

How many vibrations in a polyatomic molecule?

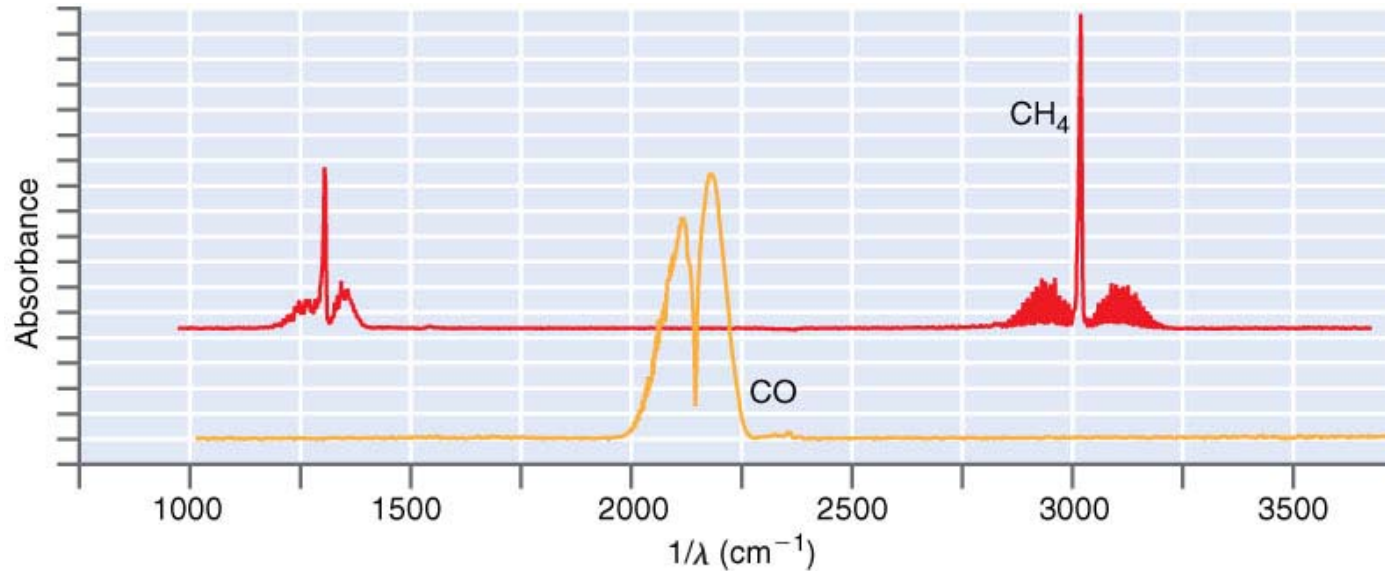
3 translation + 3 rotation

$$\begin{array}{l} \text{nonlinear} \quad 3n - 6 \\ \text{linear} \quad \quad 3n - 5 \end{array} \left. \vphantom{\begin{array}{l} \text{nonlinear} \\ \text{linear} \end{array}} \right\} n = \# \text{ atoms}$$

