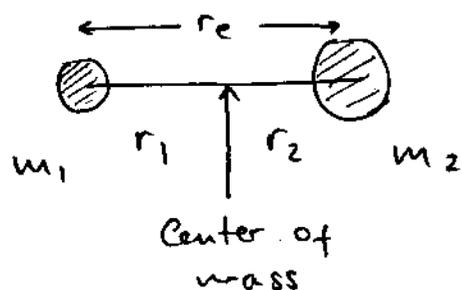


Vibrational spectroscopy

CH 3 @ HB

Diatomic molecules: Rotations and Vibrations



Center of mass:

General definition:

$$\vec{r}_c = \frac{\sum m_i \vec{r}_i}{\sum m_i}$$

Diatomic molecule:

The origin of the coordinate system $\vec{r}_c = 0$ \longrightarrow $\vec{r}_c = \frac{m_1}{m_1+m_2} \vec{r}_1 + \frac{m_2}{m_1+m_2} \vec{r}_2$

$\vec{r}_c = 0$

$$m_1 r_1 = m_2 r_2$$

Moment of inertia:

$$I = \sum_i m_i r_i^2$$

Diatomic molecule:

$$I = \frac{m_1 m_2}{m_1 + m_2} r_e^2 = \mu r_e^2$$

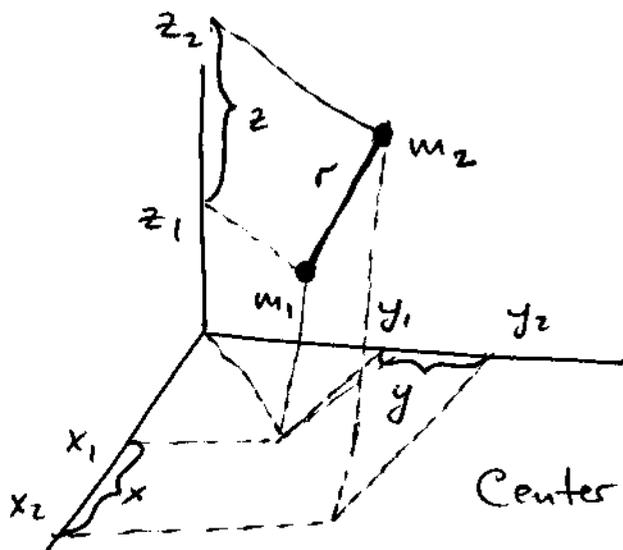
$$\mu = \frac{m_1 m_2}{m_1 + m_2} \leftarrow \text{reduced mass}$$

$$r_2 = \frac{\mu}{m_2} r_e$$

$$r_1 = \frac{\mu}{m_1} r_e$$

$$I = \frac{\mu^2}{m_2} r_e^2 + \frac{\mu^2}{m_1} r_e^2 = \mu r_e^2$$

Schrödinger equation: Vibrations and Rotations



$$\left[-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V \right] \Psi_T = E_T \Psi_T$$

total wavefunction
total energy

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

Center-of-mass coordinates:

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$X = x_2 - x_1$$

$$Y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$$

$$y = y_2 - y_1$$

$$Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

$$z = z_2 - z_1$$

Derivatives:

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial X} \frac{\partial X}{\partial x_1} + \frac{\partial}{\partial x} \frac{\partial x}{\partial x_1} = \frac{\partial}{\partial X} \frac{m_1}{M} - \frac{\partial}{\partial x}$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial^2}{\partial X^2} \frac{m_1^2}{M^2} - \frac{m_1}{M} \frac{\partial^2}{\partial x \partial X} + \frac{\partial^2}{\partial x^2}$$

$$\frac{\partial^2}{\partial x_2^2} = \frac{m_2^2}{M^2} \frac{\partial^2}{\partial X^2} + \frac{m_2}{M} \frac{\partial^2}{\partial x \partial X} + \frac{\partial^2}{\partial x^2}$$

$$\frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2^2} = \frac{1}{M} \frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial x^2}$$

$$= \frac{1}{M} \frac{\partial^2}{\partial X^2} + M \frac{\partial^2}{\partial x^2}$$

$$\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 = \frac{1}{M} \underbrace{\left[\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right]}_{\nabla_R^2} + \frac{1}{M} \underbrace{\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]}_{\nabla_r^2}$$

Splitting of the wave function

Schrödinger equation:

$$\left[-\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 \right] \Psi_T = E_T \Psi_T$$

$$\Psi_T = \Psi_t(x, y, z) \Psi_{rv}(x, y, z)$$

$$E_T = E_t + E_{rv}$$

$$-\frac{\hbar^2}{2M} \nabla_R^2 \Psi_t = E_t \Psi_t$$

describes translational motion of a molecule

$$\left[-\frac{\hbar^2}{2\mu} \nabla_r^2 + V(x, y, z) \right] \Psi_{rv} = E_{rv} \Psi_{rv}$$

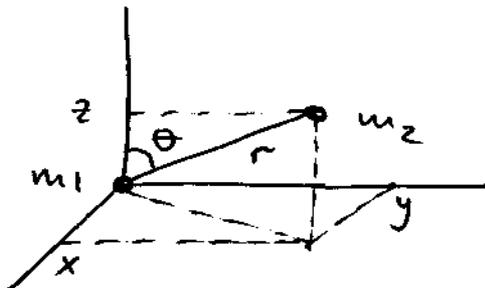
rotations + vibrations

Transition to polar coordinates:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$



$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2}$$

$$\Psi_{rv} = \underbrace{R(r)}_{\Psi_{vib}} \underbrace{\Theta(\theta) \Phi(\phi)}_{\Psi_{rot}}$$

Ψ_{vib}

Ψ_{rot}

Rotational wave functions

Eigenfunctions of the angular momentum operator are spherical harmonics $Y_{Jm}(\theta, \phi)$

$$\hat{L}^2 Y_{Jm}(\theta, \phi) = \hbar^2 \underline{J(J+1)} Y_{Jm}(\theta, \phi)$$

rotational quantum number

$$\nabla^2 \Psi_{rv} = \Psi_{rot} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{J(J+1)}{r^2} \right] R(r)$$

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - J(J+1)R + \frac{2Mr^2}{\hbar^2} [E_{rv} - V(r)] R = 0$$

this is the Schrödinger equation for the vibrational wave function

The solution of this equation is

$$\Psi_v = N_v \underline{H_v(q)} e^{-\frac{\alpha q^2}{2}}$$

Hermite polynomial

$$\alpha = \frac{\sqrt{Mk}}{\hbar}$$

For the potential

$$V(r) = \frac{1}{2} k (r - r_e)^2$$

Energy of a diatomic molecule

$$E_{v,J} = \underbrace{h\nu \left(v + \frac{1}{2}\right)}_{\text{energy of the vibrational motion}} + \underbrace{BJ(J+1)}_{\text{energy of rotations}} - \underbrace{DJ^2(J+1)^2}_{\text{centrifugal distortion, measures the increase of Bond length resulting from rotations of the molecule}}$$

energy of the vibrational motion

energy of rotations

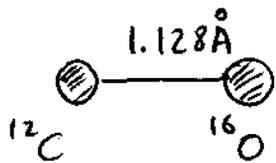
centrifugal distortion, measures the increase of Bond length resulting from rotations of the molecule

Rotational energy:

$$E_J = \frac{h^2}{2I} J(J+1), \quad B = \frac{h^2}{2I} = \frac{h^2}{2\mu r_e^2}$$

$$\bar{E}(\text{cm}^{-1}) = \frac{E(\text{joules})}{h(\text{joule-s}) \cdot c(\text{m/s}) \cdot 100(\text{cm/m})}$$

\uparrow $6.6262 \times 10^{-34} \text{ J s}$ \uparrow $3 \times 10^8 \text{ m/s}$



$$\mu = \frac{12.0 \times 16}{16 + 12} = \frac{6.86}{6.02 \times 10^{26}} = 1.14 \times 10^{-26} \text{ kg}$$

$$I = \mu r_e^2 = 1.449 \times 10^{-46} \text{ kg m}^2$$

$$E_J = \frac{(1.06 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1})^2}{2 \times 1.449 \times 10^{-46} \text{ kg m}^2} J(J+1) = 1.93 J(J+1) \text{ cm}^{-1}$$

$$1 \text{ cm}^{-1} = 30 \text{ GHz}$$

$$\text{FM: } 88 - 108 \text{ MHz} \approx 0.1 \text{ GHz}$$

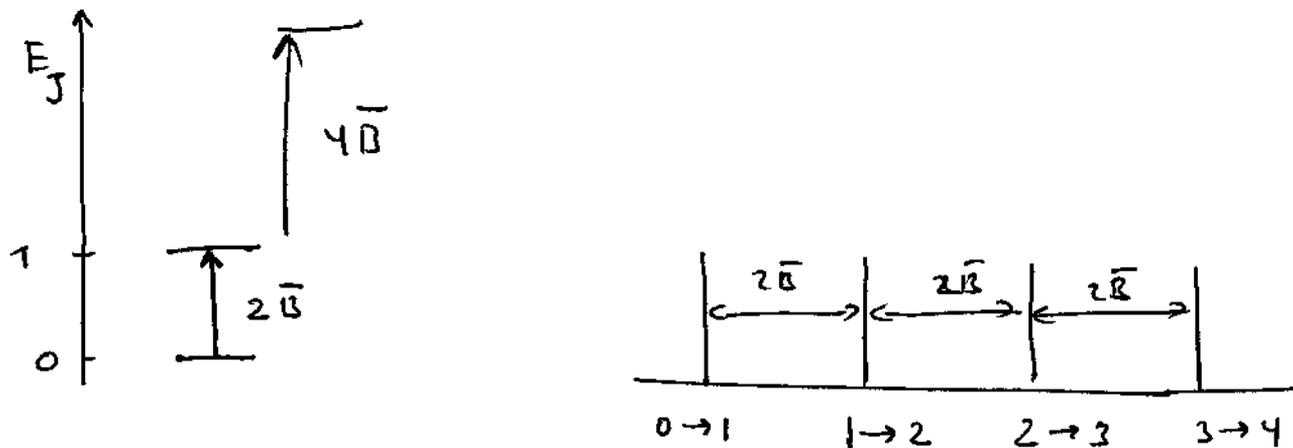
Rotational spectrum

Selection rules for the rigid rotor:

$$J \rightarrow J \pm 1$$

Absorption spectrum

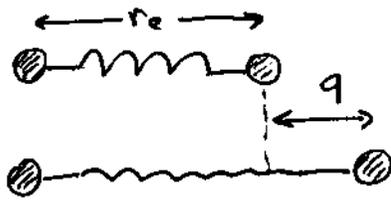
$$\Delta \bar{E}_{J+1} = \bar{B}(J+1)(J+2) - \bar{B}J(J+1) = 2\bar{B}(J+1)$$



For a nonrigid rotor

$$E_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$$

Harmonic potential



Hook's law:

$$\text{restoring force} = -kq$$

force constant

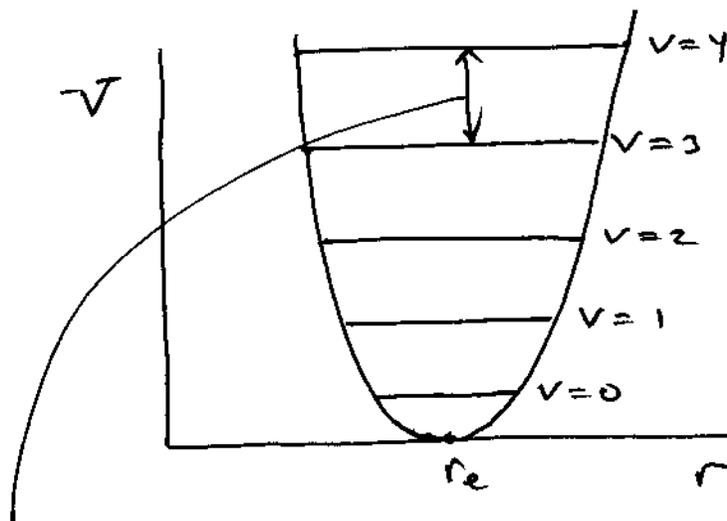
$$dV = -f dq = kq dq$$

$$V = \frac{1}{2} kq^2$$

Quantum mechanical treatment of the harmonic oscillator gives the energy in terms of the vibrational quantum number ν :

