

# Vibrational spectroscopy

Elucidation of the structure-function relationships of molecules is one of the most challenging tasks in molecular physics.

## Vibrational (Infrared and Raman) Spectroscopy:

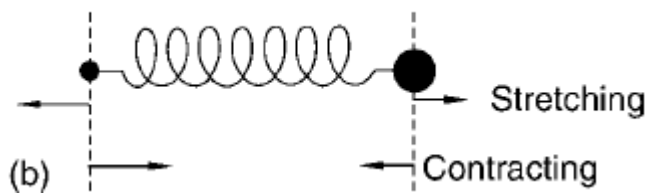
✓ provides high structural sensitivity

✓ is not restricted by the size of the sample

✓ probes molecular events under conditions that are closely related to the physico-chemical environment of the reaction

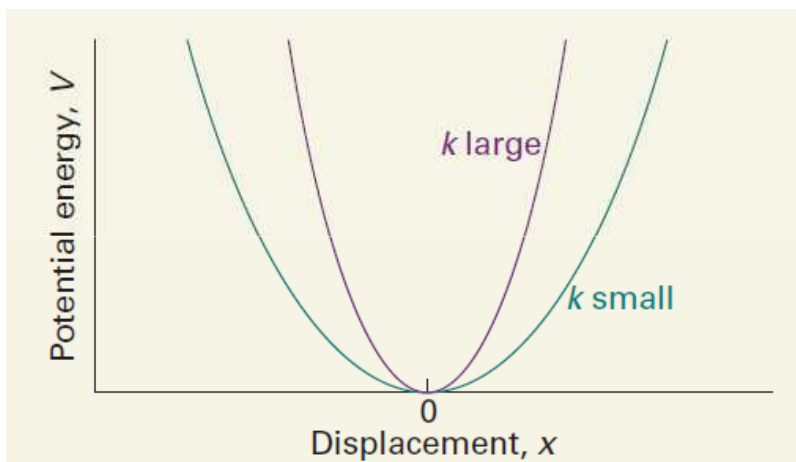
✓ can be a time-resolved method

## Diatomic molecules: harmonic oscillator



$$V(x) = \frac{1}{2}kx^2 \quad (1)$$

$$\frac{d^2\psi_v}{dx^2} + \left( \frac{2\mu E_v}{\hbar^2} - \frac{\mu kx^2}{\hbar^2} \right) \psi_v = 0 \quad (2)$$



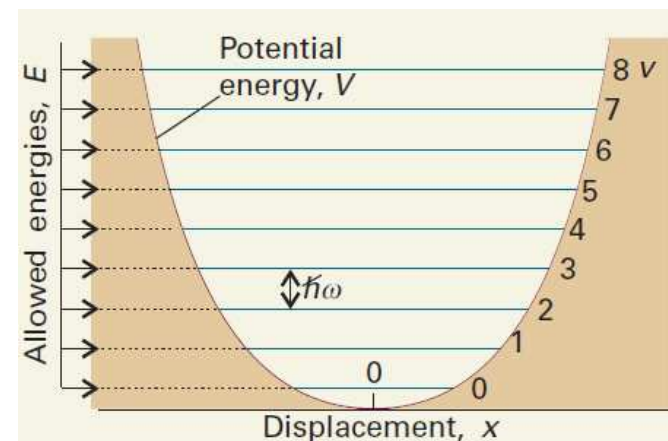
Vibrational energy:

$$E_v = \left( v + \frac{1}{2} \right) h\nu \quad v = 0, 1, 2, \dots \quad (3)$$

$$\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \quad (4)$$

(5) Vibrational terms:

$$\tilde{G}(v) = \left( v + \frac{1}{2} \right) \tilde{\nu}$$

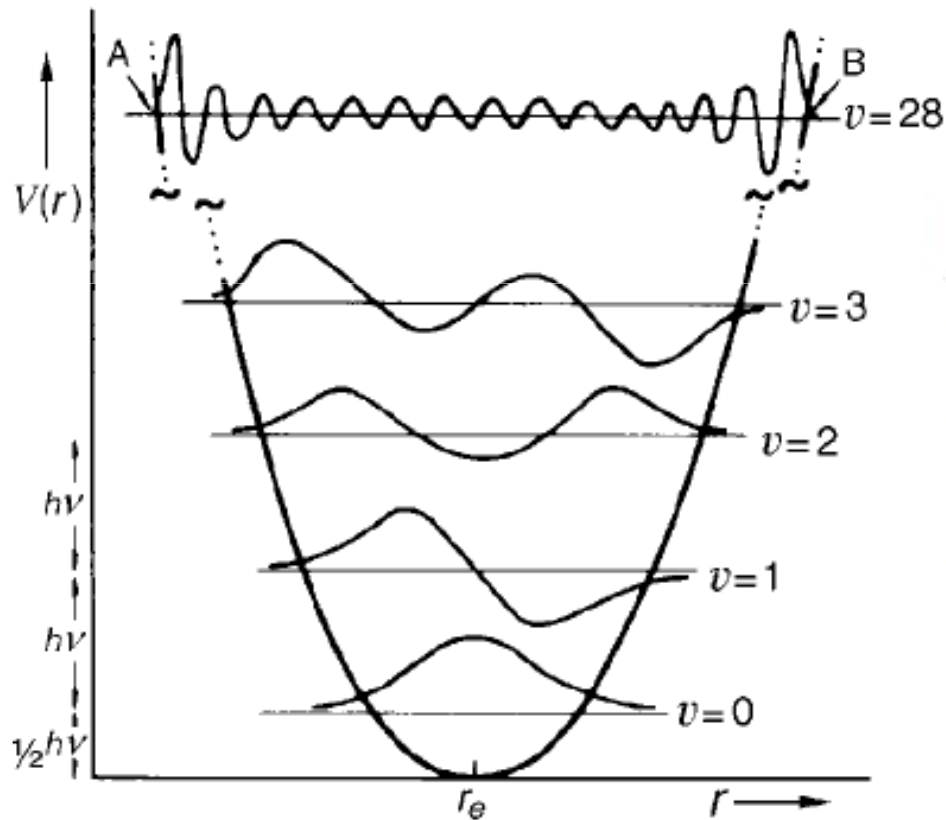


## Diatomic molecules: harmonic oscillator

$$\psi_v = \left( \frac{1}{2^v v! \pi^{1/2}} \right)^{1/2} H_v(y) \exp\left(-\frac{y^2}{2}\right)$$

where  $y = \left( \frac{4\pi^2 \nu \mu}{h} \right)^{1/2} (r - r_e)$  (6)