$$H_2O \quad 3 \cdot 3 - 6 = 3$$

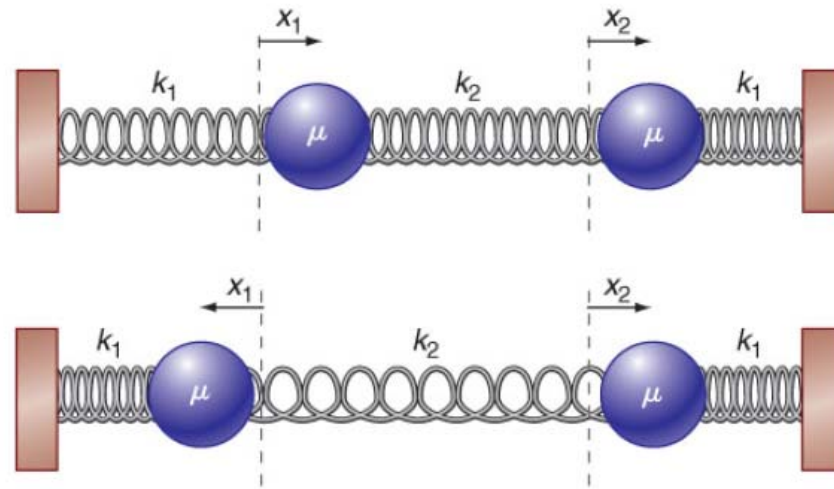
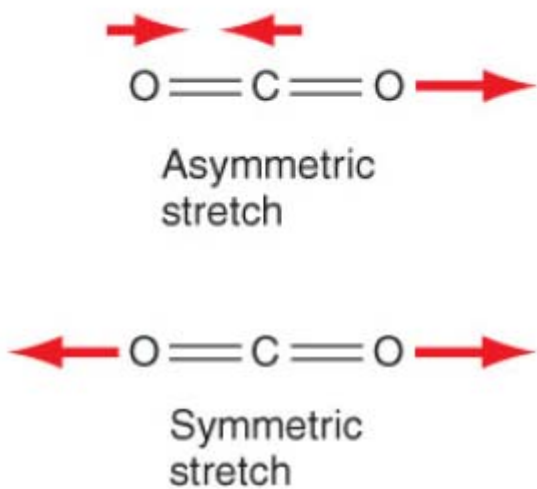
$$CH_4 \quad 3 \cdot 5 - 6 = 9$$

$$C_6H_6 \quad 3 \cdot 12 - 6 = 30 \quad \longrightarrow \quad 20 \text{ distinct frequencies after allowing for degeneracies}$$



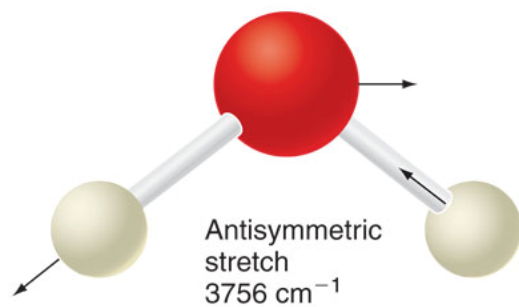
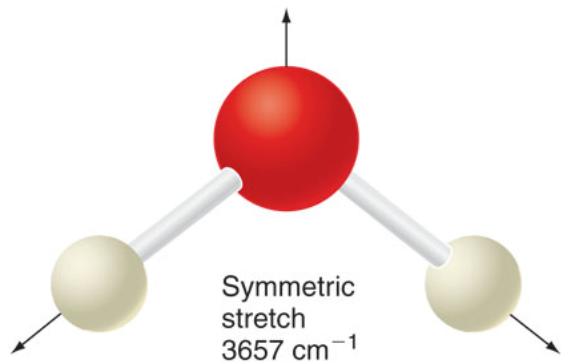
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The extra structure in the above spectra is a consequence of rotational transitions accompanying the vibrational transitions. In solution the rotational lines are not resolved → broad bands



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$$\nu = \frac{1}{2\pi} \sqrt{\frac{(k_1 + 2k_2)}{\mu}} \leftarrow \text{higher frequency}$$



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rotational transitions $\Delta J = \pm 1, \Delta M_J = 0$

Need a permanent dipole moment for a rotational transition

Rotational energy of a linear molecule: $E = \frac{\hbar^2}{2\mu r_o^2} J(J+1) = \frac{h^2}{8\pi^2 \mu r_o^2} J(J+1) = hcBJ(J+1)$

B = rotational constant in cm^{-1}

$J \rightarrow J+1: \Delta E_+ = 2hcB(J+1)$ (R branch)	$0 \rightarrow 1$ $2hcB$ $1 \rightarrow 2$ $4hcB$ $2 \rightarrow 3$ $6hcB$ $3 \rightarrow 4$ $8hcB$	}	energies of transitions
$J \rightarrow J-1: \Delta E_- = -2hcBJ$ (P branch)			