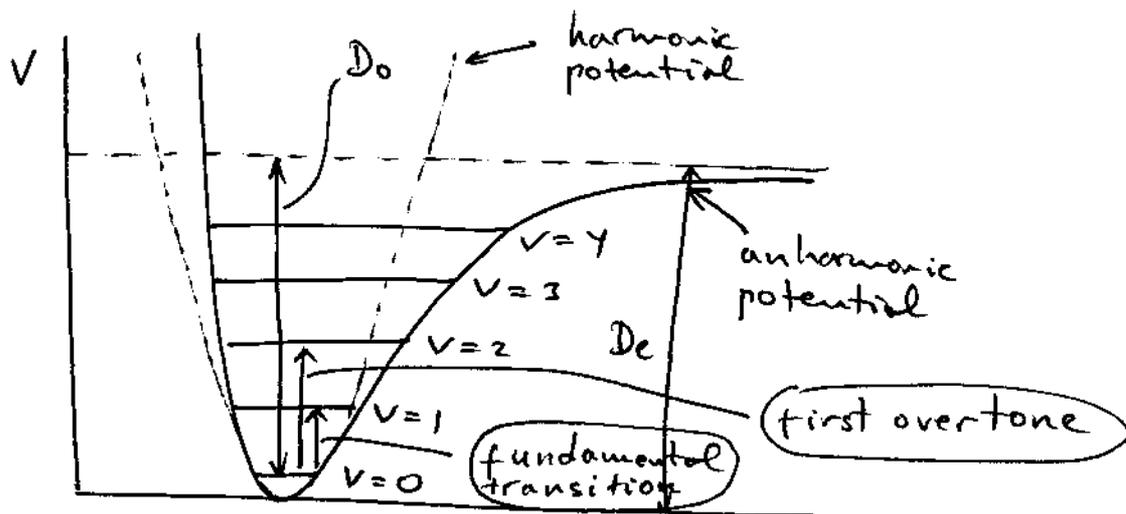
$$E_\nu = h\nu(\nu + \frac{1}{2}), \quad \omega = \sqrt{\frac{k}{m}}, \quad \nu = 0, 1, 2, \dots$$

$$E_0 = E(\nu=0) = \frac{h\nu}{2} \leftarrow \text{zero point energy}$$



equal spacing between the energy levels equal to $h\nu$

The anharmonic oscillator



Morse potential:

$$V = D_e (1 - e^{-\rho q})^2$$

$$\bar{E}_v = \bar{\omega}_e (v + \frac{1}{2}) - \bar{\omega}_e x_e (v + \frac{1}{2})^2$$

Vibrational spacing decreases with increasing v for the anharmonic potential.

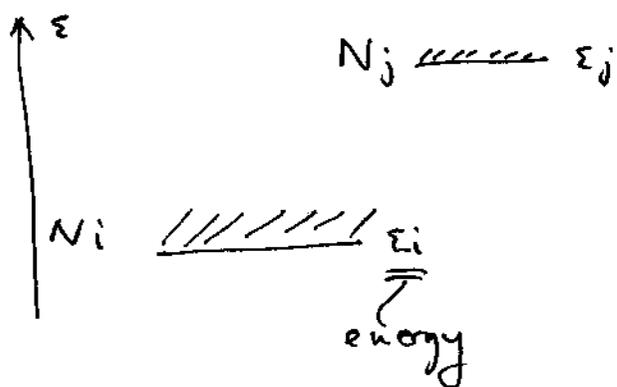
$$E_{v,J} = (v + \frac{1}{2}) h \bar{\omega}_e - (v + \frac{1}{2})^2 h \bar{\omega}_e x_e + B_e J(J+1)$$

$$- D J^2(J+1)^2 - \underline{\underline{\alpha_e (v + \frac{1}{2}) J(J+1)}}$$

the interaction between vibration and rotation

The population of energy levels

The Maxwell-Boltzmann distribution of populations



$$\frac{N_j}{N_i} = \frac{g_j e^{-\epsilon_j/kT}}{g_i e^{-\epsilon_i/kT}}$$

g_j and g_i are degeneracies of j th and i th states

Energy level diagram showing two levels, ϵ_i and ϵ_j , with energy difference $\Delta\epsilon = \epsilon_j - \epsilon_i$. The population ratio is given as $\frac{N_j}{N_i} = e^{-\frac{\Delta\epsilon}{kT}}$.

Energy level diagram showing two levels, ϵ_i and ϵ_j , with energy difference $\Delta\epsilon$. The population ratio is given as $\frac{N_j}{N_i} = \frac{1}{2} e^{-\frac{\Delta\epsilon}{kT}}$.

For harmonic oscillator $g_v = 1$ (all states are not degenerate) and

$$\frac{N_v}{N_0} = \frac{e^{-(v+1/2)\frac{h\nu}{kT}}}{e^{-\frac{1}{2}\frac{h\nu}{kT}}} = e^{-v\frac{h\nu}{kT}}$$

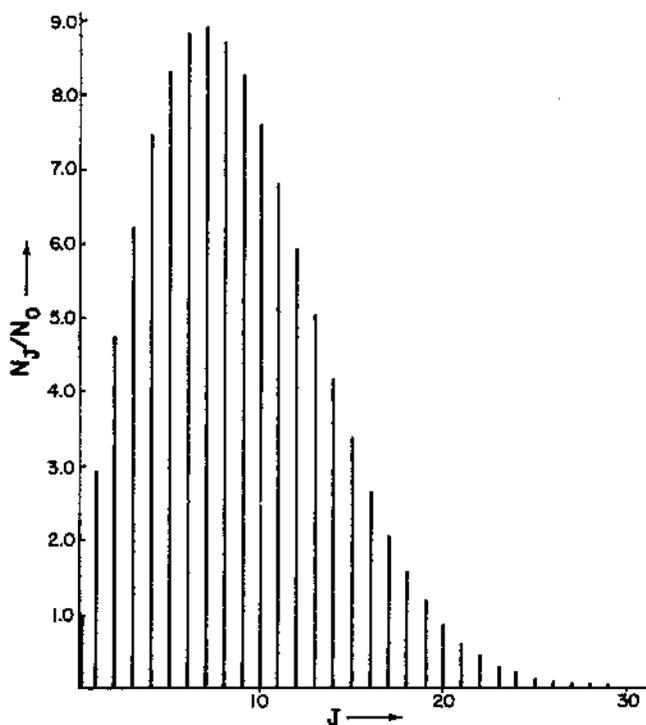
$$kT \approx 200 \text{ cm}^{-1} \text{ at } T \approx 300 \text{ K}$$

	$\bar{\omega} (\text{cm}^{-1})$	$1/\theta$
H_2	4159	2.2×10^{-9}
I_2	213	0.359

Population of rotational states

- * ΔE for rotations is much smaller than the splitting between vibrational levels
- * The J th rotational level is $(2J+1)$ -fold degenerate

$$\frac{N_J}{N_0} = \frac{(2J+1) e^{-BJ(J+1)/kT}}{(2 \times 0 + 1) e^{-B \cdot 0(0+1)/kT}} = (2J+1) e^{-BJ(J+1)/kT}$$



$$\frac{d}{dJ} \frac{N_J}{N_0} = 0 \leftarrow J_{\max}$$

$$\frac{d}{dJ} \frac{N_J}{N_0} = 2 e^{-\frac{BJ(J+1)}{kT}} - (2J+1)^2 \frac{B}{kT} e^{-\frac{BJ(J+1)}{kT}} = 0$$

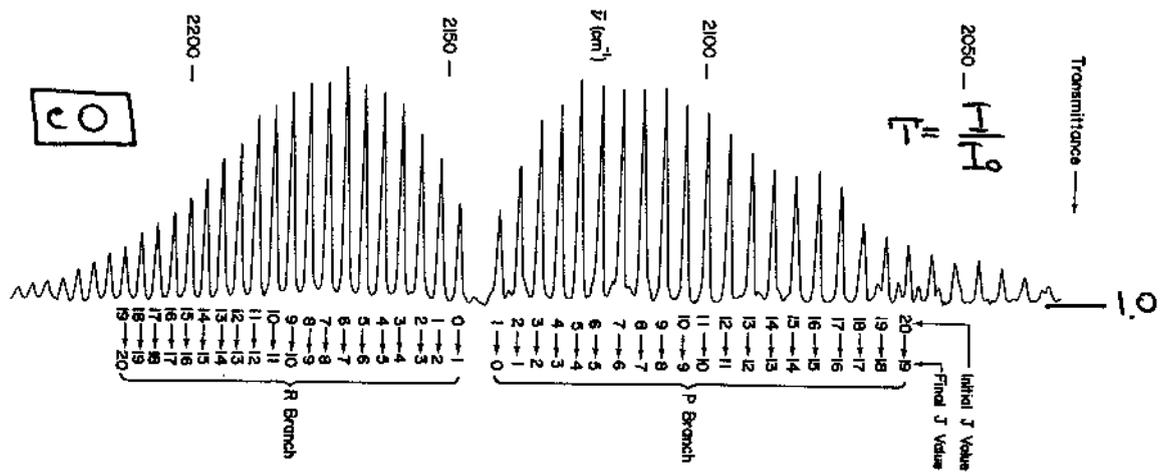
$$2J_{\max} + 1 = \sqrt{\frac{2kT}{B}}$$

$$J_{\max} = -\frac{1}{2} + \frac{1}{2} \sqrt{\frac{2kT}{B}}$$

Fig. 3-18. Relative thermal populations of the rotational energy levels of CO at 300 K.

Homework: Evaluate the temperature at which the maximum in the rotational progression disappears ($J_{\max} < 2$). Assume $B = 4 \text{ cm}^{-1}$.

R and P branches



Selection rules for vibrational-rotational transitions (IR spectrum):

$$\Delta v = \pm 1$$

$$\Delta J = \pm 1$$

For the vibrational absorption $v=0 \rightarrow v=1$
rotational transitions $J \rightarrow J \pm 1$ are allowed:

$$(0, J) \rightarrow (1, J \pm 1)$$

P-branch: $(0, J) \rightarrow (1, J-1)$, $\Delta J = -1$

R-branch: $(0, J) \rightarrow (1, J+1)$, $\Delta J = +1$

Q-branch: $(0, J) \rightarrow (1, J)$ ← is not allowed by selection rules for IR transitions

Vibrational-rotational energies

Rotational energy levels:

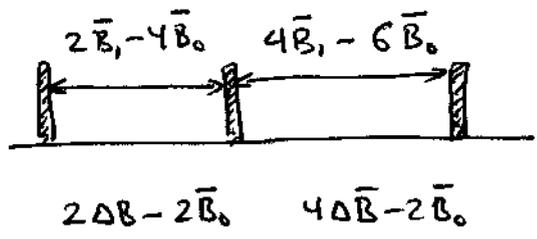
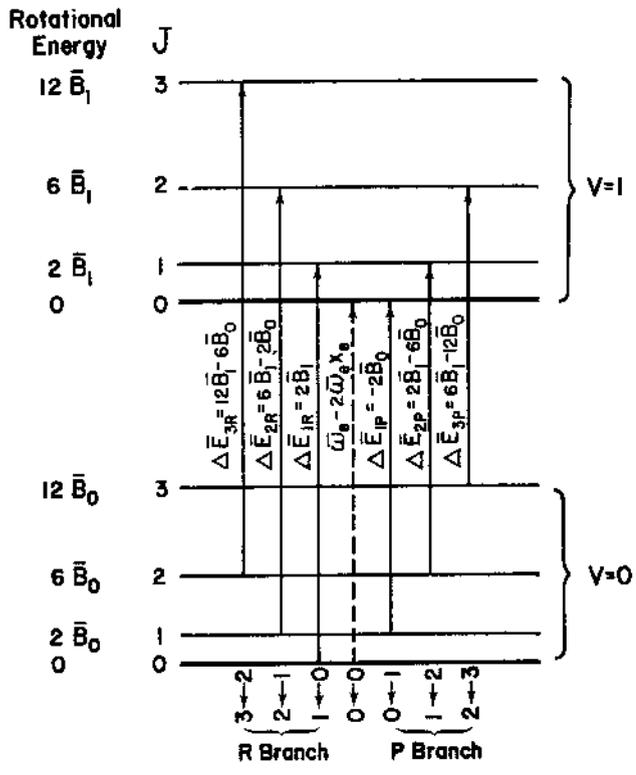
$$\bar{E}_j = \bar{B} J(J+1), \quad \bar{B} = \frac{h}{800\pi^2 I c} = \frac{h}{800\pi^2 \mu r^2 c}$$

B is different for each vibrational state because the equilibrium distance changes

$$B_v = \frac{h}{800\pi^2 \mu r_v^2 c} \quad \text{depends on the vibrational state}$$

Symmetry and spectroscopy

P Branch:

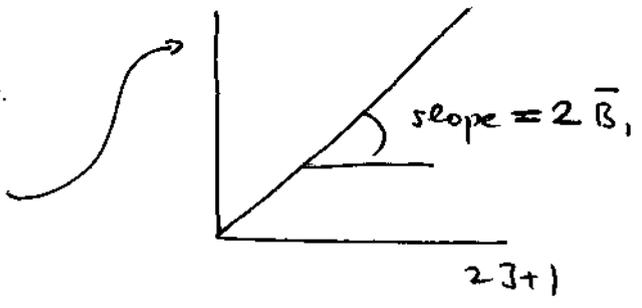


Because of the difference in rotational constants the spacing between the rotational lines is not constant

Fig. 3-21. Some energy levels and transitions of a rotating anharmonic oscillator.

$$\bar{V}_R(J) - \bar{V}_P(J) = 2B_1(2J+1)$$

$$\bar{V}_R(J) - \bar{V}_P(J+2) = 2B_0(2J+3)$$



Normal coordinates (normal modes)

For a nonlinear molecule with n atoms there are $3n-6$ modes of vibration. A linear molecule will have $3n-5$ modes of vibration.

