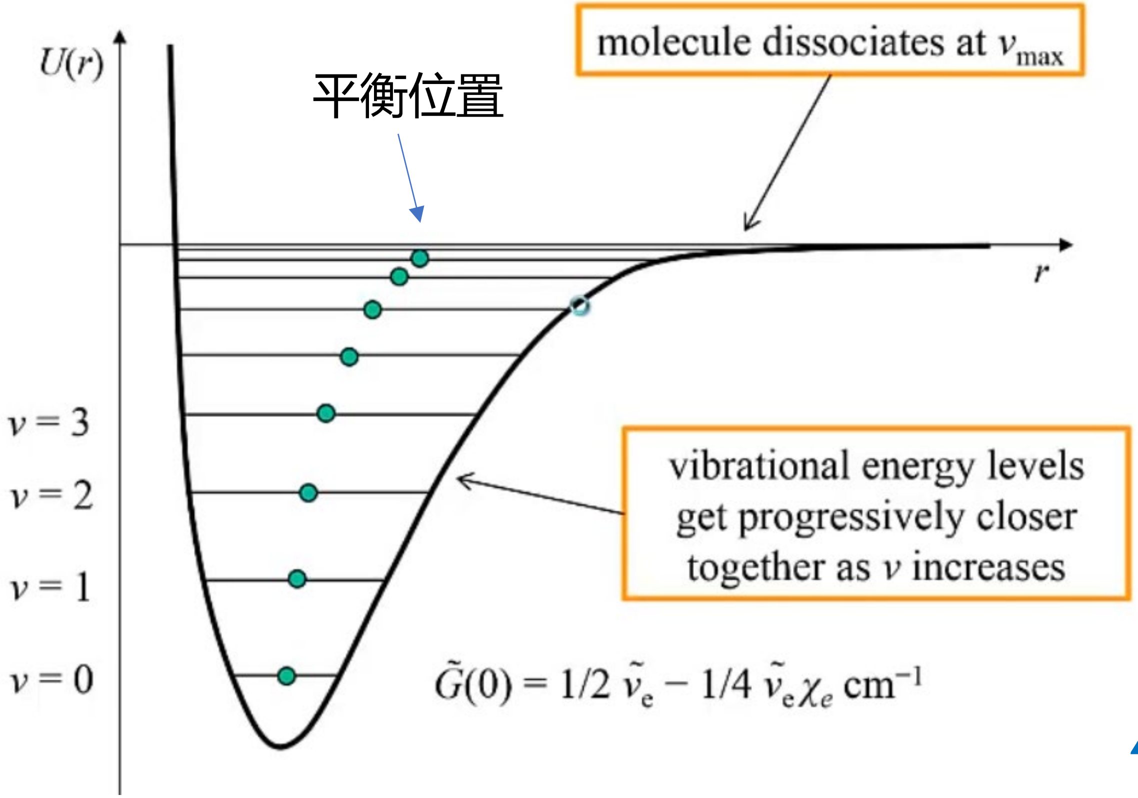
低分辨率 → 高分辨率 → 更高分辨率

(H^{35}Cl and H^{37}Cl)

4. 双原子分子的振-转跃迁

振转光谱（考虑振动非谐性）

振动非谐性对转动的影响（振转耦合）



高振动能级 ➡ 键长变长 ➡ 转动惯量变大

$$B = \frac{h}{8\pi^2 I} \Rightarrow \boxed{B_{v=0} > B_{v=1}}$$

P 分支 $\Delta J = -1$

$$\tilde{\nu}_{P(J)} = \tilde{\nu}_0 - J(\tilde{B}_0 + \tilde{B}_1)\boxed{-J^2(\tilde{B}_0 - \tilde{B}_1)}$$