Depending on the molecule the rotational constant can be $0.03 - 20 \text{ cm}^{-1}$

Room temperature corresponds to about 200 cm^{-1}

So many rotational levels will be populated at room temperature

$$Y_0^0 \sim 1$$

$$Y_1^0 \sim \cos \theta$$

$$Y_2^0 \sim (3 \cos^2 \theta - 1)$$

radiation: electromagnetic field in the z direction

$$\mu_z = \mu \cos \theta$$

$$Y_0^0 \rightarrow Y_1^0$$

$$\mu \frac{\sqrt{3}}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta = \mu \frac{\sqrt{3}}{3}$$

General selection rule: $\Delta J = \pm 1$

Rotational spectroscopy is an important method for determining geometries of small molecules.

$${}^1\text{H}{}^{35}\text{Cl} \rightarrow B = 10.59342 \text{ cm}^{-1}$$

Ex.

$$B = \frac{h}{8\pi^2 \mu c r_o^2} \Rightarrow r_o = 1.274553 \times 10^{-10} \text{ m}$$

In general, $\Delta E_{\text{rot}} \ll kT \Rightarrow$ many levels are populated

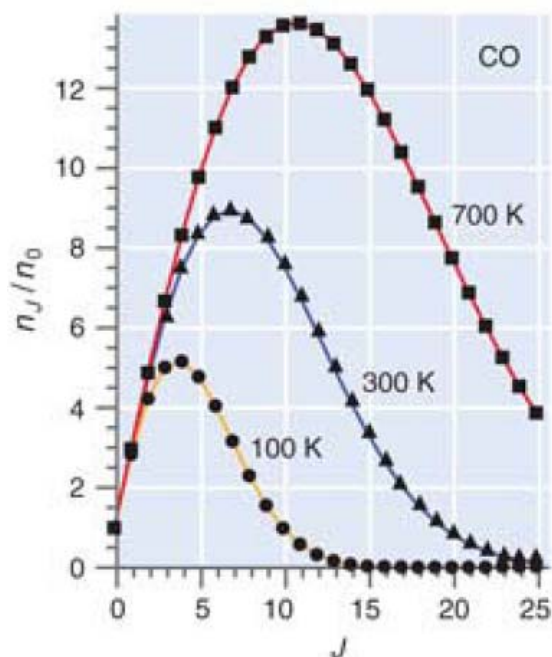
microwave spectroscopy: pure rotational transitions

infrared spectroscopy: vibrational and rotational transitions

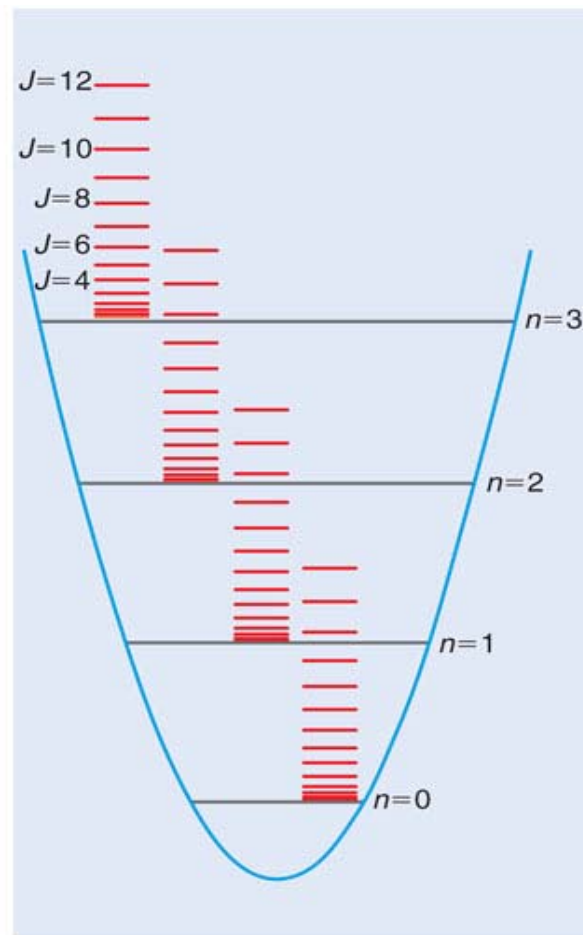
Population of rotational levels

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(\varepsilon_j - \varepsilon_0)/kT} = (2J + 1) e^{-\hbar^2 J(J+1)/2IkT}$$