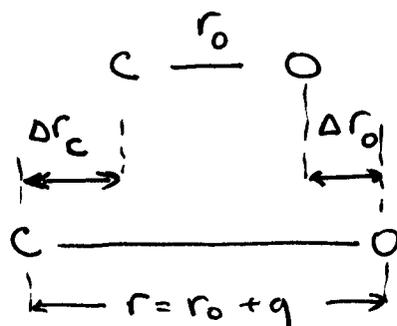
The complete set of molecular vibrations is the result of the superposition of a number of relatively simple vibrations known as the normal modes. Each normal mode has a fixed frequency.

Diatomic molecule:

$$q = r - r_0 = \Delta r_C + \Delta r_O$$

The center of mass does not move:

$$m_C \Delta r_C = m_O \Delta r_O$$



$$\frac{\Delta r_C}{\Delta r_O} = \frac{m_O}{m_C} = \frac{16}{12} = \frac{4}{3}$$

q is the normal coordinate

Normal coordinates diagonalize the energy of the molecule:

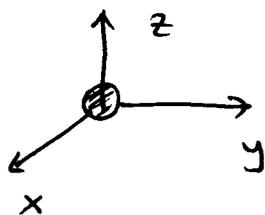
$$K = \frac{1}{2} \sum_i \left(\frac{dq_i}{dt} \right)^2$$

$$V = \frac{1}{2} \sum_i \lambda_i q_i^2$$

Degrees of freedom

Degrees of freedom are independent coordinates that are sufficient to describe the motions of the molecule.

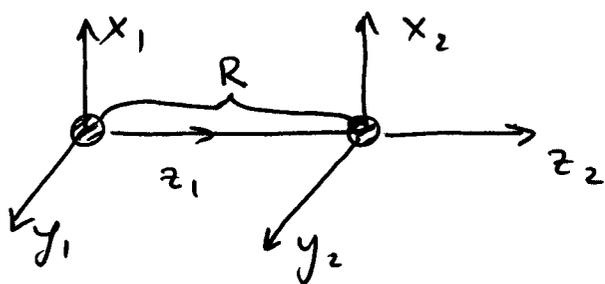
A single particle :



x, y, z are three independent coordinates that completely define the position of the particle

$$NDF = 3$$

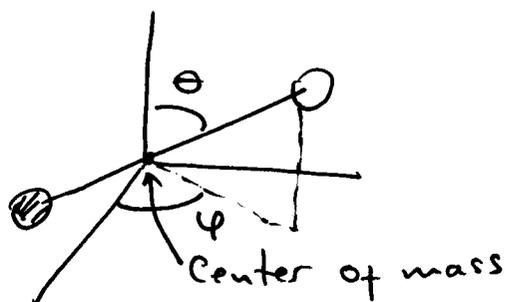
Diatomic molecule :



$x_1, y_1, z_1 + x_2, y_2, z_2$
However, they are not independent since

$$(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 = R^2$$

$$NDF = 6 - 1 = 5$$



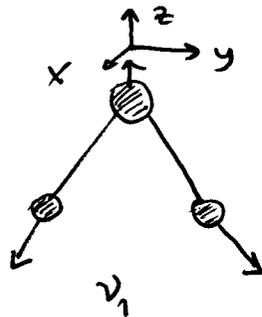
$x_c, y_c, z_c, \theta, \varphi$

$$NDF = 5$$

Symmetries of normal modes

Each normal mode of vibration will form a basis for an irreducible representation of the point group of the molecule.

H₂O

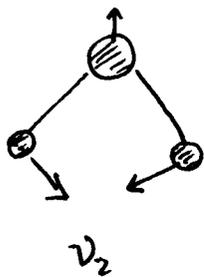


$$C_2 \nu_1 = \nu_1$$

$$\sigma(xz) \nu_1 = \nu_1$$

$$\sigma(yz) \nu_1 = \nu_1$$

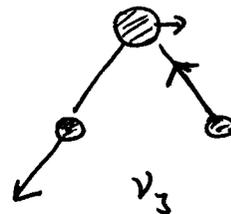
C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
ν_1	1	1	1	1	= a_1



$$C_2 \nu_2 = \nu_2$$

$$\sigma(xz) \nu_2 = \nu_2$$

$$\sigma(yz) \nu_2 = \nu_2$$



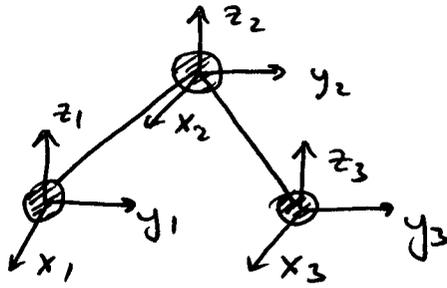
$$C_2 \nu_3 = -\nu_3$$

$$\sigma(xz) \nu_3 = -\nu_3$$

$$\sigma(yz) \nu_3 = \nu_3$$

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
ν_2	1	1	1	1	= a_1
ν_3	1	-1	-1	1	= b_2

Vibrations: irreducible representations



$$E: \quad \begin{aligned} x_1 &\rightarrow x_1, & x_2 &\rightarrow x_2, & \dots \\ y_1 &\rightarrow y_1, & y_2 &\rightarrow y_2, & y_3 \rightarrow y_3 \\ z_1 &\rightarrow z_1, & z_2 &\rightarrow z_2, & z_3 \rightarrow z_3 \end{aligned}$$

$$\begin{pmatrix} 1 & & & & & & & & \\ & 1 & & & & & & & \\ & & 1 & & & & & & \\ & & & 1 & & & & & \\ & & & & 1 & & & & \\ & & & & & 1 & & & \\ & & & & & & 1 & & \\ & & & & & & & 1 & \\ & & & & & & & & 1 \end{pmatrix} \quad 9 \times 9$$

$$\chi(E) = 9$$

$$C_2: \quad \begin{aligned} x_1 &\rightarrow -x_3 & x_2 &\rightarrow -x_2 & x_3 &\rightarrow -x_1 \\ y_1 &\rightarrow -y_3 & y_2 &\rightarrow -y_2 & y_3 &\rightarrow -y_1 \\ z_1 &\rightarrow z_3 & z_2 &\rightarrow z_2 & z_3 &\rightarrow z_1 \end{aligned}$$

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

$$\chi(C_2) = -1$$

Procedure to calculate characters of reducible vibrational representations:

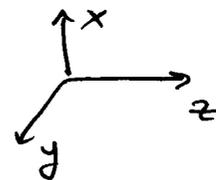
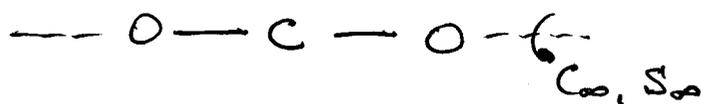
- ①. Determine the number of atoms which do not change location during each symmetry operation
- ②. For each operation, multiply the number of unmoved atoms by the character of $P_{x,y,z}$
- ③. Subtract characters of translations (P_{trans}) and rotations (P_{rot})

P_{trans} is the set of irreducible representations for x, y, z coordinates

P_{rot} are irreducible representations for rotations.

<u>H₂O</u>	<u>C_{2v}</u>	<u>E</u>	<u>C₂</u>	<u>z(xz)</u>	<u>z(yz)</u>	
$P_{x,y,z}$	3	-1	1	1	1	
Atoms	3	1	1	1	3	
P_{tot}	9	-1	1	1	3	$= 3a_1 + a_2 + 2b_1 + 3b_2$
P_{trans}	3	-1	1	1	1	
P_{rot}	3	-1	-1	-1	-1	
P_{vib}	3	1	1	1	3	$= 2a_1 + b_2$

CO₂



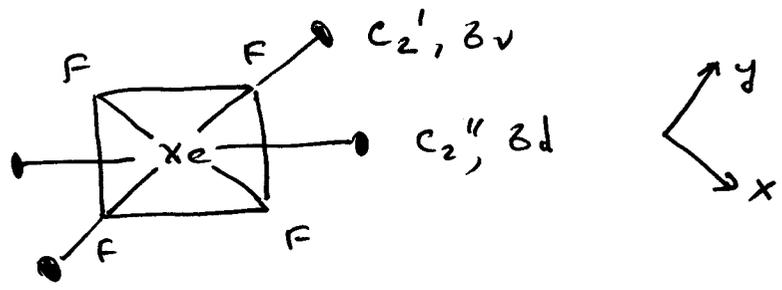
D _{∞h}	E	2 C _{∞^φ}	∞ C _v	i	2 S _{∞^φ}	∞ C ₂	
Σ _g ⁻	1	1	-1	1	1	-1	R _z
Π _g	2	2 cos φ	0	2	-2 cos φ	0	(R _x , R _y)
Σ _u ⁺	1	1	1	-1	-1	-1	z
Π _u	2	2 cos φ	0	-2	2 cos φ	0	(x, y)
ρ _{x,y,z}	3	1 + 2 cos φ	1	-3	-1 + 2 cos φ	-1	
Atoms	3	3	3	1	1	1	
ρ _{tot}	9	3 + 6 cos φ	3	-3	-1 + 2 cos φ	-1	
ρ _{trans}	3	1 + 2 cos φ	1	-3	-1 + 2 cos φ	-1	
ρ _{rot}	2	2 cos φ	0	2	-2 cos φ	0	
ρ _{vib}	4	2 + 2 cos φ	2	-2	2 cos φ	0	

$$\rho_{vib} = \underbrace{\Sigma_g^+ + \Sigma_u^+ + \Pi_u}$$

$$3N - 5 = 3 \times 3 - 5 = 4$$

Two modes transforming as a single degenerate irreducible representation have the same energy and are degenerate.