Hermite polynomial



Hermite polynomials for  $v=0$  to 5

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

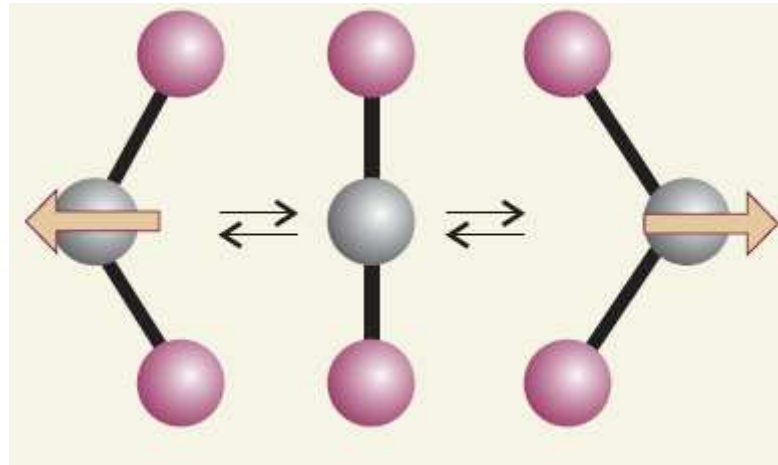
## Diatomic molecules: Harmonic oscillator

**Selection rule:** the electric dipole moment of the molecule must change when the vibrational transition occur.

$$d\mu / dx \neq 0$$

$$\Delta v = \pm 1$$

$$\Delta \tilde{G}(v) = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{\nu}$$



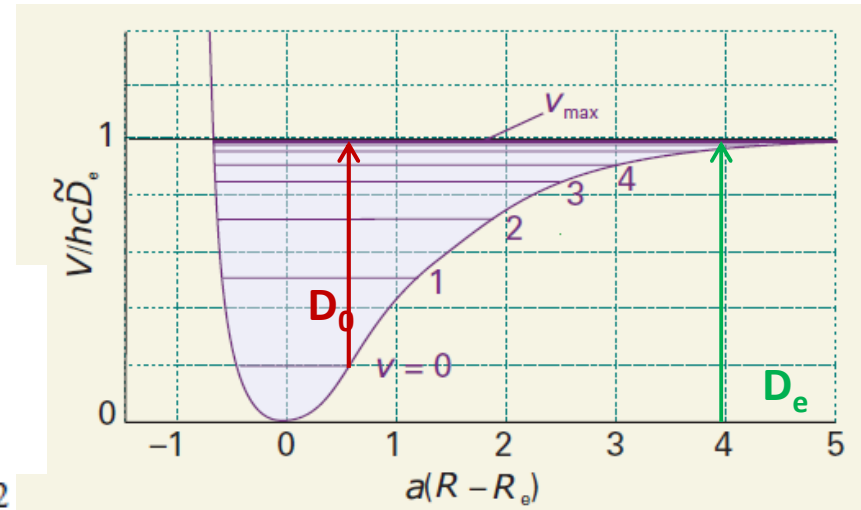
# Diatomic molecules: Anharmonic oscillator

$$V(x) = V(0) + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2} \left(\frac{d^2V}{dx^2}\right)_0 x^2 + \dots \quad (7)$$

$$\mu = \mu_0 + \left(\frac{d\mu}{dx}\right)_0 x + \frac{1}{2} \left(\frac{d^2\mu}{dx^2}\right)_0 x^2 + \dots$$

Morse potential:

$$V = hc\tilde{D}_e \{1 - e^{-a(R-R_e)}\}^2 \quad a = \left(\frac{m_{\text{eff}}\pi V}{\hbar c\tilde{D}_e}\right)^{1/2} \quad (8)$$

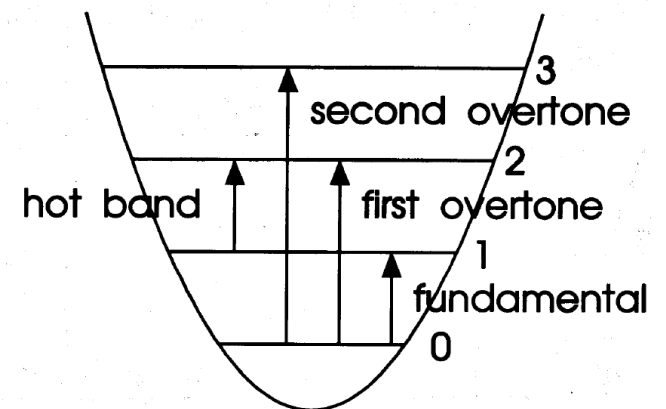


Vibrational terms:  $\tilde{G}(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e \tilde{\nu}$ ,  $x_e = \frac{a^2 \hbar}{4\pi m_{\text{eff}} V} = \frac{\tilde{\nu}}{4\tilde{D}_e}$  (9)

$$v = 0, 1, 2, \dots, v_{\text{max}}$$

$$E_0 = \frac{1}{2} \hbar \omega \left(1 - \frac{1}{2} x_e\right) \quad D_0 = D_e - E_0/hc$$