J越大，P分支的间隔越大

R 分支 $\Delta J = +1$

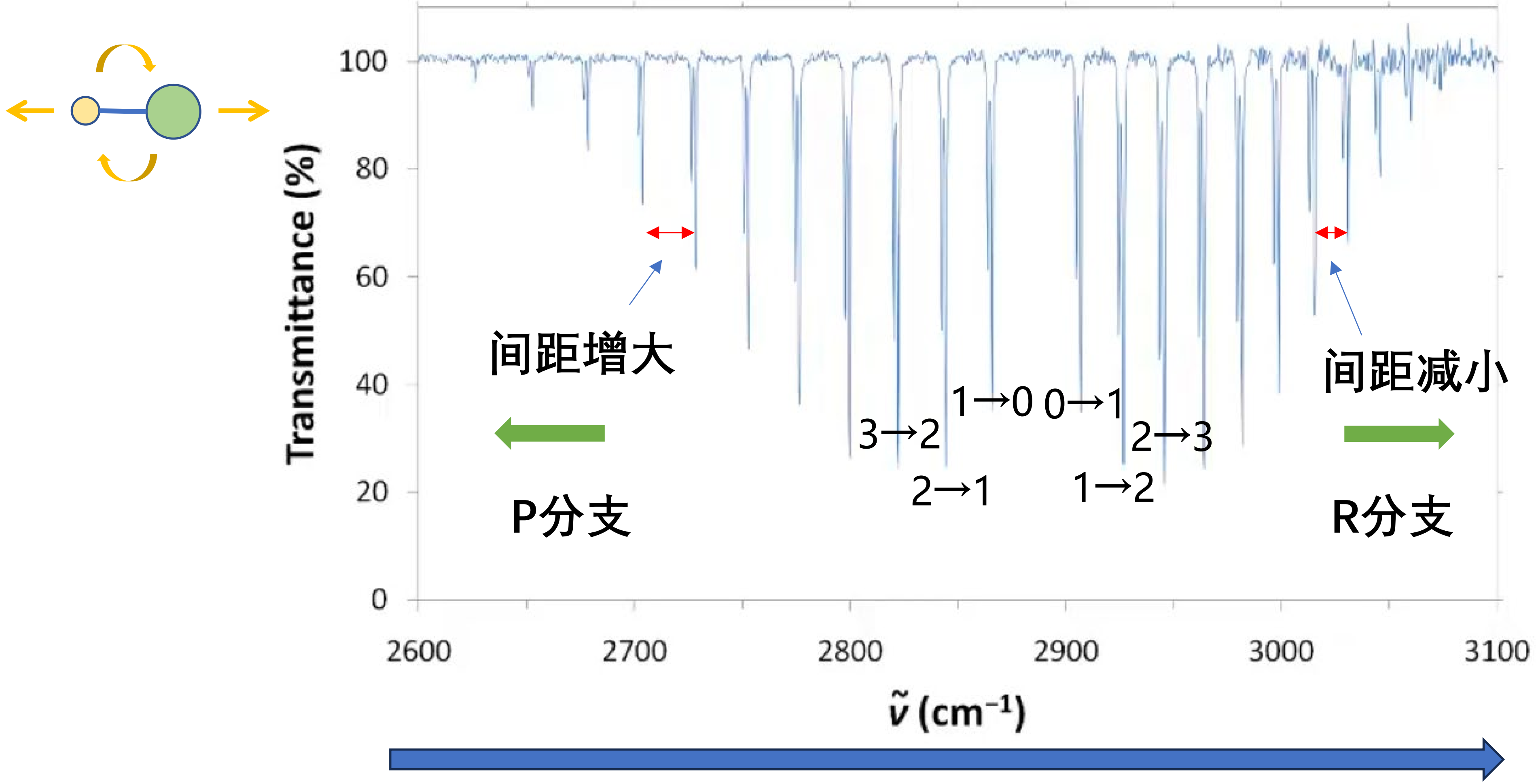
$$\tilde{\nu}_{R(J)} = \tilde{\nu}_0 + (J+1)(\tilde{B}_0 + \tilde{B}_1)\boxed{-(J+1)^2(\tilde{B}_0 - \tilde{B}_1)}$$