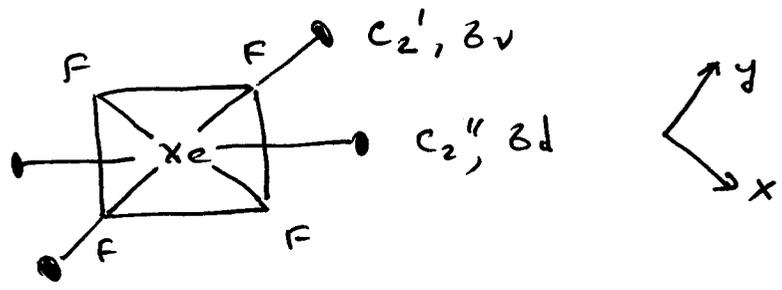
XeF_4



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	C_4	$2C_2$	$2C_2'$
$P_{x,y,z}$	3	1	-1	-1	-1	-3	-1	1	1	1
Atoms	5	1	1	3	1	1	1	5	3	1
P_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	1	-1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
P_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1
P_{vib}	9	-1	1	-1	1	-3	-1	5	3	1

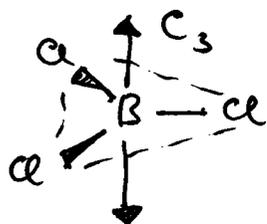
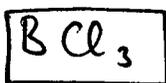
$P_{vib} = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$

XeF_4



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2\sigma_v$	σ_h	$2\sigma_v$	$2\sigma_d$
$P_{x,y,z}$	3	1	-1	-1	-1	-3	-1	1	1	1
Atoms	5	1	1	3	1	1	1	5	3	1
P_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
P_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1
P_{vib}	9	-1	1	-1	1	-3	-1	5	3	1

$P_{vib} = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$

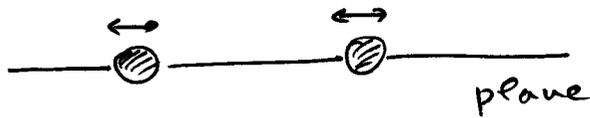


D_{3h}	E	$2C_3$	$2C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	R_z
E'	2	-1	0	2	-1	0	(x, y)
A_1''	1	1	1	-1	-1	-1	z
A_2''	1	1	-1	-1	-1	1	
E''	2	-1	0	-2	1	0	(R_x, R_y)
$P_{x,y,z}$	3	0	-1	1	-2	1	
Atoms	4	1	2	4	1	2	
P_{tot}	12	0	-2	4	-2	2	
P_{rot}	3	0	-1	-1	2	-1	
P_{vib}	6	0	0	4	-2	2	

$P_{vib} = a_1' + a_2'' + 2e'$

Classification of vibrations

ν Stretching vibration

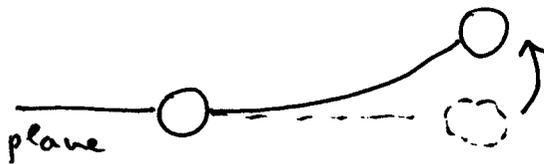


δ in-plane bend

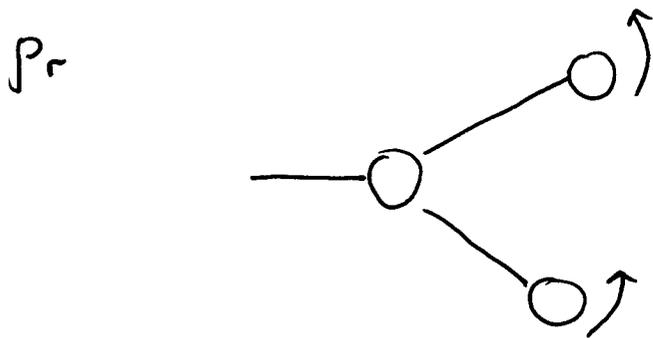
+ toward you
- away from you



δ out-of-plane bend

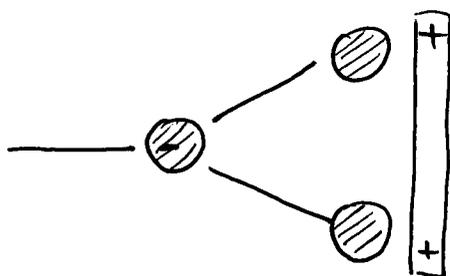


ρ rock - in-plane bend of X-H₂ group



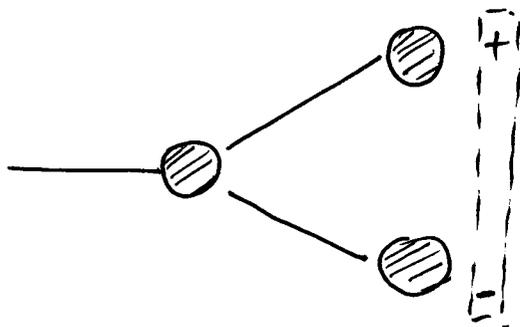
χ WAG - out-of-plane bend of $X-H_2$ group

β_w



τ TWIST - a restricted rotation of an $X-H_2$ group

β_t



π - out of plane

as - asymmetric

s - symmetric

d - degenerate

Vibrational excitations

Wave function

$$\psi_i(v_i)$$

v th vibrational quantum number

i th normal mode

For several vibrational modes (normal modes):

$$\Psi_{\text{vib}} = \psi_1(v_1) \psi_2(v_2) \dots \psi_n(v_n)$$

A fundamental transition corresponds to $0 \rightarrow 1$ excitation of only one vibrational normal mode:

$$\psi_1(0) \psi_2(0) \dots \psi_n(0) \rightarrow \psi_1(0) \dots \psi_i(1) \dots \psi_n(0)$$

The selection rules define which transitions will have zero intensity based on the molecular symmetry.

Transition $v \rightarrow v'$:

$$M_{vv'} = 0 \quad \leftarrow \text{forbidden transition}$$

$$M_{vv'} \neq 0 \quad \leftarrow \text{allowed transition}$$

$$I_{\text{IR}} = M_{vv'} = \langle v | \vec{\mu} | v' \rangle \quad \leftarrow \text{IR active}$$

$$M_{vv'} = \langle v | \vec{\alpha} | v' \rangle \quad \leftarrow \text{Raman active.}$$

Fundamental transitions

- * A vibrational transition is active in IR if the dipole moment of the molecule changes during the vibration.
- * A transition is Raman active if the polarizability of the molecule changes during the vibration.

$$M_{v'v} = \langle v' | \hat{O} | v \rangle \stackrel{\uparrow}{=} \hat{O} \langle v' | v \rangle = \hat{O} \delta_{v'v}$$

if \hat{O} is independent of the vibration

- * For a molecule belonging to a particular point group, the MOs Φ_a, Φ_b, Φ_c will form a basis for some irreducible representation of the group.

- * The integral $\int_{-\infty}^{\infty} \Phi_a \Phi_b dx$ will have a nonzero value only if the direct product $\Gamma_a \times \Gamma_b$ contains the totally symmetric irreducible representation of the point group.

e.g., for C_{4v} $a_2 \times b_2 = B_1$ and

$$\langle \Psi_{a_2} | \Psi_{b_2} \rangle = 0$$

Harmonic wave function:

$$\Psi_i(r) = N_i e^{-\frac{\alpha_i}{2} q_i^2} H_\nu(\underbrace{\sqrt{\alpha_i} q_i}_{\frac{\sqrt{m k_i}}{\hbar}})$$

$$H_0(x) = 1 \quad H_1(x) = 2x$$

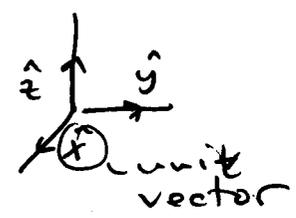
$$H_2(x) = 4x^2 - 2 \quad H_3(x) = 8x^3 - 12x$$

$\Psi_i(0) = N_i e^{-\frac{\alpha_i}{2} q_i^2}$ transforms as the totally symmetric irreducible representation

Even wave functions ($\nu=2, 4, 6, \dots$) are totally symmetric and odd wave functions have the symmetry of the vibration, e.g. $\Gamma(\Psi(1)) = \Gamma(q)$

The wave function of a fundamental transition transforms according to the irreducible representation of the excited normal mode

$$\vec{\mu} = \hat{x} \sum_i e_i x_i + \hat{y} \sum_i e_i y_i + \hat{z} \sum_i e_i z_i$$



$\vec{\mu}$ transforms as $x, y,$ and z

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

The six components of α transform as the binary products $x^2, y^2, z^2, xy, xz, yz$

Selection Rules

IR: $\langle \psi | \vec{\mu} | \psi' \rangle$

Raman: $\langle \psi | \vec{\alpha} | \psi' \rangle$

If $\Gamma[\psi(v)] \times \Gamma[\vec{\mu}] \times \Gamma[\psi(v')]$ contains the totally symmetric irreducible representation, the transition is IR active

If $\Gamma[\psi(v)] \times \Gamma[\vec{\alpha}] \times \Gamma[\psi(v')]$ contains the totally symmetric irreducible representation, the transition is Raman active.

N₂ :

Dash	E	2 cos φ	∞ 3 _v	i	2 sin φ	∞ C ₂	
P _{x,y,z}	3	1+2cosφ	1	-3	-1+2cosφ	-1	
Atoms	2	2	2	0	0	0	
P _{tot}	6	2+4cosφ	2	0	0	0	
P _{tr}	3	1+2cosφ	1	-3	-1+2cosφ	-1	= Σ _u ⁺ + Π _u
P _{rot}	2	2cosφ	0	2	-2cosφ	0	= Π _g
P _{vib}	1	1	1	1	1	1	= Σ _g ⁺

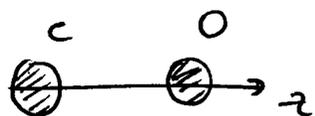
IR: $M_{01} = \int \psi(1) \vec{\mu} \psi(0) d\vec{r}$, $\psi(1) \vec{\mu} \psi(0) \sim \Sigma_g^+ \begin{pmatrix} \delta_u^+ \\ \pi_u \end{pmatrix} \Sigma_g^+ = \begin{pmatrix} \delta_u^+ \\ \pi_u \end{pmatrix}$

Raman: $M_{01} = \int \psi(1) \vec{\alpha} \psi(0) d\vec{r}$, $\psi(1) \vec{\alpha} \psi(0) \sim \Sigma_g^+ \begin{pmatrix} \delta_g^+ \\ \pi_g \\ \delta_g \end{pmatrix} \Sigma_g^+ = \begin{pmatrix} \delta_g^+ \\ \pi_g \\ \delta_g \end{pmatrix}$

CO

$C_{\infty v}$	E	$2C_{\infty}^{\phi}$	∞C_2
$P_{x,y,z}$	3	$1+2\cos\phi$	1
Atoms	2	2	2
P_{tot}	6	$2+4\cos\phi$	2
P_{trans}	3	$1+2\cos\phi$	1
P_{rot}	2	$2\cos\phi$	0
P_{vib}	1	1	1 = δ^+

$$\Psi(1) \vec{M} \Psi(0) \sim \delta^+ \begin{pmatrix} \delta^+ \\ \pi \end{pmatrix} \delta^+ = \begin{pmatrix} \delta^+ \\ \pi \end{pmatrix}$$



Only z-component of \vec{M} is IR active

$$\Psi(1) \vec{\alpha} \Psi(0) \sim \delta^+ \begin{pmatrix} \delta^+ \\ \pi \\ \delta \end{pmatrix} \delta^+ = \begin{pmatrix} \delta^+ \\ \pi \\ \delta \end{pmatrix}$$

Selection rules for fundamental transitions

The only way to get a totally symmetric component in $\psi(1)\hat{O}$ is if one of the components of \hat{O} has the same symmetry as $\psi(1)$.

The only IR active modes will have the symmetries of the three components of $\vec{\mu}$. The only Raman active modes will have the symmetries of the six components of $\hat{\alpha}$.

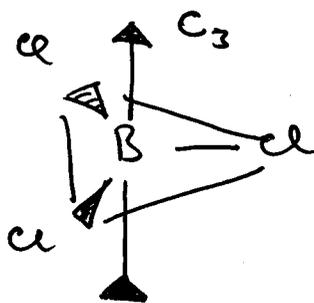
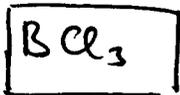
XeF₄

Duh	E	2e _g	e ₂	2e ₂ '	2e ₂ "	i	2d ₄	6h	2g _v	2g _d
P _{x,y,z}	3	1	-1	-1	-1	-3	-1	1	1	1
Atoms	5	1	1	3	1	1	1	5	3	1
P _{tot}	15	1	-1	-3	-1	-3	-1	5	3	1
P _{trans}	3	1	-1	-1	-1	-3	-1	1	1	1
P _{vib}	3	1	-1	-1	-1	3	+1	-1	-1	-1
P _{vib}	9	-1	1	-1	1	-3	-1	5	3	1

$$a(a_{1g}) = \frac{1}{16} [9 - 2 + 1 - 2 + 2 - 3 - 2 + 5 + 6 + 2] = 1$$

$$a(b_{1g}) = \frac{1}{16} [9 + 2 + 1 - 2 - 2 - 3 + 2 + 5 + 2 \times 3 + (-2)] = 1$$

$$P_{vib} = a_{1g} + b_{1g} + b_{2g} + \overset{\mu_z}{a_{2u}} + \overset{(\mu_x, \mu_y)}{b_{2u}} + 2e_u$$



