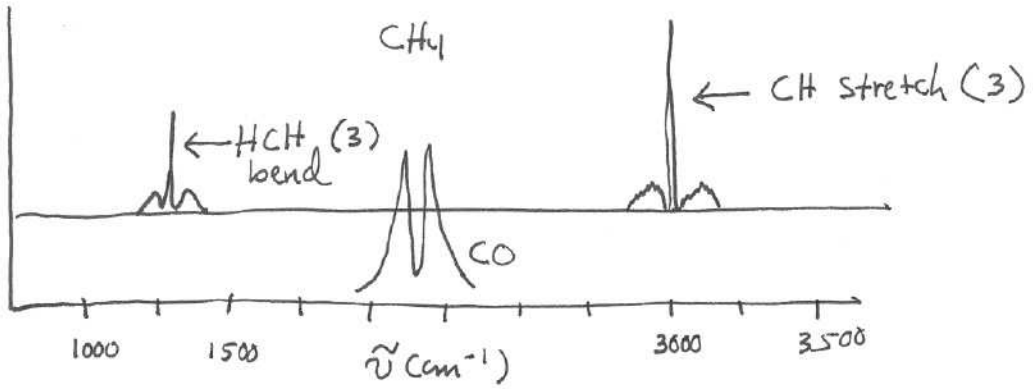
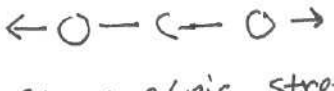
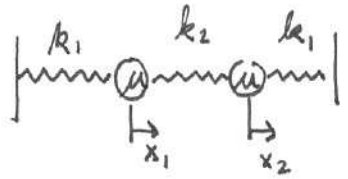


The extra structure in the above spectra is a consequence of rotational transitions accompanying the vibrational transitions.

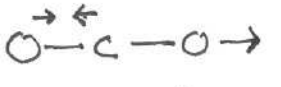
In solution the rotational lines are not resolved → broad bands



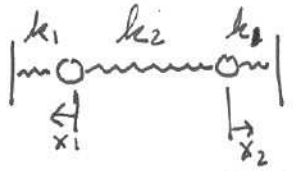
symmetric stretch



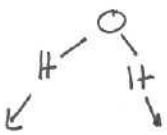
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_1}{\mu}}$$



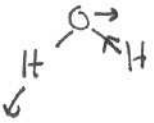
asymmetric stretch



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



symmetric
3657 cm⁻¹



asymmetric
3756 cm⁻¹

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

Need a permanent dipole moment for a rotational transition

Rotational energy: $E = \frac{\hbar^2}{2\mu r_0^2} J(J+1) = \frac{h^2}{8\pi^2 \mu r_0^2} J(J+1) = hcBJ(J+1)$

B = rotational constant in cm^{-1}.

$J \to J+1$: $\Delta E_+ = 2hcB(J+1)$

$J \to J-1$: $\Delta E_- = -2hcBJ$

$0 \to 1$	$2hcB$
$1 \to 2$	$4hcB$
$2 \to 3$	$6hcB$
$3 \to 4$	$8hcB$

energies of transitions

$Y_0^0 \sim 1$

$Y_1^0 \sim \cos\theta$

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

radiation: electromagnetic field in the z direction

$\mu_z = \mu\cos\theta$

$Y_0^0 \to Y_1^0$

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

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

Ex. $^1H^{35}Cl \longrightarrow B = 10.59342\ cm^{-1}$

$$B = \frac{h}{8\pi^2 \mu c r_0^2} \Rightarrow r_0 = 1.274553 \times 10^{-10}\ m$$