J越大，R分支的间隔越小

4. 双原子分子的振-转跃迁

振转光谱（考虑振动非谐性）

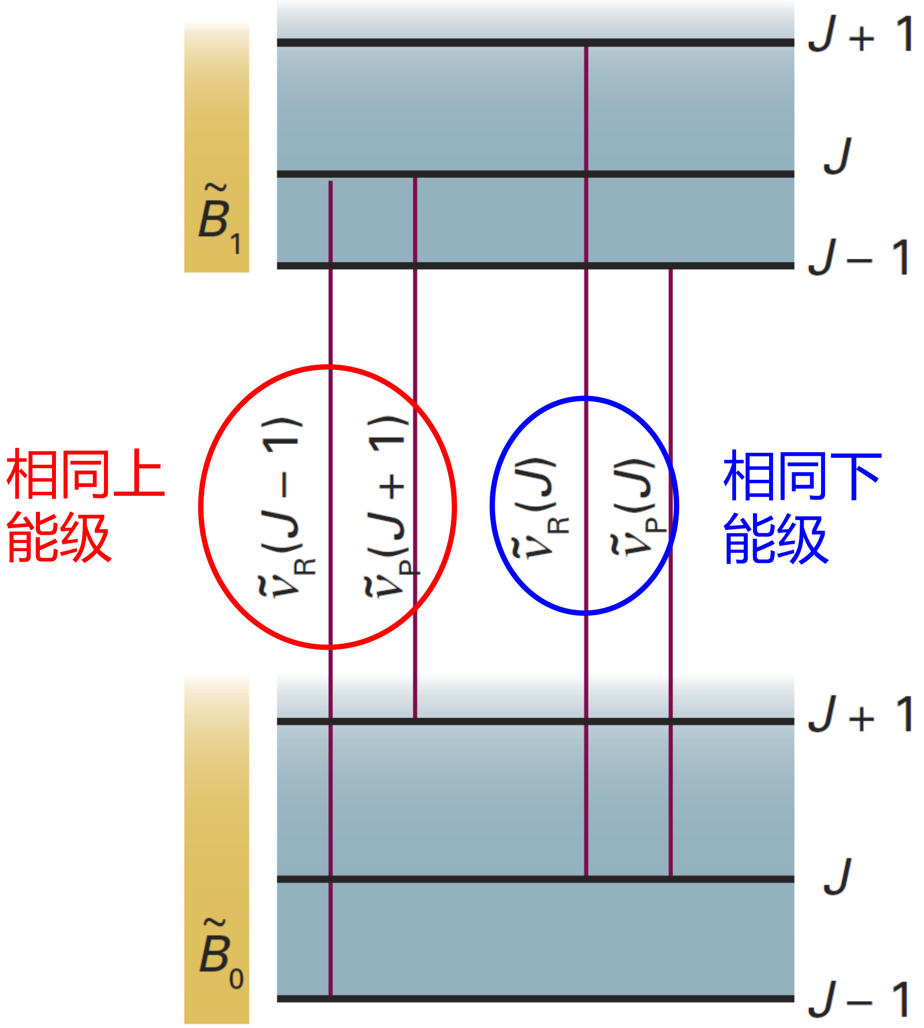
HCl伸缩振动+转动



间距越来越小

4. 双原子分子的振-转跃迁

振转光谱（考虑振动非谐性）



$$\boxed{\tilde{\nu}_R(J)-\tilde{\nu}_P(J)=4\tilde{B}_1(J+\tfrac{1}{2})}$$

$\Rightarrow \tilde{B}_1$

$$\boxed{\tilde{\nu}_R(J-1)-\tilde{\nu}_P(J+1)=4\tilde{B}_0(J+\tfrac{1}{2})}$$

$\Rightarrow \tilde{B}_0$

例： $^1H^{35}Cl$, $\tilde{B}_0$ = 10.440 cm^{-1}, $\tilde{B}_1$ =10.136 cm^{-1}