D_{3h}	E	$2C_3$	$3C_2$	$3\sigma_h$	$2S_3$	$3\sigma_v$
$P_{x,y,z}$	3	0	-1	1	-2	1
Atoms	4	1	2	4	1	2
P_{tot}	12	0	-2	4	-2	2
P_{trans}	3	0	-1	1	-2	1
P_{rot}	3	0	-1	-1	2	-1
P_{vis}	6	0	0	4	-2	2

$$a(a_1') = \frac{1}{12} [6 + 4 - 4 + 6] = 1$$

$$a(a_2'') = \frac{1}{12} [6 - 4 + 4 + 6] = 1$$

$$a(e') = \frac{1}{12} [6 \times 2 + 8 + 4] = 2$$

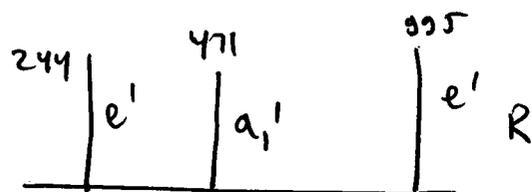
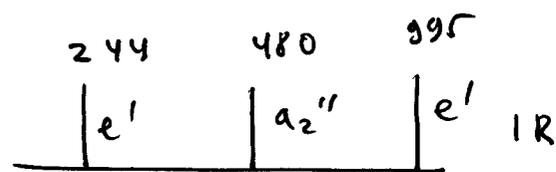
$$P_{vis} = a_1' + 2e' + a_2''$$

x^2+y^2, z^2

(μ_x, μ_y)

x^2-y^2, xy

μ_z



Polarization

$$\Gamma_{\text{vib}}(\text{H}_2\text{O}) = 2a_1 + b_2$$

\uparrow
 $\nu_1 + \nu_2$

\uparrow
 ν_3

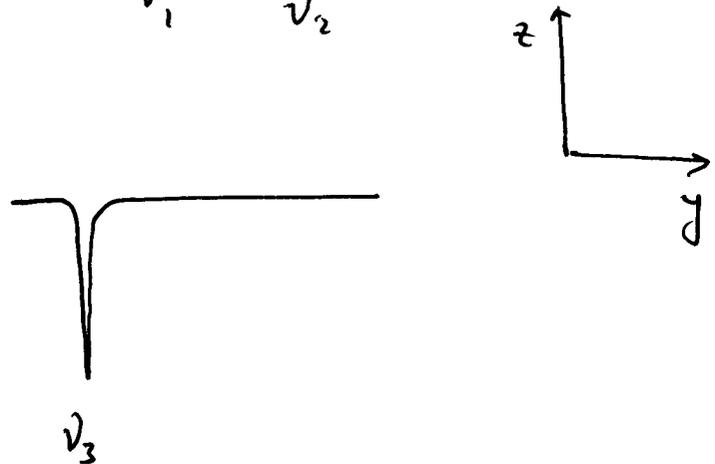
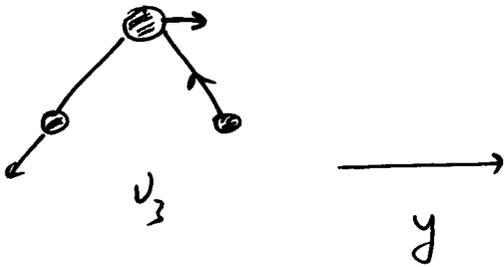
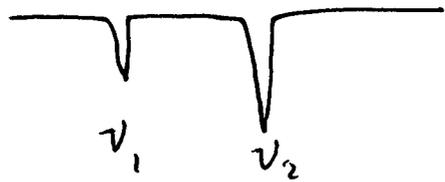
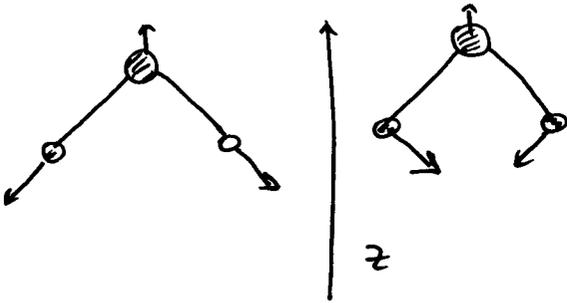
$$\hat{M} = \begin{pmatrix} \hat{M}_x \\ \hat{M}_y \\ \hat{M}_z \end{pmatrix} \leftarrow \begin{pmatrix} b_1 \\ b_2 \\ a_1 \end{pmatrix}$$

$\nu_1 + \nu_2$: $\Psi(1) \hat{\mu} \Psi(0) \sim a_1 \begin{pmatrix} b_1 \\ b_2 \\ a_1 \end{pmatrix} a_1 = \begin{pmatrix} b_1 \\ b_2 \\ \boxed{a_1} \end{pmatrix}$

z -polarization

ν_3 : $\Psi(1) \hat{\mu} \Psi(0) \sim b_2 \begin{pmatrix} b_1 \\ b_2 \\ a_1 \end{pmatrix} a_1 = \begin{pmatrix} a_2 \\ \boxed{a_1} \\ b_2 \end{pmatrix}$

y -polarized

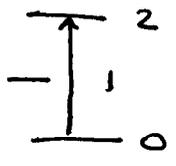


Overtones, Combination bands, Hot bands

Overtone: $0, \dots, 0 \rightarrow n+1, 0, 0 \quad (n > 0)$

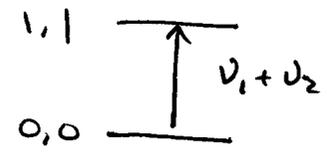
example: $\psi_1(0) \rightarrow \psi_1(2)$

second overtone of ν_2



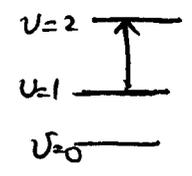
Combination Band: $0, 0, \dots, 0 \rightarrow n+1, k+1, \dots$

example: $\psi_1(0) \psi_2(0) \rightarrow \psi_1(1) \psi_2(1)$



Hot Band: $0, n+1, \dots, 0 \rightarrow 0, n+k, \dots, 0$

example: $\psi_1(1) \psi_2(0) \rightarrow \psi_1(2) \psi_2(0)$



Overtone selection rules:

$$M = \langle \psi_e | \hat{O} | \psi_g \rangle$$

If ν_i is not degenerate,

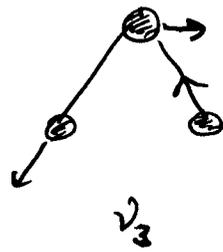
ψ_e is totally symmetric for ν even

ψ_e transforms as ν_i if ν is odd

For example, for ν_1 of b_2 symmetry

- $\nu=3$ — b_2
- $\nu=2$ — a_1
- $\nu=1$ — b_2
- $\nu=0$ — a_1

Example: Overtones of b_2 vibrations of H_2O



Transition	IR	Raman
$0 \rightarrow 1$	M_y	$y z$
$0 \rightarrow 2$	M_z	z^2 , Polarized
$0 \rightarrow 3$	M_y	$y z$

ν_3 is double degenerate (e)

fundamental: $\psi_a(0)\psi_b(0) \rightarrow \begin{matrix} \psi_a(1)\psi_b(0) \\ \psi_a(0)\psi_b(1) \end{matrix}$

first overtone: $\psi_a(0)\psi_b(0) \rightarrow \begin{matrix} \psi_a(2)\psi_b(0) \\ \psi_a(1)\psi_b(1) \\ \psi_a(0)\psi_b(2) \end{matrix}$

The symmetry of $[\psi_a(1)\psi_b(0), \psi_a(0)\psi_b(1)]$ is e;

the symmetry of $[\psi_a(2)\psi_b(0), \psi_a(1)\psi_b(1), \psi_a(0)\psi_b(2)]$

is not e x e

Doubly degenerate vibration (Appendix C)

Recursion formula:

$$\chi_{\nu}^{(R)} = \frac{1}{2} [\chi(R) \chi_{\nu-1}(R) + \chi(R^{\nu})]$$

symmetry operation

νth energy level

C_{4v}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
E	2	0	-2	0	0
R	E	C_4	C_2	$2C_2'$	$2C_2''$
R^2	E	C_2	E	E	E
R^3	E	C_4	C_2	$2C_2'$	$2C_2''$
R^4	E	E	E	E	E
$\chi(R)$	2	0	-2	0	0
$\chi(R^2)$	2	-2	2	2	2
$\chi(R^3)$	2	0	-2	0	0
$\chi(R^4)$	2	2	2	2	2
$\chi_1(R)$	2	0	-2	0	0 = e
$\chi_2(R)$	3	-1	3	1	1 = $a_1 + b_1 + b_2$
$\chi_3(R)$	4	0	-4	0	0 = 2e
$\chi_4(R)$	5	1	5	1	1 = $2a_1 + a_2 + b_1 + b_2$

3-29 Find symmetries of $\nu=0,1,2,3$ of e' in D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
e'	2	-1	0	2	-1	0	
R	E	C_3	C_2	σ_h	S_3	σ_v	
R^2	E	C_3	E	E	σ_h	E	
R^3	E	E	C_2	σ_h	σ_h	σ_v	
$\chi(R)$	2	-1	0	2	-1	0	
$\chi(R^2)$	2	-1	2	2	-1	2	
$\chi(R^3)$	2	2	0	2	2	0	
$\chi_1(R)$	2	-1	0	2	-1	0	$= e'$
$\chi_2(R)$	3	0	1	3	0	1	$= e' + a_1'$
$\chi_3(R)$	4	1	0	4	1	0	$= e' + a_1' + a_2'$

$\nu=0 \sim a_1'$, $\nu=1 \sim e'$, $\nu=2 \sim e' + a_1'$, $\nu=3 \sim e' + a_1' + a_2'$

Is the first overtone ($\nu=2$) allowed in IR and Raman?

IR: (x, y) $\begin{pmatrix} e' \\ a_1' \end{pmatrix} \begin{pmatrix} e' \\ a_2'' \end{pmatrix} a_1' = \begin{pmatrix} a_1' + a_2' + e' \\ e'' \end{pmatrix} + \begin{pmatrix} e' \\ a_2'' \end{pmatrix}$

allowed

Raman: $\begin{pmatrix} e' \\ a_1' \end{pmatrix} \begin{pmatrix} a_1' \\ e' \\ e'' \end{pmatrix} a_1' \sim \begin{pmatrix} a_1' + e' + e'' + a_2' \end{pmatrix}$

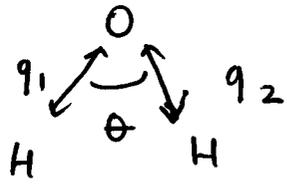
allowed

Symmetry coordinates

Symmetry coordinates analysis:

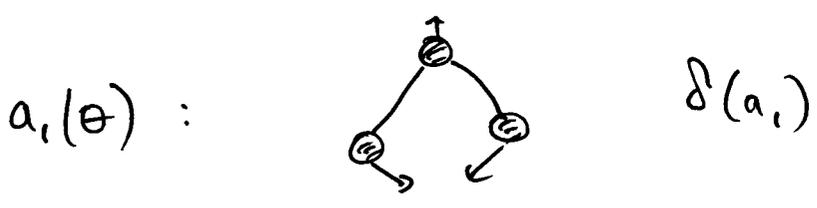
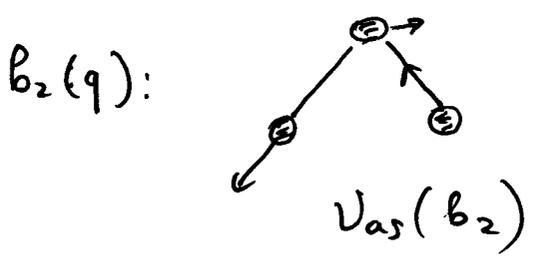
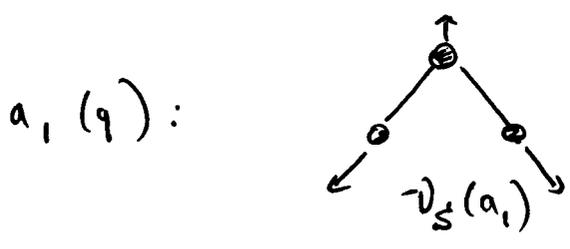
- ①. Obtain the full list of irreducible representations.
- ②. Using a set of $3n - 5/6$ internal coordinates as basis functions generate symmetry coordinates by using projection operator technique

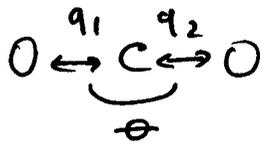
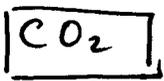
Normal coordinates can be expressed as functions of a set of internal displacement vectors:



internal displacements = $\{q_1, q_2, \theta\}$

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
Γ_q	2	0	0	2	$= a_1 + b_2$
Γ_θ	1	1	1	1	$= a_1$



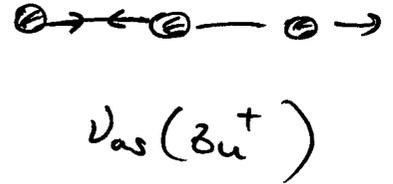
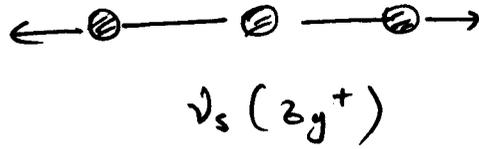