In general $\Delta E_{rot.} << kT \Rightarrow$ many levels are populated

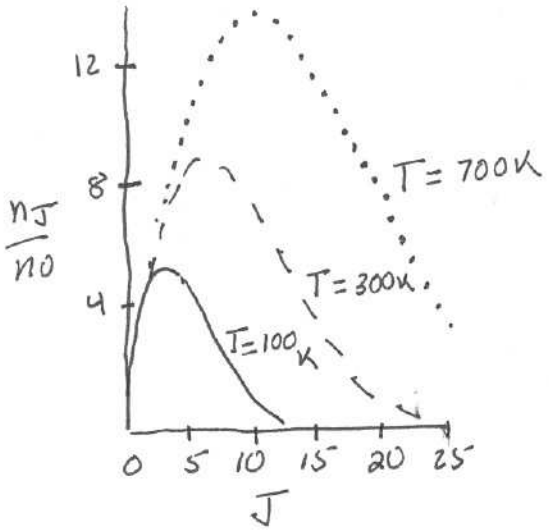
microwave spectroscopy: pure rotational transitions

infrared spectroscopy: vibrational + rotational transitions

Population of rotational levels

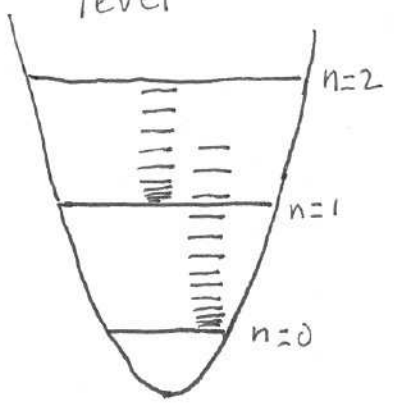
$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(\varepsilon_j - \varepsilon_0)/kT} = (2J+1)\, e^{-\hbar^2 J(J+1)/2IkT}$$

degeneracy



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

There are multiple rot. levels associated with each vibr. level



$E_0 = 0$

$E_1 = 2(1)\, hcB$

$E_2 = 3(2)\, hcB$

$E_4 = 4(3)\, hcB$

$0 \to 1$	$2hcB$
$1 \to 2$	$4hcB$
$1 \to 0$	$-2hcB$
$2 \to 1$	$-4hcB$

HCl
T = 300 K
n = 0 → 1

P Branch R branch

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

Allows spectrum to be determined much faster

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

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

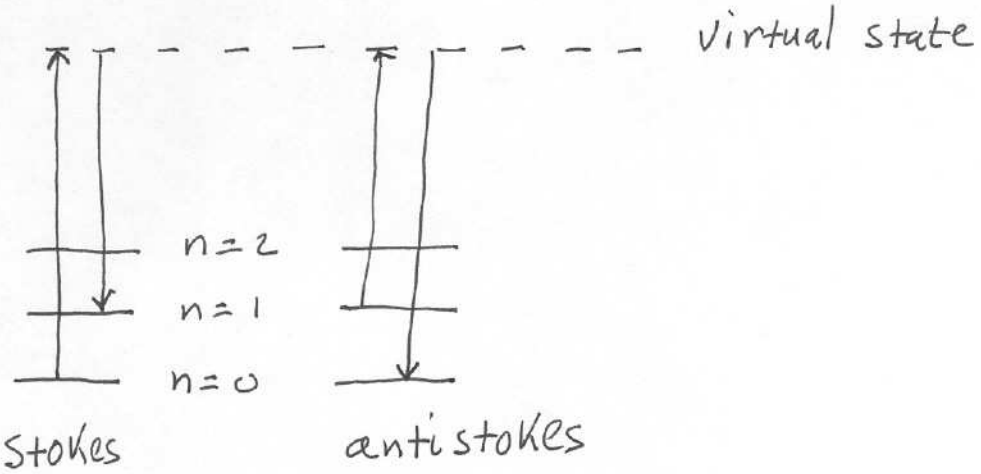
$$x(t) = x_{max} \cos(2\pi\nu_{vib} t)$$

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

light will be scattered at original (incident) ν — Rayleigh

$\nu + \nu_{vib}$ — anti-stokes

$\nu - \nu_{vib}$ — stokes



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

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

In general population of $n=0 \gg n=1$, 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)