Selection rule:  $\Delta v = \pm 1, \pm 2, \pm 3, \dots$



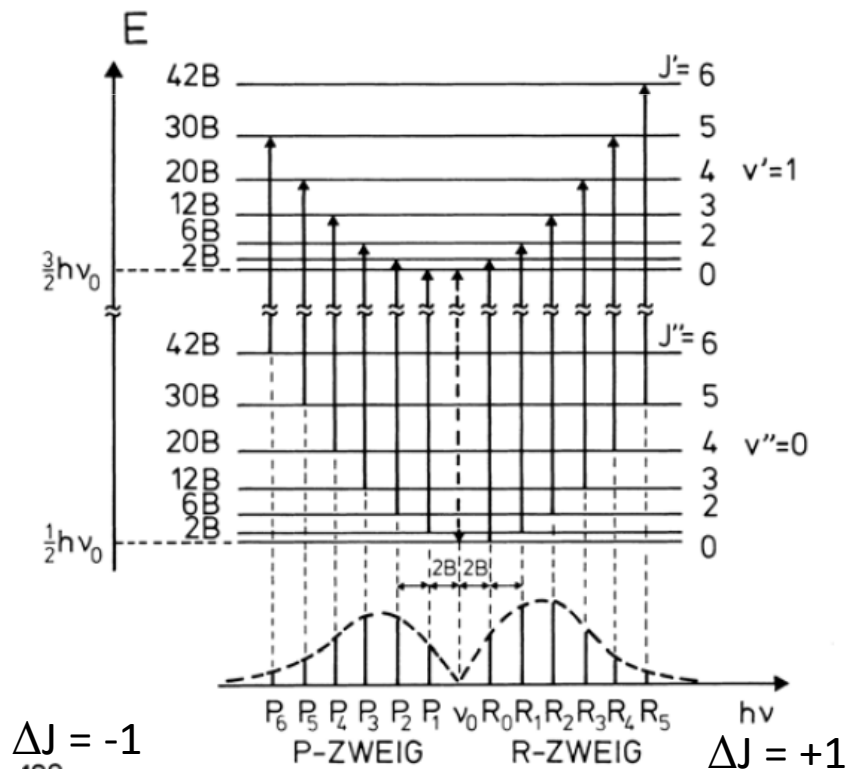
# Diatomic molecules: Vibrotor

A vibrational transition is accompanied by a simultaneous rotational transition

$$\tilde{S}(v,J) = \tilde{G}(v) + \tilde{F}(J) \quad (10)$$

$$E(v,J) = (v + \frac{1}{2})\hbar\omega - (v + \frac{1}{2})^2\hbar\omega x_e + \dots + hcB_v J(J+1) - hcD_v J^2(J+1)^2 + \dots \quad (11)$$

Selection rules:  $\Delta v = \pm 1$        $\Delta J = \pm 1$       (12)