$\rho_{vib}(CO_2) = 3g^+ + 3u^+ + \pi_u$

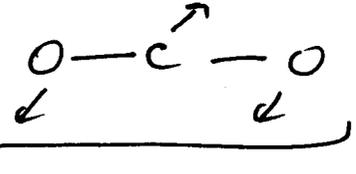
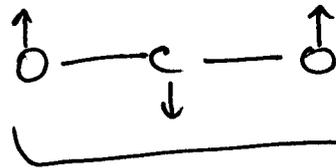
D_{ooh}	E	$2C_{\infty}^{\Phi}$	∞C_v	i	$2S_{\infty}^{\Phi}$	∞C_2	
ρ_g	2	2	2	0	0	0	$= 3g^+ + 3u^+$

$\rho_{\theta} = \pi_u$

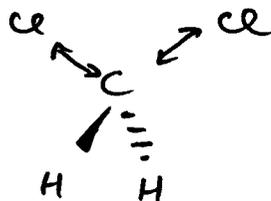
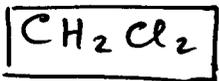
$\rho_g:$



$\rho_{\theta}:$



bending $\rightarrow \rho_d(\pi_u)$
 \uparrow
 degenerate



①. Irreducible representations

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma_{x,y,z}$	3	-1	1	1	
Atoms	5	1	3	3	
Γ_{tot}	15	-1	3	3	
Γ_{tr}	3	-1	1	1	
Γ_{rot}	3	-1	-1	-1	
Γ_{vib}	9	1	3	3	$= \sum_i a_i \Gamma_i$

$a(a_1) = \frac{1}{4} (9+1+3+3) = 4$

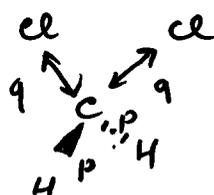
$a(b_1) = \frac{1}{4} (9-1+3-3) = 2$

$a(a_2) = \frac{1}{4} (9+1-3-3) = 1$

$a(b_2) = \frac{1}{4} (9-1-3+3) = 2$

$\Gamma_{vib} = 4a_1 + a_2 + 2b_1 + 2b_2$

②. Stretching modes



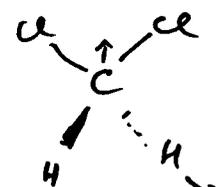
C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma(C-Cl)$	2	0	2	0	$= a_1 + b_1$
$\Gamma(C-H)$	2	0	0	2	$= a_1 + b_2$



$\nu_s(C-Cl)$



$\nu_{as}(Cl-C)$

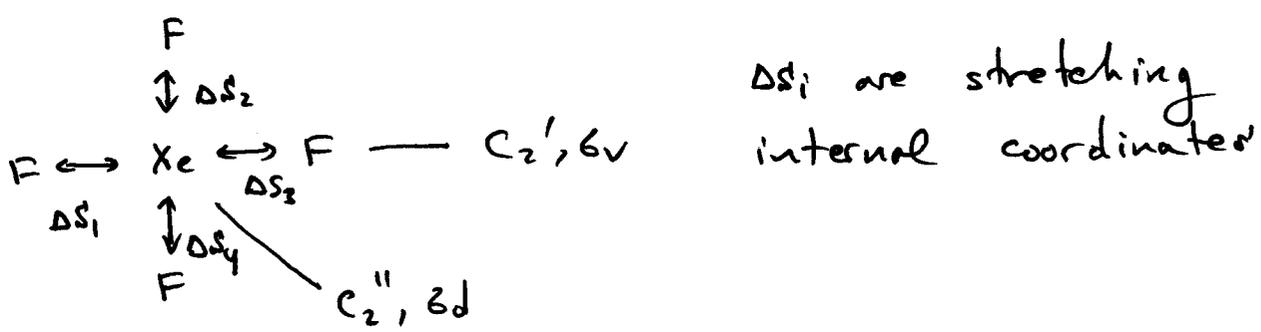


$\nu_s(C-H)$



$\nu_{as}(CH)$

Projection operators : XeF₄



Δs_i are stretching internal coordinates

①. Separation of stretching and bending irreducible representations

$$P_{vib} = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$$

D _{4h}	E	2C ₄	C ₂	2C ₂ '	2C ₂ ''	i	2S ₄	3C ₂	2C _{2v}	2C _{2d}
P _{st}	4	0	0	2	0	0	0	4	2	0

$$P_{st} = a_{1g} + b_{1g} + e_u$$

$$P_{bend} = b_{2g} + a_{2u} + b_{2u} + e_u$$

②. Use of projection operators to produce symmetry coordinates

$$S_{a_{1g}} = \hat{P}^{a_{1g}} \Delta s_1 \propto \Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4$$

$$S_{b_{1g}} = \hat{P}^{b_{1g}} \Delta s_1 \propto \Delta s_1 - \Delta s_2 + \Delta s_3 - \Delta s_4$$

$$S_{e_u(1)} \propto \Delta s_1 - \Delta s_3$$

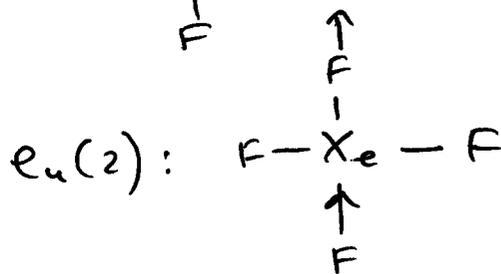
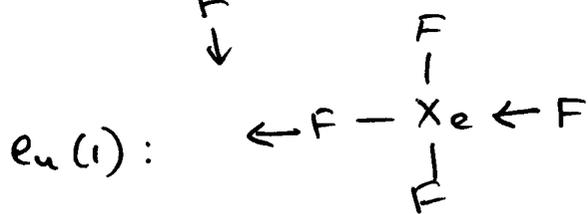
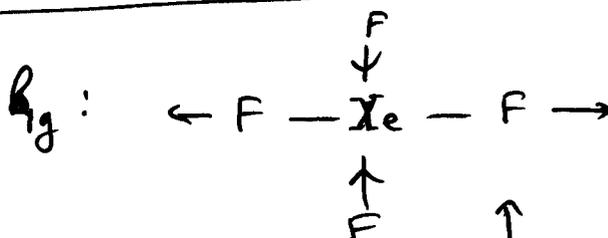
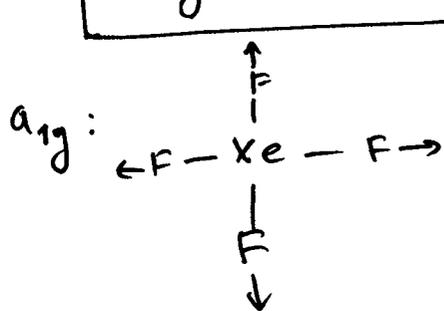
$$S_{e_u(2)} \propto \Delta s_2 - \Delta s_4$$

C_4	E	C_4	C_2	C_4^3
A	1	1	1	1
B	1	-1	1	-1
E	1	i	-1	-i

\Rightarrow

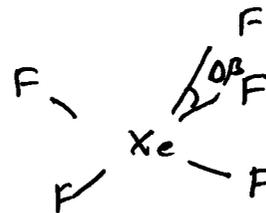
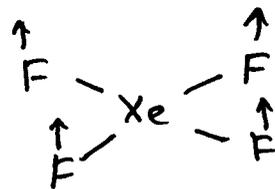
C_4	E	C_4	C_4^2	C_4^3
A	1	1	1	1
B	1	-1	1	-1
E	1	0	-1	0
	0	1	0	-1

$$S_{b_{1g}} \propto \Delta s_1 - \Delta s_2 + \Delta s_3 - \Delta s_4$$

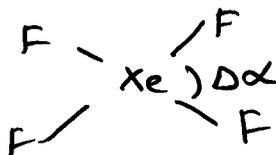


XeF₄: bending vibrations

Out-of-plane:



In-plane:



D _{4h}	E	2C ₄	C ₂	2C ₂ '	2C ₂ "	i	2S ₄	σ _h	2σ _v	2σ _d
out-of-plane	4	0	0	-2	0	0	0	-4	2	0
in-plane	4	0	0	-2	0	0	0	4	-2	0

$$\Gamma_{\text{out}} = a_{2u} + b_{2u} + e_g$$

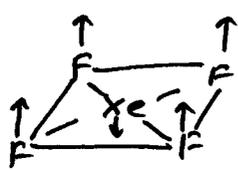
$$\Gamma_{\text{in}} = a_{2g} + b_{2g} + e_u$$

$$\pi(a_{2u}) \propto \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4$$

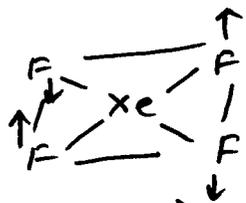
$$e_g(x) \propto \Delta\beta_1 - \Delta\beta_3$$

$$\pi(b_{2u}) \propto \Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4$$

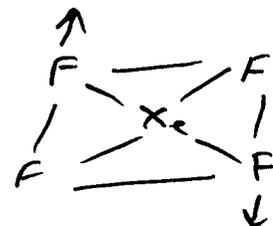
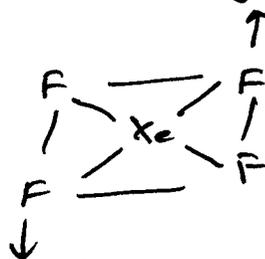
$$e_g(y) \propto \Delta\beta_2 - \Delta\beta_4$$



$\pi(a_{2u})$



$\pi(b_{2u})$

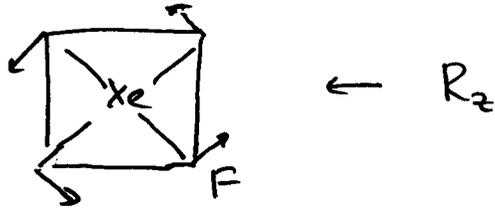


$R_x + R_y (e_g)$

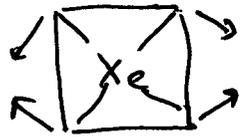
XeF₄: in-plane Bending

$P_{in} = a_{2g} + b_{2g} + e_u, \quad N_{st} + N_{out} = 4 + 2$

$R_2(a_{2g}) \propto \Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4$



$\delta(b_{2g}) \propto \Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4$



$\delta(e_u) \propto \begin{cases} \Delta\alpha_1 - \Delta\alpha_3 \\ \Delta\alpha_2 - \Delta\alpha_4 \end{cases}$



Symmetry coordinates: $\nu_s(a_{1g}), \nu_{as}(b_{1g}), \nu_d(e_u)$
 $\pi(a_{2u}), \pi(b_{2u}), \delta(b_{2u}), \delta_d(e_u)$

3-31



IR+R: 2421, 2327, 1121, 991

Suggest an assignment of these frequencies and draw a picture of each normal mode

①. Splitting into irreducible representations

C_{3v}	E	$2C_3$	$3C_2$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)
$P_{x,y,z}$	3	0	1		
Atoms	4	1	2		
P_{tot}	12	0	2		
P_{rot}	3	0	-1		
P_{vib}	6	0	2		

$P_{vib} = 2a_1 + 2e$

②. Selection rules

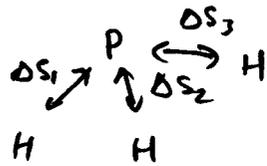
$$\hat{\mu} \sim \begin{pmatrix} a_1 \\ e \end{pmatrix}$$

$$\hat{d} \sim \begin{pmatrix} a_1 \\ e \end{pmatrix}$$

$$a_1 \begin{pmatrix} a_1 \\ e \end{pmatrix} a_1 \sim \begin{pmatrix} \boxed{a_1} \\ e \end{pmatrix} \leftarrow \text{IR+R active}$$

$$e \begin{pmatrix} a_1 \\ e \end{pmatrix} a_1 \sim \begin{pmatrix} e \\ \boxed{a_1} + a_2 + e \end{pmatrix} \leftarrow \text{IR+R active}$$

③. Stretching modes

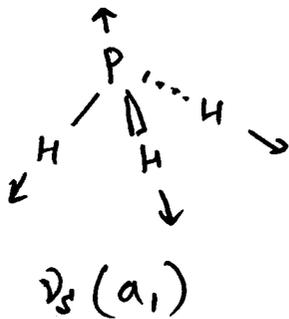


C_{3v}	E	$2C_3$	$3C_2$	
$\nu_{stretch}$	3	0	1	$= a_1 + e$

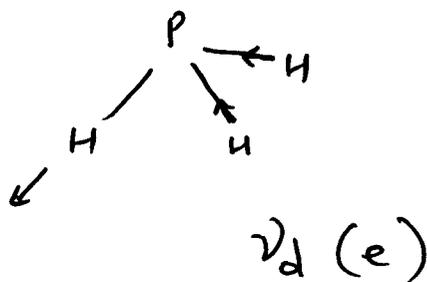
C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{Bmatrix} \epsilon \\ \epsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \epsilon^* \\ \epsilon \end{Bmatrix}$