\uparrow
 degeneracy



rotational distributions for CO.
 At 300 K, even levels as high as
 J = 20 have significant population.



$$E_0 = 0$$

$$E_1 = 2(1)hcB$$

$$E_2 = 3(2)hcB$$

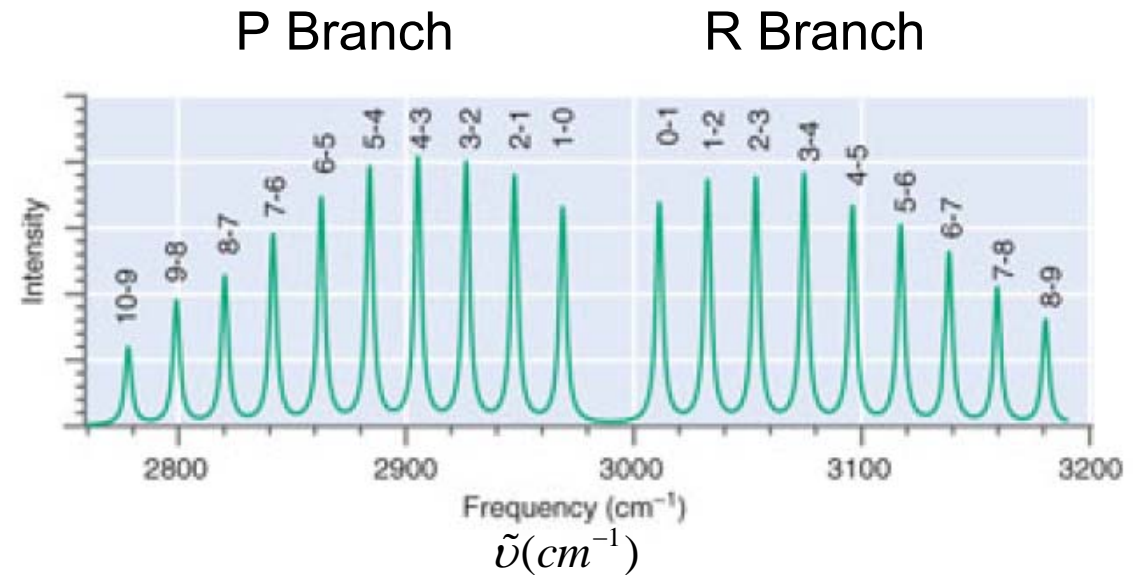
$$E_4 = 4(3)hcB$$

$$0 \rightarrow 1 \quad 2hcB$$

$$1 \rightarrow 2 \quad 4hcB$$

$$1 \rightarrow 0 \quad -2hcB$$

$$2 \rightarrow 1 \quad -4hcB$$



gap between branches = $4hcB$

In some polyatomic molecules, $\Delta J = 0$ (Q branch) is seen in vibrational transitions.

Fourier Transform IR

essentially expose the molecule to all frequencies
at once → intensity vs. time

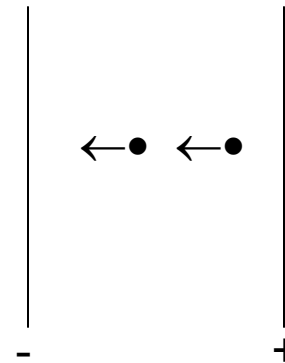


I vs. frequency
fourier transform

Raman Spectroscopy

Consider a molecule in a field $E = E_0 \cos(2\pi\nu t)$

the field distorts the molecule, inducing a
time-dependent dipole



$$\mu_{ind}(t) = \alpha E_0 \cos(2\pi\nu t)$$

polarizability

$$\alpha(x) = \alpha(x_e) + x \left(\frac{d\alpha}{dx} \right)_{x=x_e} + \dots, \quad x = \text{bondlength}$$