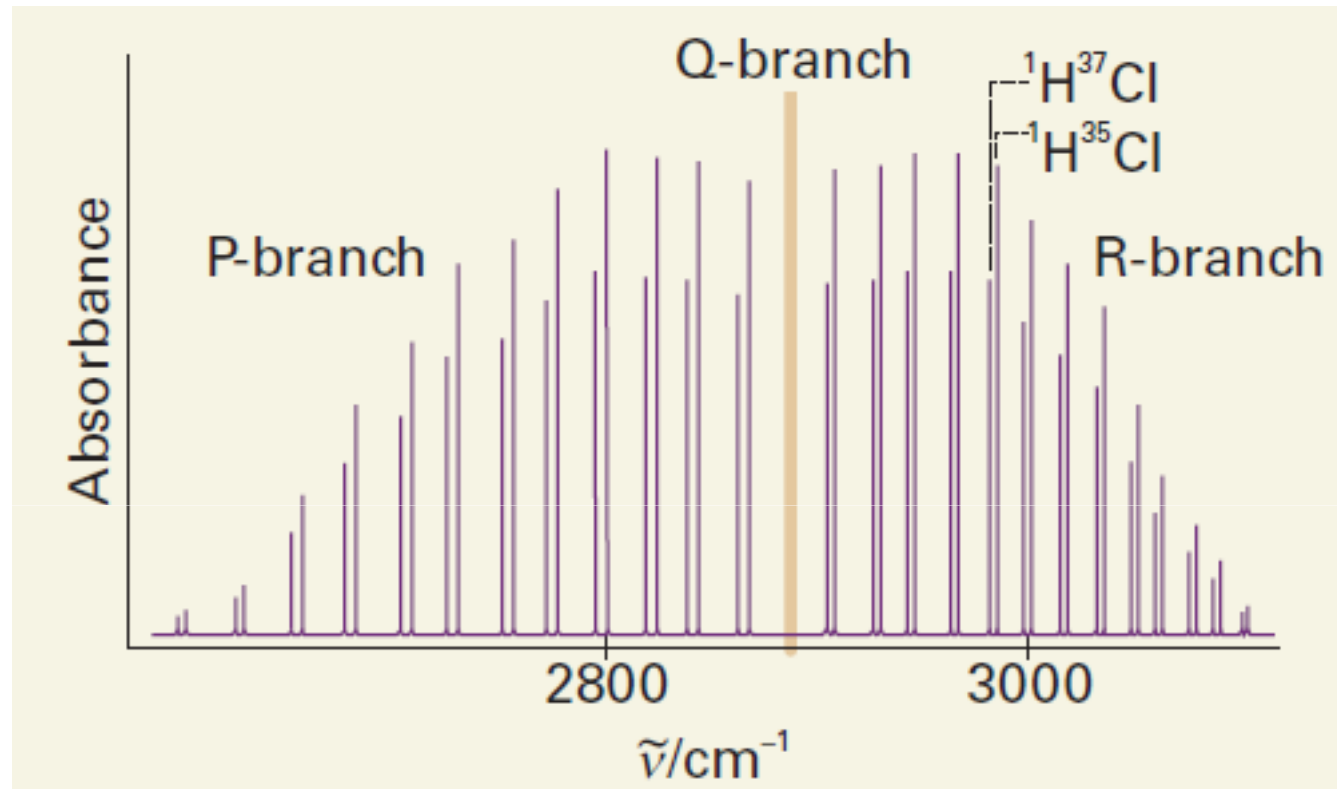


$$\tilde{\nu}^P(v,J) = \tilde{\nu} - 2BJ \quad J = 1, 2, \dots$$

$$\tilde{\nu}^R(v,J) = \tilde{\nu} + 2B(J+1) \quad J = 0, 1, 2, \dots$$

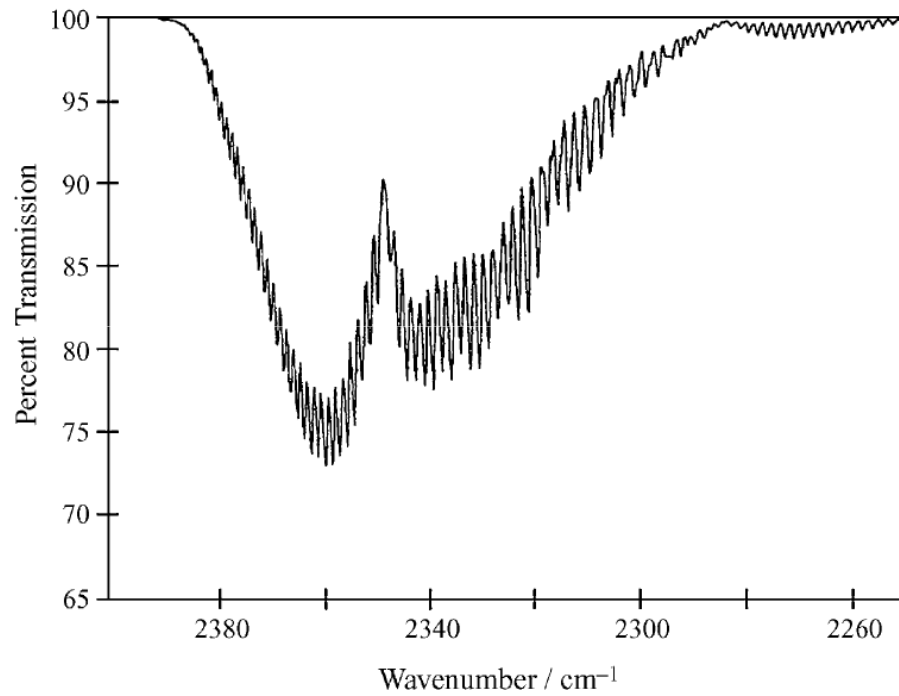
$\Delta J = -1$

$\Delta J = +1$

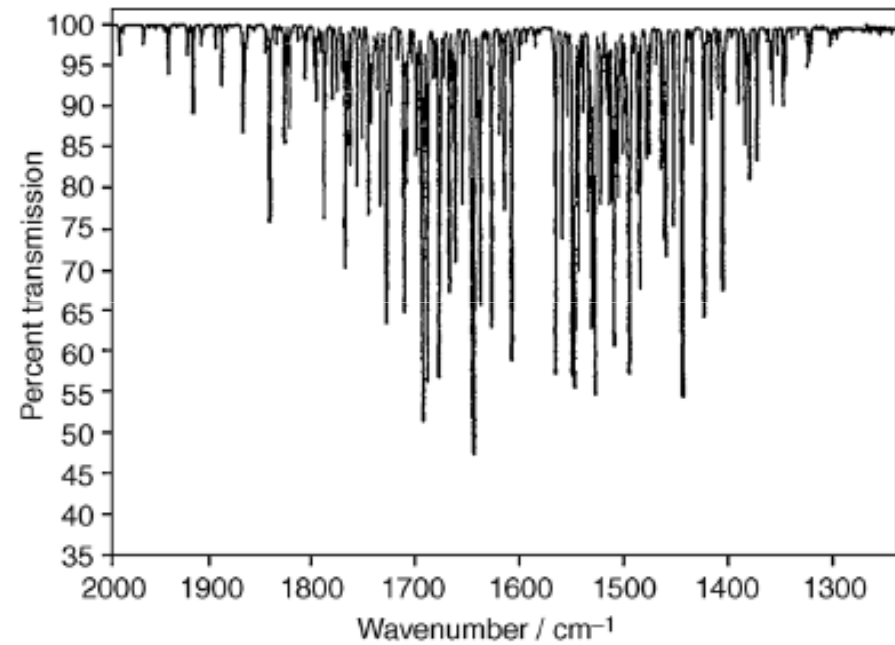


$$\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$$

IR active vibration-rotation fundamental bands of carbon dioxide: antisymmetric stretching mode

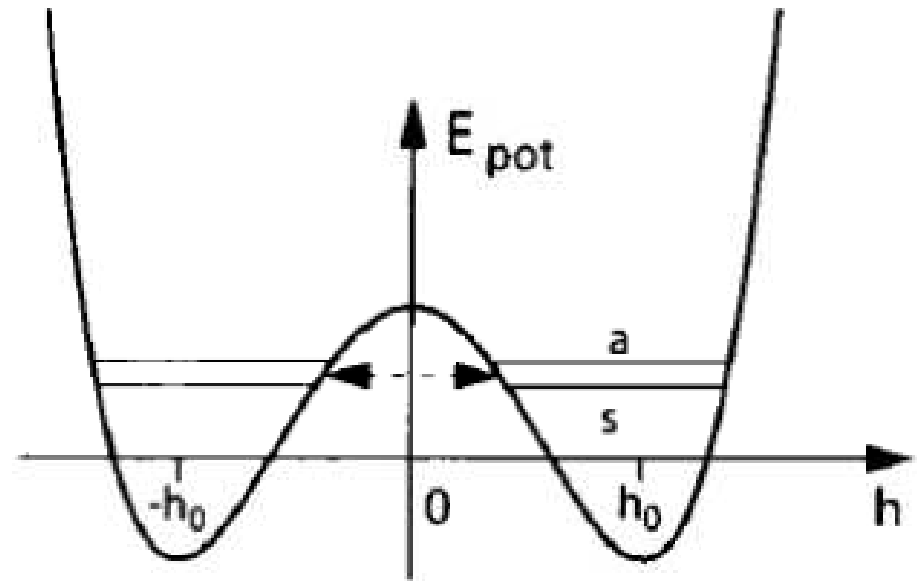
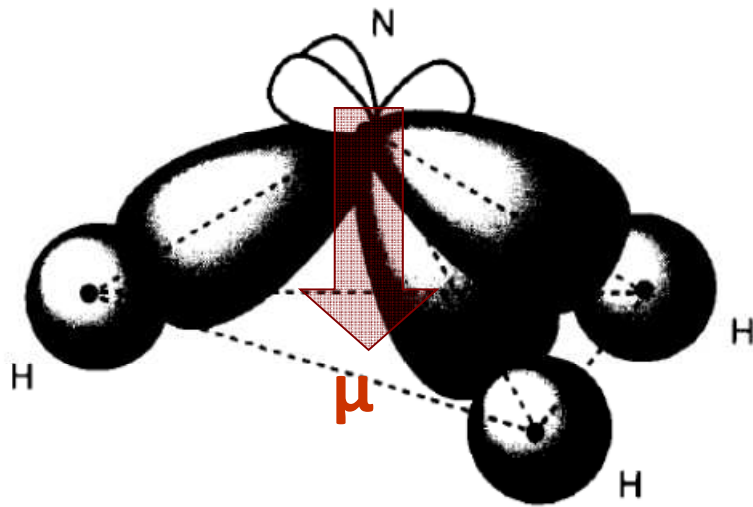