C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{Bmatrix} 1 \\ 0 \end{Bmatrix}$	$\begin{Bmatrix} \cos \frac{2\pi}{3} \\ \sin \frac{2\pi}{3} \end{Bmatrix}$	$\begin{Bmatrix} \cos \frac{2\pi}{3} \\ \sin \frac{2\pi}{3} \end{Bmatrix}$

$$S_{a_1} = \hat{P}^{a_1} \Delta s_1 \propto \Delta s_1 + \Delta s_2 + \Delta s_3$$



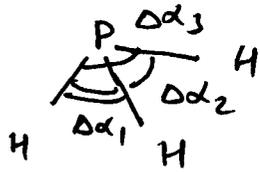
$$S(e) \propto \begin{cases} \Delta s_1 - \frac{1}{2} \Delta s_2 - \frac{1}{2} \Delta s_3 \\ \Delta s_2 + \Delta s_3 \end{cases}$$



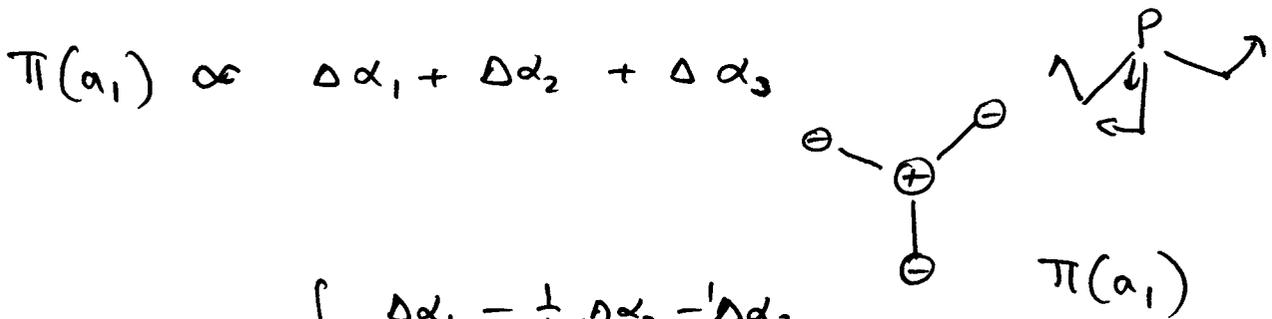
$$\frac{\sqrt{3}}{2}$$

$$-\frac{1}{2}$$

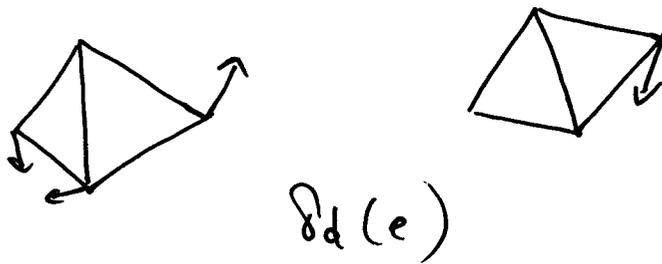
④. Bending modes



C_{3v}	E	$2 C_3$	$3 C_2$	$3 \sigma_v$	
Γ_{Bend}	3	0	1	1	$= a_1 + e$

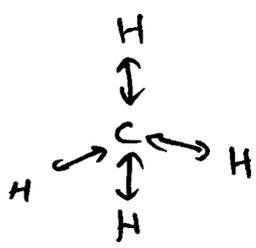


$$\delta_d(e) \propto \begin{cases} \Delta\alpha_1 - \frac{1}{2}\Delta\alpha_2 - \frac{1}{2}\Delta\alpha_3 \\ \Delta\alpha_2 + \Delta\alpha_3 \end{cases}$$



Stretching Mode Analysis

How many C-H vibrations will be seen for CH₄?

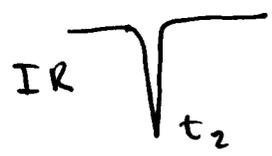


T _d	E	8C ₃	3C ₂	6S ₄	6σ _d
Γ _{st}	4	1	0	0	2

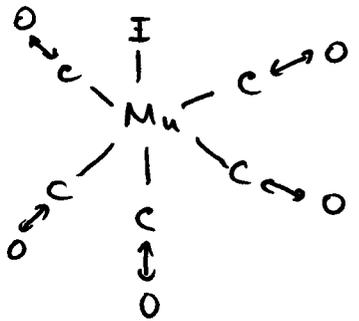
$$\Gamma_{st} = a_1 + t_2$$

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d		
T ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
a ₁	1	1	1	1	1		x ² +y ² +z ²

t₂ ← IR active + Raman active
 a₁ ← Raman active



Mn(CO)₅I

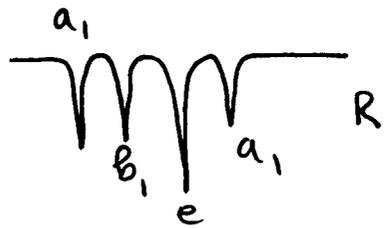
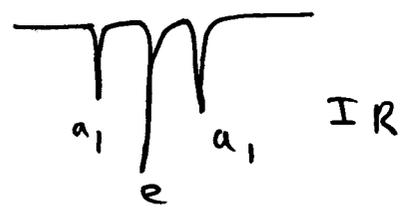


C _{4v}	E	2C ₄	C ₂	2σ _v	2σ _d
Γ _{st}	5	1	1	3	1

$$\Gamma_{st} = 2a_1 + b_1 + e$$

$\hat{\mu} = \begin{pmatrix} a_1 \\ e \end{pmatrix}$
 IR active

$\hat{\alpha} = \begin{pmatrix} a_1 \\ b_1 \\ e \end{pmatrix}$
 R active





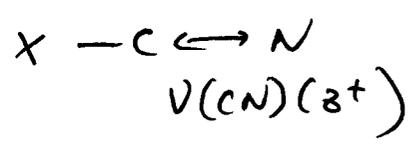
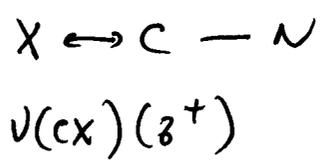
$C_{\infty v}$	E	$2C_{\infty}^{\phi}$...	$\infty \sigma_v$
P_{tot}	9	$3 + 6\cos\phi$		3
P_{tr}	3	$1 + 2\cos\phi$		1
P_{rot}	2	$2\cos\phi$		0

$P_{vib} \quad 4 \quad 2 + 2\cos\phi \quad 2 = 2\sigma^+ + \pi$

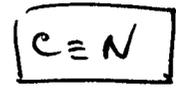
Stretch:



$C_{\infty v}$	E	$2C_{\infty}^{\phi}$...	$\infty \sigma_v$
P_{st}	2	2		$2 = 2\sigma^+$



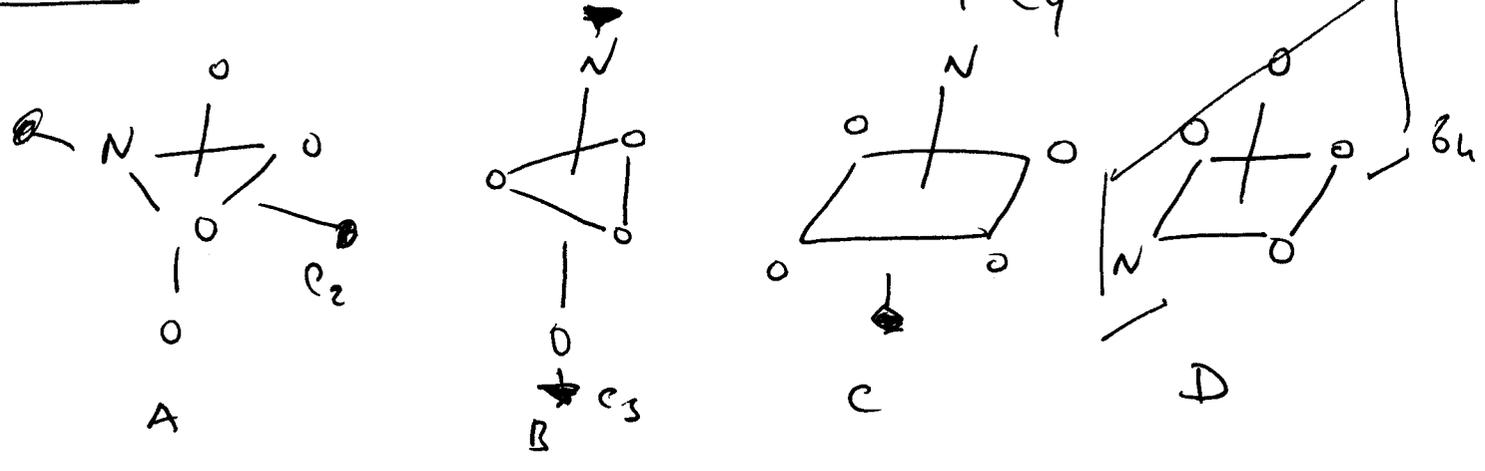
	σ^+	σ^+	π
description	CX	CN	δ_d
symmetry	σ^+	σ^+	π
HCN	3311	2097	712
FCN	1077	2290	449
BrCN	574	2200	342
ICN	470	2158	321



2200-2300

3-43

O_s O₄ N:



IR: 926, 915, 908, 885

R: 928 (p), 916 (p), 907 (p), 886 (dp)

O_s-O stretches

structure	Group	IR Bands	R Bands	IR+R	polarized R
A	C _{2v}	4	4	4	2
B	C _{3v}	3	3	3	2
C	C _{4v}	2	3	2	1
D	C _s	4	4	4	3

C_{2v} | E C₂ 2C_{2'} 2C_{2''} | 4 0 2 2 = 2a₁ + b₁ + b₂

↓ x² ↓ xz ↓ yz

↑ z ↑ x ↑ y

C_s | E σ_h | 4 2 = 3a₁' + a₁''

↑ x, y ↑ z

C_{3v} | E 2C₃ 3C₂ | 4 1 2 = 2a₁ + e

↓ x²+y² ↓ xz, yz

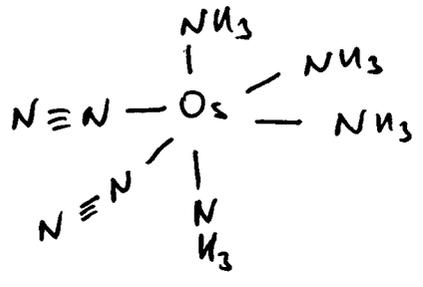
↑ z ↑ (x, y)

C_{4v} | E 2C₄ C₂ 2C_{2'} 2C_{2''} | 4 0 0 2 0 = a₁ + b₁ + e

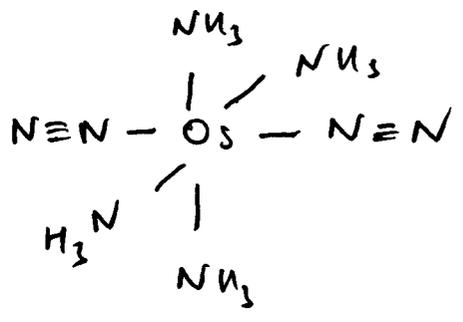
↓ z² ↓ x²-y² ↓ xz, yz

↑ z ↑ x, y

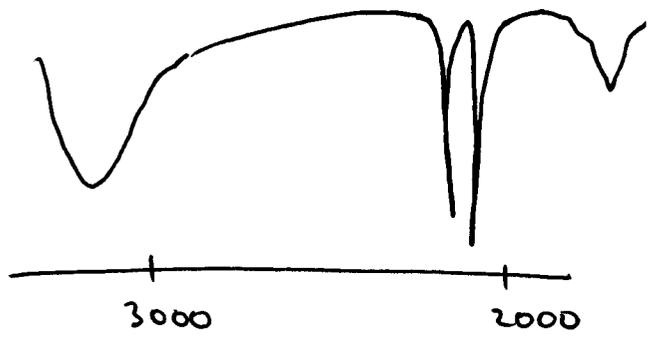
3-45



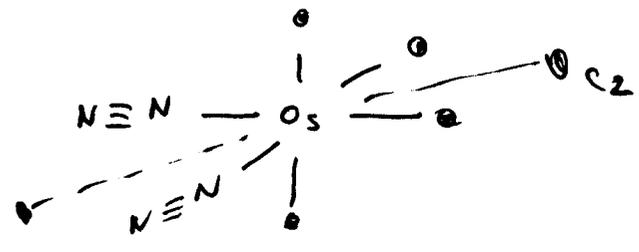
cis



trans



cis :