$$x(t) = x_{\max} \cos(2\pi\nu_{vib} t)$$

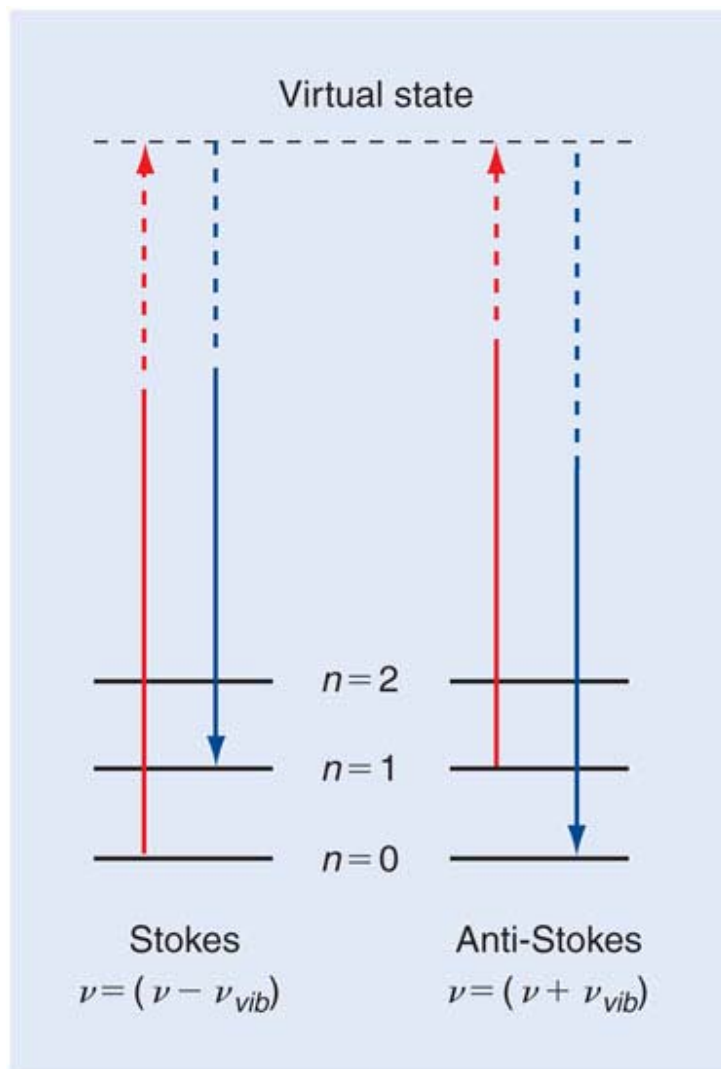
$$\mu_{ind}(t) = \alpha(x_e) E_0 \cos(2\pi\nu t) + \left(\frac{d\alpha}{dx} \right)_{x_e} x_{\max} E_0 \left[\cos(2\pi\nu + 2\pi\nu_{vib})t + \cos(2\pi\nu - 2\pi\nu_{vib})t \right]$$

light will be scattered at original (incident) ν

$$\nu + \nu_{vib}$$

$$\nu - \nu_{vib}$$

Rayleigh
anti-stokes
Stokes



Need $\frac{d\alpha}{dx} \neq 0$ for vibration to be Raman active

For H_2 , N_2 , and CO_2 (symmetric stretch), this is true. So can observe these vibrations in Raman spectroscopy although not in IR spectroscopy.

In general, population of $n = 0 \gg$ population $n = 1$, so Stokes dominates.

Raman vibrational transitions are also accompanied by rotations

for linear rotors, $\Delta J = 0, \pm 2$

for symmetric rotors, $\Delta J = 0, \pm 1, \pm 2$
(example NH_3)