Vibration-rotation spectrum of the H-O-H bending mode of water vapor



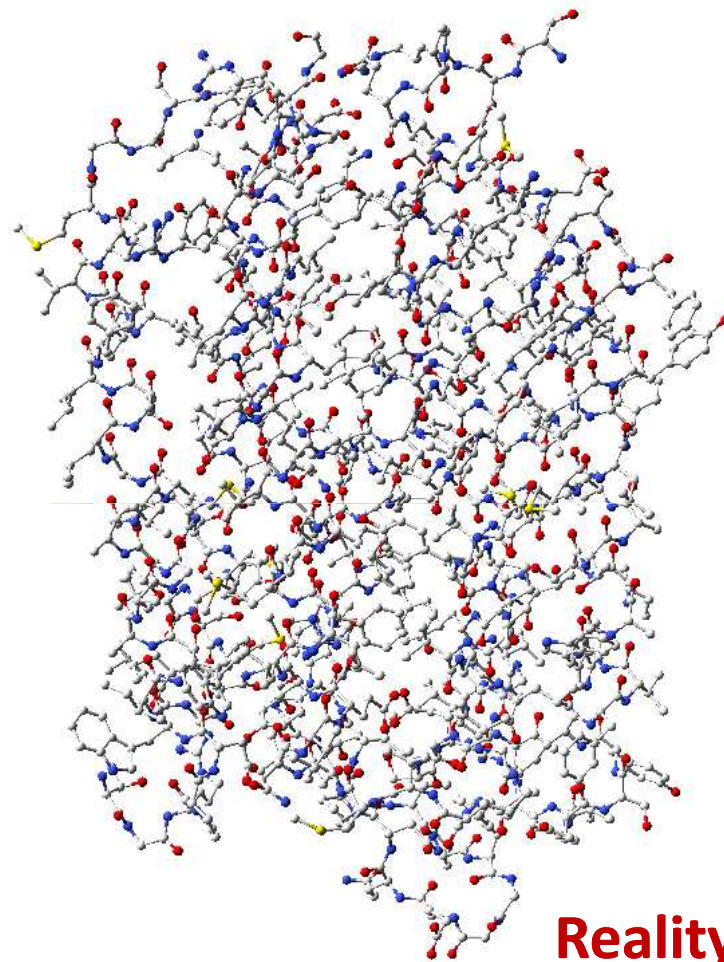
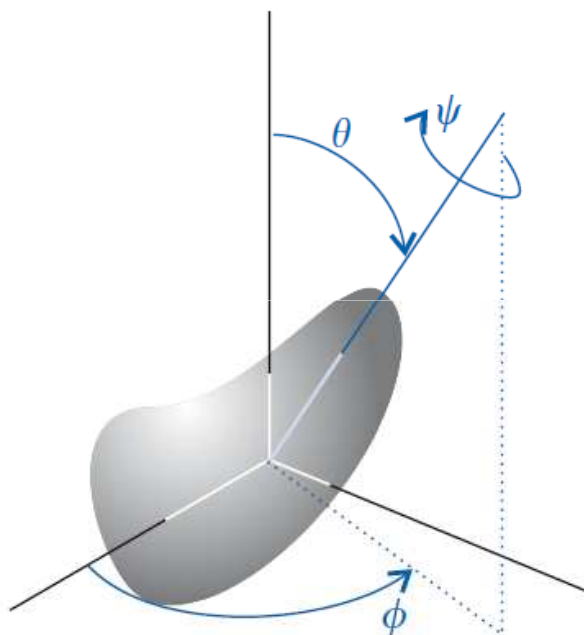


# NH<sub>3</sub> molecule



$$\Psi_{\text{sym}} = N_1(\Phi_1 + \Phi_2) ; \quad \Psi_{\text{asym}} = N_2(\Phi_1 - \Phi_2)$$

# The vibrations of polyatomic molecules



**Reality**

## Normal modes

Potential energy for a polyatomic molecule

$$V = V(0) + \sum_i \left( \frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right) x_i x_j + \dots \quad (13)$$

3N cartesian displacement coordinates for the N atoms,  $i = 1, 2, \dots, 3N$

mass-weighted coordinates:  $q_i = m_i^{1/2} x_i$  (14)

$$V = V_0 + \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots \quad (16)$$

Potential energy:  $V \cong \frac{1}{2} \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 = \frac{1}{2} \sum_{i,j=1}^{3N} f_{ij} q_i q_j$  (17)

$f_{ij}$  = force constants

Kinetic energy:  $T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$  (18)

## Normal modes

Lagrangian:

$$L = T(\dot{q}_i) - V(q_i); \mathbf{F} = m\mathbf{a} \Rightarrow \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right)_{q_i} - \left( \frac{\partial L}{\partial q_i} \right)_{\dot{q}_i} = 0 \quad (19)$$

$$\ddot{q}_j + \sum_{i=1}^{3N} f_{ij} q_i = 0 \quad (20)$$

Solutions:  $q_i = A_i \cos(\sqrt{\lambda}t + \varphi) \quad (21)$

$$-A_j \lambda + \sum_{i=1}^{3N} f_{ij} A_i = 0 \quad (22)$$

Secular determinant

$$\begin{vmatrix} f_{11} - \lambda & f_{12} & f_{13} & \cdots & f_{1,3N} \\ f_{21} & f_{22} - \lambda & f_{23} & \cdots & f_{2,3N} \\ f_{31} & f_{32} & f_{33} - \lambda & \cdots & f_{3,3N} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ f_{3N,1} & f_{3N,2} & f_{3N,3} & \cdots & f_{3N,3N} - \lambda \end{vmatrix} = 0 \quad (23)$$

## Normal modes

Amplitudes  $A_{ik}$ :

$$\begin{aligned}
 (f_{11} - \lambda_k)A_{1k} + f_{12}A_{2k} + \dots + f_{1,3N}A_{3N,k} &= 0 \\
 f_{21}A_{1k} + (f_{22} - \lambda_k)A_{2k} + \dots + f_{2,3N}A_{3N,k} &= 0 \\
 \dots & \\
 f_{3N,1}A_{1k} + f_{3N,2}A_{2k} + \dots + (f_{3N,3N} - \lambda_k)A_{3N,k} &= 0
 \end{aligned}
 \tag{24}$$

In a given vibr. mode  $k$  all atoms vibrate in-phase and with the same frequency  $\lambda^{1/2}$ , but with different amplitudes.