C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ	2	0	2	0	$= a_1 + b_1$

$\begin{matrix} \text{IR}(z) \\ \downarrow \\ a_1 \end{matrix}$
 $\begin{matrix} \text{IR}(x) \\ \swarrow \\ b_1 \end{matrix}$

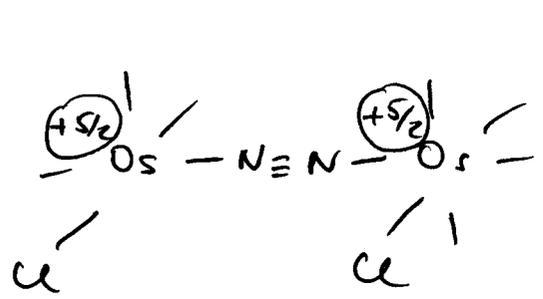
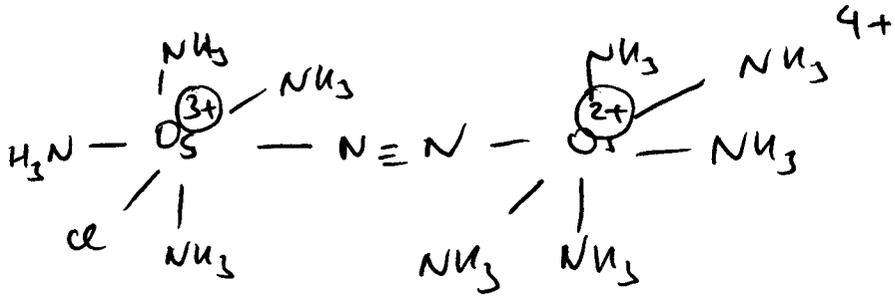
trans

D_{2h}	E	$C_2(x)$	$C_2(y)$	$C_2(z)$	σ_h	...
Γ	2	0	2	0	2	0 ...

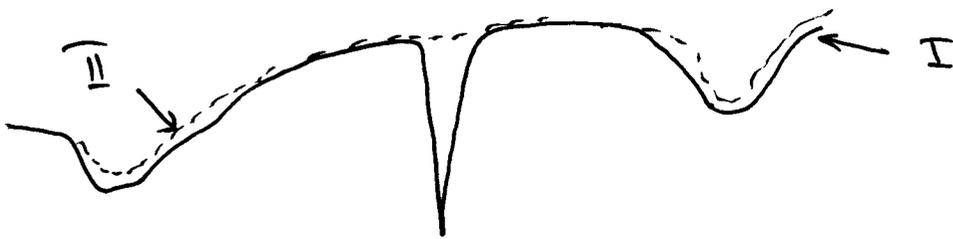
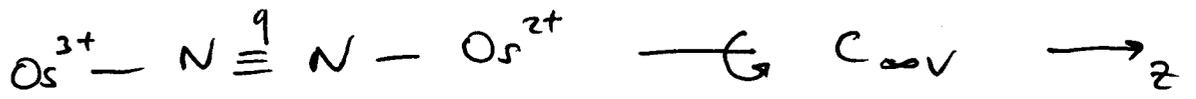
$$\Gamma = a_g + b_{2u}$$

\uparrow
 IR(y)

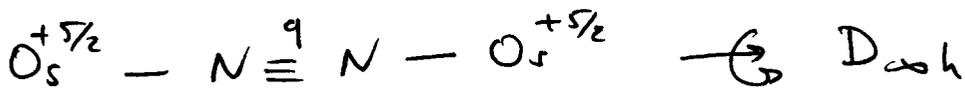
Two active vibrations in CO stretch region imply cis symmetry.



If Os^{3+} and Os^{2+} are different, the electron is said to be localized

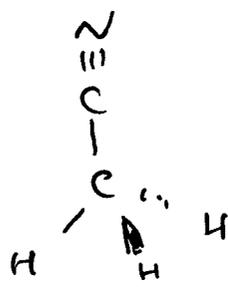


$\text{C}_{\infty v}$	E	$2 \text{C}_{\infty}^{\text{p}}$	$2 \text{C}_{\infty}^{2\text{p}}$...	$\infty \text{ } \delta v$	= $\Sigma^+ (z)$
Γ_g	1	1	1		1	



$\text{D}_{\infty h}$	E	$2 \text{C}_{\infty}^{\text{p}}$...	$\infty \text{ } \delta v$	$i \text{ } 2 \text{ } s_{\text{d}}^{\text{p}}$...	$\infty \text{ } \text{C}_2$	= Σ_g^+
Γ_g	1	1		1	1		1	

3-50



Stretching:

C-H	alkane	2800-3000
C≡N	nitrile	2200-2300

Bending:

CH₃ 1350-1400

C _{3v}	E	2C ₃	3C _{2v}
n _{tot}	18	0	4
n _{tr}	3	0	1
n _{rot}	3	0	-1
n _{vib}	12	0	4 = 5a ₁ + a ₂ + 6e

C-H st:

C _{3v}	E	2C ₃	3C _{2v}
n _{st}	3	0	1 = a ₁ + e

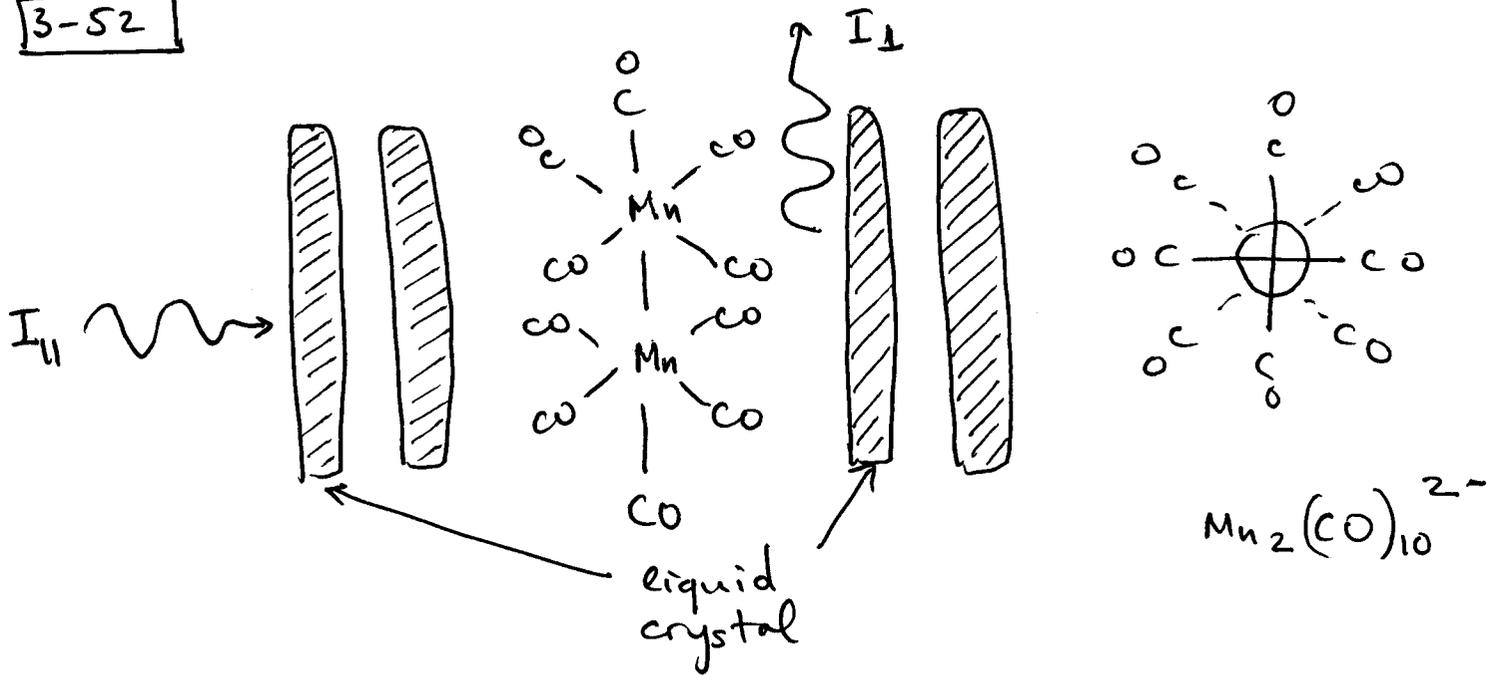
C-H Bend:

C _{3v}	E	2C ₃	3C _{2v}
n _{bend}	3	0	1 = a ₁ + e

CH₃CN : 2999, 2942, 2249, 1440, 1376

↑	↑	↑	↑	↑
ν ₂ (CN)(e)	ν ₂ (CH)(a ₁)	ν(CN)(a ₁)	δ _d (CH ₃)(e)	δ _s (CH ₃)(a ₁)
1124	918		380	
ν(cc)(a ₁)	δ(ucc)(e)		δ(ccn)(e)	

3-52



IR:

	2045	2009	1980
$A_{ }$	0.62	0.81	0.21
A_{\perp}	0.54	0.92	0.19

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4C_2''$
$\nu(\text{CO})$	10	0	2	0	2	0	4

$$= 2a_1 + 2b_2 + e_1 + e_2 + e_3$$

\uparrow \uparrow \uparrow \uparrow \uparrow
 x^2+y^2, z^2 z x, y (x^2-y^2, xy) (xz, yz)

IR spectrum: $2b_2(z) + e_1(x, y)$

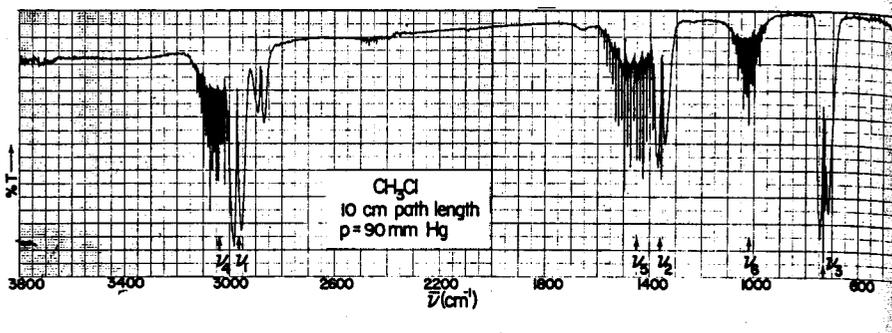
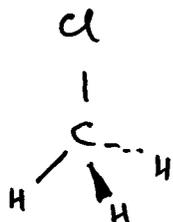
$$\frac{A_{||}}{A_{\perp}} > 1 : \quad \nu(b_2) = \begin{cases} 2045 \\ 1980 \end{cases}$$

$$\frac{A_{||}}{A_{\perp}} < 1 : \quad \nu(e_1) = 2009$$

3-53

Fundamentals of CH₃Cl :

2966, 1355, 732, 3042, 1455, 1015
 ν_1 ν_2 ν_3 ν_4 ν_5 ν_6



C_{3v}	E	$2C_3$	$3C_2$
ρ_{tot}	15	0	3
ρ_{tr}	3	0	1
ρ_{rot}	3	0	-1
ρ_{vib}	9	0	3 = $3a_1 + 3e$

C-H ← 2800-3000

$\delta(CH_3)$ ← 1350-1400

1450-1480

C_{3v}	E	$2C_3$	$3C_2$
$\rho_{bent}(CH)$	3	0	1 = $a_1 + e$

- 3042 ← $\nu_d(CH_3)$ (e)
- 2966 ← $\nu_s(CH_3)$ (a_1)
- 1355 ← $\delta_s(CH_3)$ (a_1)
- 1455 ← $\delta_d(CH_3)$ (e)
- 1015 ← $\delta_d(HCl)$ (e)
- 732 ← $\nu_s(CCl)$ (a_1)

C_{3v}	E	$2C_3$	$3C_2$
$\rho_{st}(C-Cl)$	1	1	1 = a_1

ν_5 first overtone is a good candidate for the double split line at 2879 cm^{-1}

$$\chi_\nu(R) = \frac{1}{2} [\chi(R) \chi_{\nu-1}(R) + \chi(R^\nu)]$$

C_{3v}	E	$2C_3$	$3C_2$	
E	2	-1	0	
R^2	E	C_3	E	
$\chi(R)$	2	-1	0	
$\chi(R^2)$	2	-1	2	
$\chi_2(R)$	3	0	1	$= a_1 + e$