~~group frequency~~

$q_i$  are converted into **normal coordinates** (orthogonalization):

$$Q_k = \sum_{i=1}^{3N} l_{ik} q_i \tag{25}$$

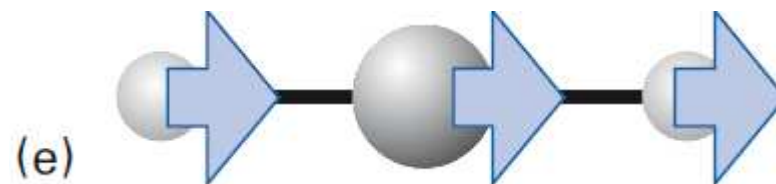
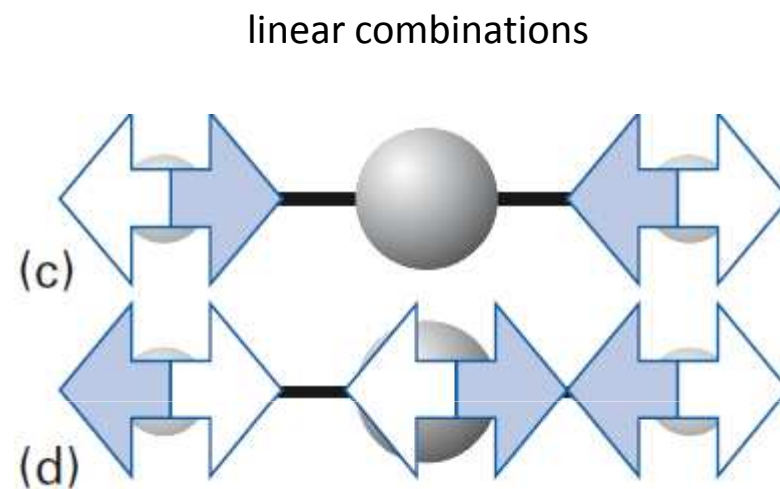
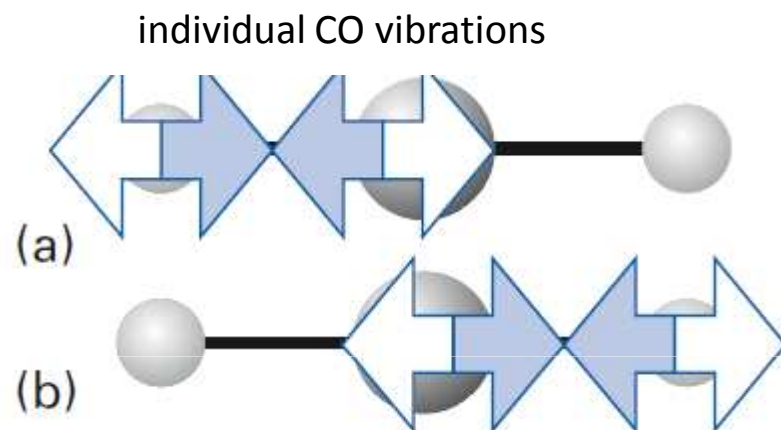
$$Q_k = K_k \cos(\sqrt{\lambda_k} t + \varphi_k) \tag{26}$$


  
**normal modes**

# Normal coordinates

$$Q_k = \sum_{i=1}^{3N} l_{ik} q_i$$

CO<sub>2</sub> vibrations:



## Normal modes

(G. M. Barrow – Introduction to molecular spectroscopy – Mc GrawHill)

Total energy: 
$$E = \frac{1}{2} \sum_i \dot{Q}_i^2 + \frac{1}{2} \sum_i \lambda_i Q_i^2 \quad (27)$$

Hamiltonian: 
$$H = \sum_i H_i \quad H_i = -\frac{1}{2}\hbar^2 \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\lambda_i Q_i^2 \quad (28)$$

Wavefunction:  
3N-6 (5) factors 
$$\psi = \psi_{v_1}(Q_1)\psi_{v_2}(Q_2)\cdots = \prod_i \psi_{v_i}(Q_i) \quad (29)$$

Schrödinger eq.: 
$$-\frac{1}{2}\hbar^2 \frac{\partial^2 \psi(Q_i)}{\partial Q_i^2} + \frac{1}{2}\lambda_i Q_i^2 \psi(Q_i) = E\psi(Q_i) \quad (30)$$

Solutions: 
$$E_{v_i} = \left(v_i + \frac{1}{2}\right)\hbar\omega_i \quad \omega_i = \lambda_i^{1/2} \quad v_i = 0, 1, 2, \dots \quad (31)$$

$$\psi_{v_i}(Q_i) = N_{v_i} H_{v_i}(\alpha_i Q_i) e^{-\alpha_i^2 Q_i^2 / 2} \quad \alpha_i = \left(\frac{\omega_i}{\hbar}\right)^{1/2} \quad (32)$$

## Normal modes

$$E = \sum_i \left( v_i + \frac{1}{2} \right) \hbar \omega_i \quad (33)$$

Vibrational state j:  $|v_1 v_2 \dots\rangle$  1, 2,.. modes (34)

Ground state:  $E = \frac{1}{2} \sum_i \hbar \omega_i$

Ex: N = 50 atoms, 144 modes,  $\bar{\nu} = \bar{\nu}$  cm<sup>-1</sup>, E<sub>0</sub> = 2.7 eV

**Selection rules:** 
$$\mu = \mu_0 + \sum_i \left( \frac{\partial \mu}{\partial Q_i} \right)_0 Q_i + \dots \quad (35)$$

Transition dipole moment  $\mu_{ij}$

$$\langle 00 \dots v'_i \dots 0 | \mu | 00 \dots v_i \dots 0 \rangle = \left( \frac{\partial \mu}{\partial Q_i} \right)_0 \langle v'_i | Q_i | v_i \rangle \quad (36)$$

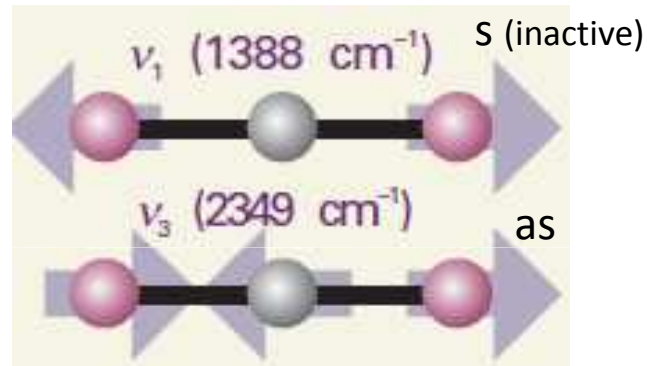
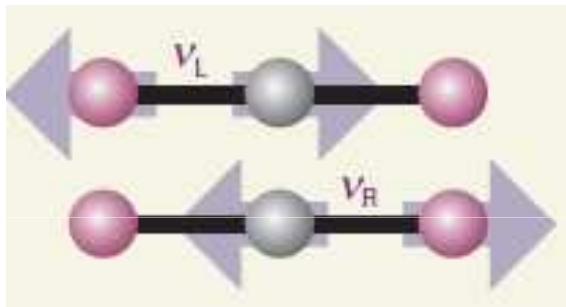
$$\left( \frac{\partial \mu}{\partial Q_i} \right)_0 \neq 0$$

$$v'_i = v_i \pm 1 \quad (37)$$

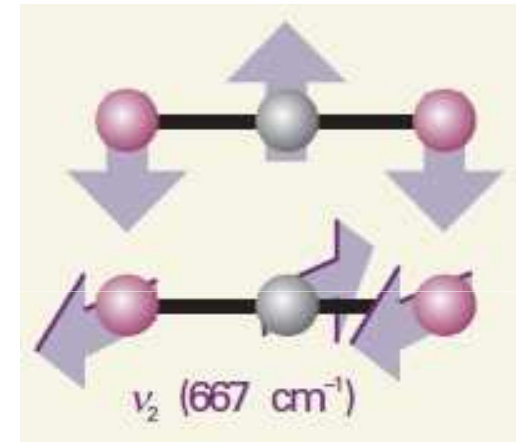


# Normal modes

Normal modes of CO<sub>2</sub> (4 modes = 9-5):



parallel bands

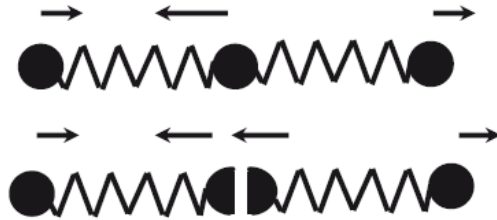


perpendicular bands

$$A_k = \int_{\nu \text{ band}} \epsilon(\nu) d\nu = \frac{N\pi}{3c} \left\{ \left| \frac{\partial \mu_x}{\partial Q_k} \right|^2 + \left| \frac{\partial \mu_y}{\partial Q_k} \right|^2 + \left| \frac{\partial \mu_z}{\partial Q_k} \right|^2 \right\}$$

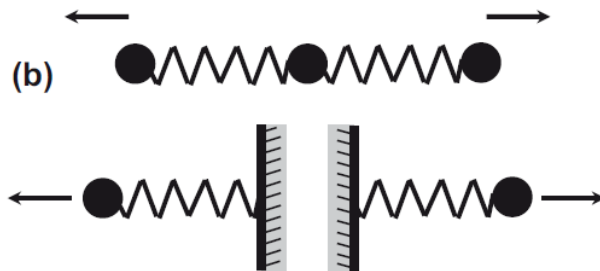
## Normal modes

Asymmetric  
2349 cm<sup>-1</sup>:



$$\bar{\nu}_{\mathbf{3}} = 1303 \sqrt{K \left( \frac{1}{m_1} + \frac{2}{m_2} \right)} = 1303 \sqrt{\frac{K}{m}} \sqrt{3}$$

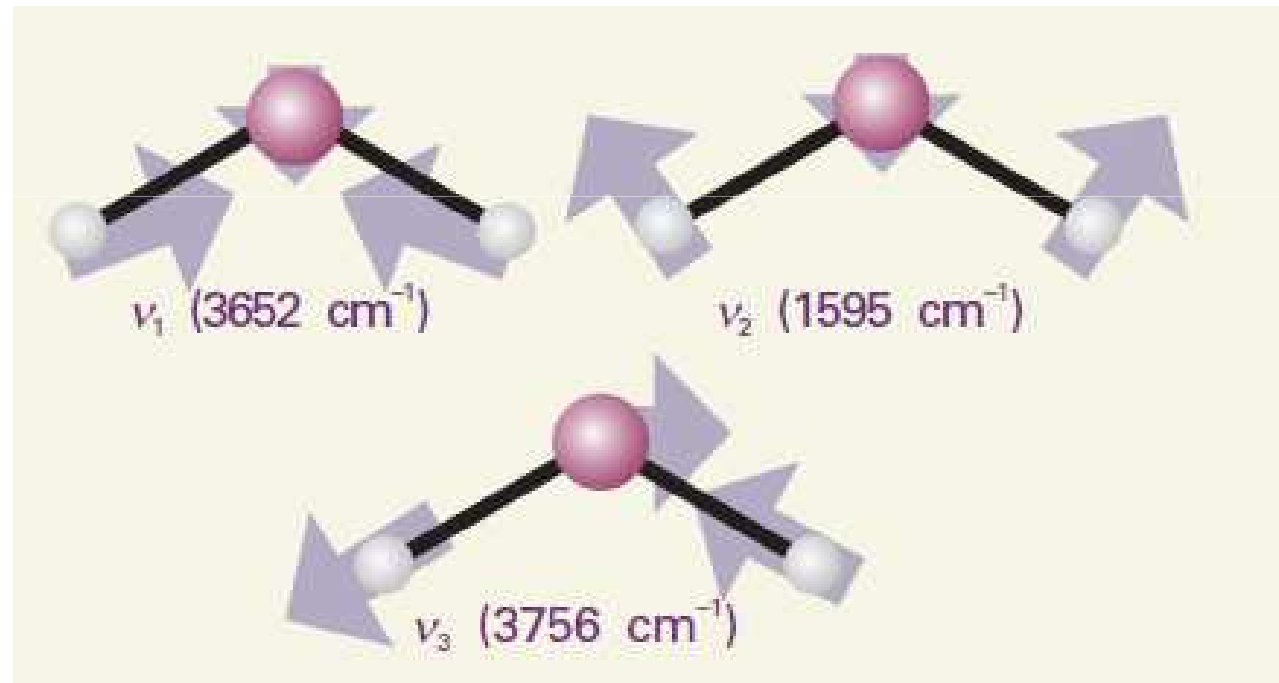
Symmetric:  
1388 cm<sup>-1</sup>



$$\bar{\nu}_{\mathbf{1}} = 1303 \sqrt{K \left( \frac{1}{m_1} + \frac{1}{\infty} \right)} = 1303 \sqrt{\frac{K}{m}} \sqrt{1}$$

## Normal modes

Normal modes of H<sub>2</sub>O (3 modes = 9-6):



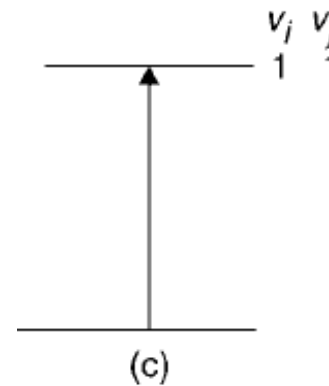
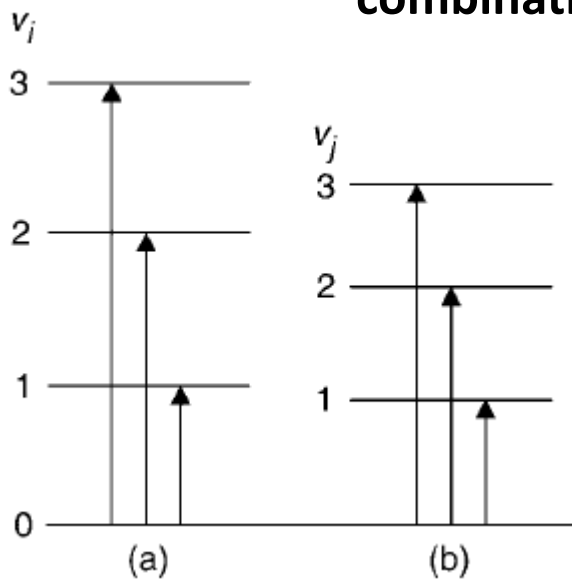
## The effects of anharmonicity

$$\mu_z = \mu_{0z} + \sum_i \left( \frac{\partial \mu_z}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 \mu_z}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j + \dots \quad (38)$$

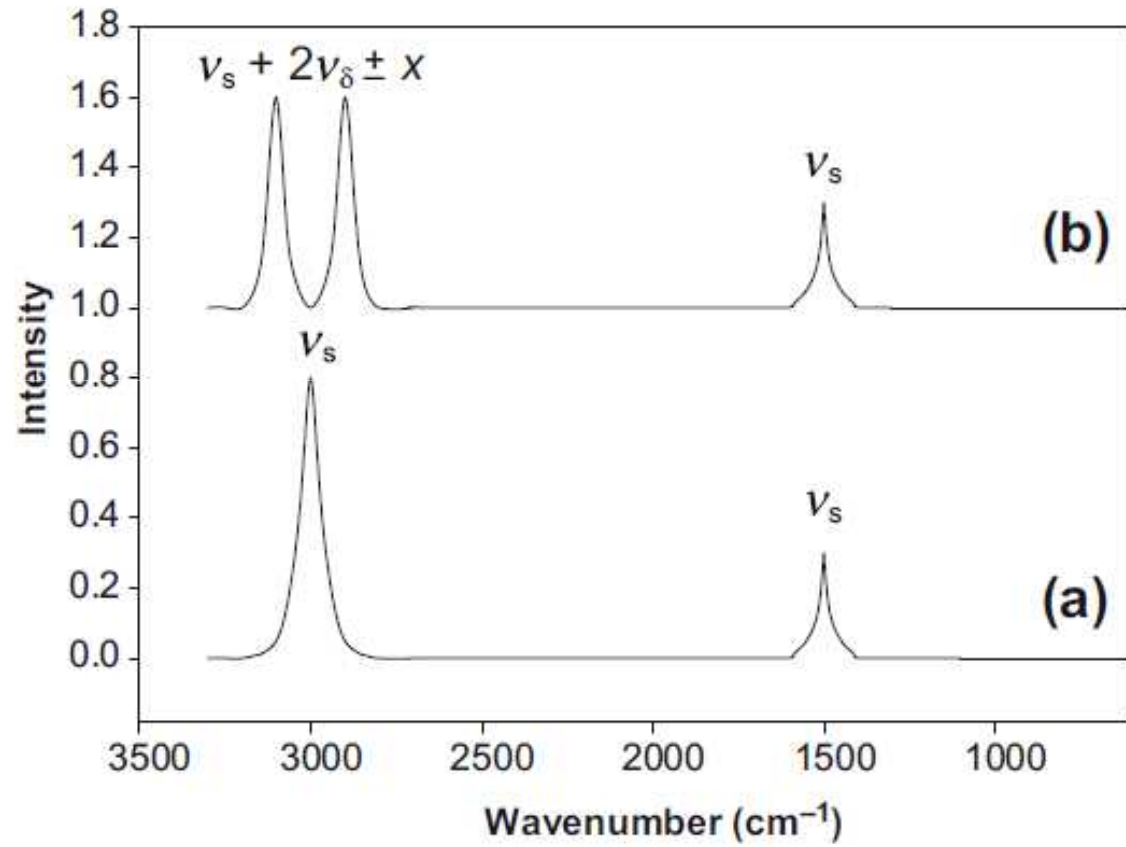
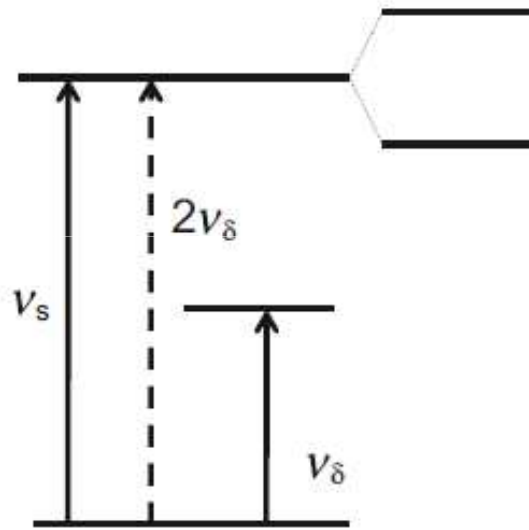
$$Q_k = K_k \cos(\sqrt{\lambda_k t} + \varphi_k)$$

**overtone:  $\nu_i, 2\nu_i, 3\nu_i, \dots$**

**combination bands:  $\nu_i + \nu_j, \nu_i - \nu_j, \nu_i + 2\nu_j, \dots$**



## Fermi resonance



## Normal modes: classification

### Skeletal vibrations (fingerprint) 1400-200 $\text{cm}^{-1}$ :

involve significant displacements of almost all atoms in the molecule.

**Far IR:** C-Cl, C-Br, C-I bending modes below  $400 \text{ cm}^{-1}$ ; restricted rotational oscillations (librations) of molecules in liquid state, ring breathing benzene  $260 \text{ cm}^{-1}$

### Group frequencies 4000-1400 $\text{cm}^{-1}$ : stretching, bending modes

involve only a small group of the molecule, the rest is almost stationary.

$\nu(\text{O-H})$  :  $3590\text{-}3650 \text{ cm}^{-1}$

