

Molecular Vibrations

Read:

- Cotton, *Chemical Applications...*, Chapter 10.
- Harris & Bertolucci, *Symmetry and Spectroscopy...*, Chapter 3, pp. 93-117; 135-167; 170-201.

Diatomic Molecules

The harmonic oscillator Hamiltonian is

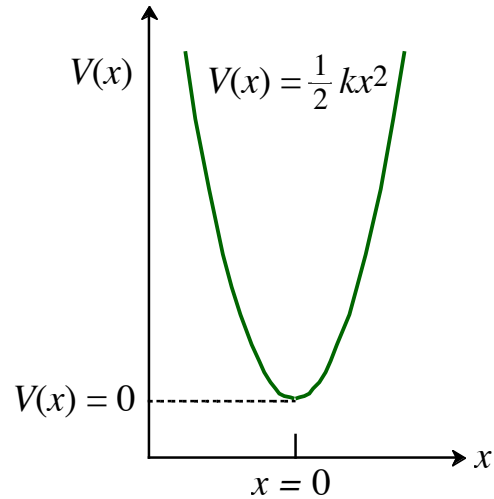
$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \varphi = E\varphi \quad V(x) = \frac{1}{2} kx^2$$

$x =$ distance from x_0

$$\left(\text{Hooke's Law: Force} = F = -\frac{dV(x)}{dx} = -kx \right)$$

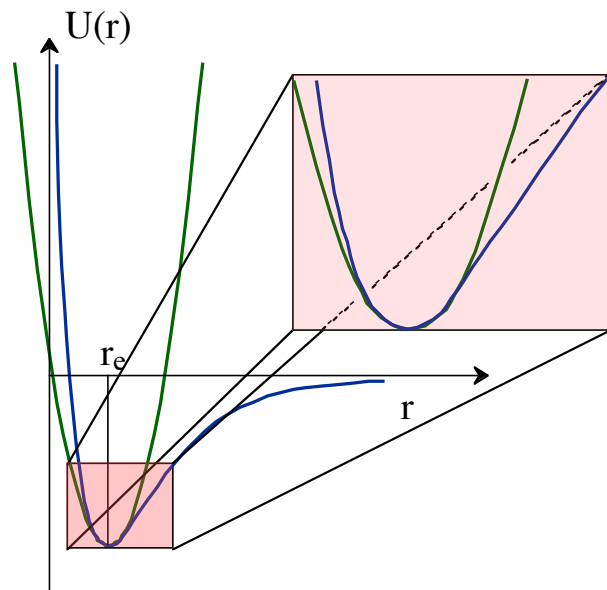
Diatomic Molecules

- The effective potential, $V(x)$, in which the nuclei move is determined by the electronic energy & nuclear-nuclear repulsion.
- k , the force constant, is linked to vibrational frequency, $\nu = (1/2\pi)(k/\mu)^{1/2}$



Real vs. Harmonic Potential

Harmonic (quadratic) potential is an approximation of the true ground state binding curve for the diatomic molecule.



Normal Coordinate for diatomics

The Hamiltonian is rewritten (change of variables to mass weighted coordinate):

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \Rightarrow -\hbar^2 \frac{d^2}{dq^2} + \frac{1}{2} \lambda q^2$$

$$q = \sqrt{m}x ; \quad \lambda = k/m ; \quad V(q) = \frac{1}{2} \lambda q^2$$

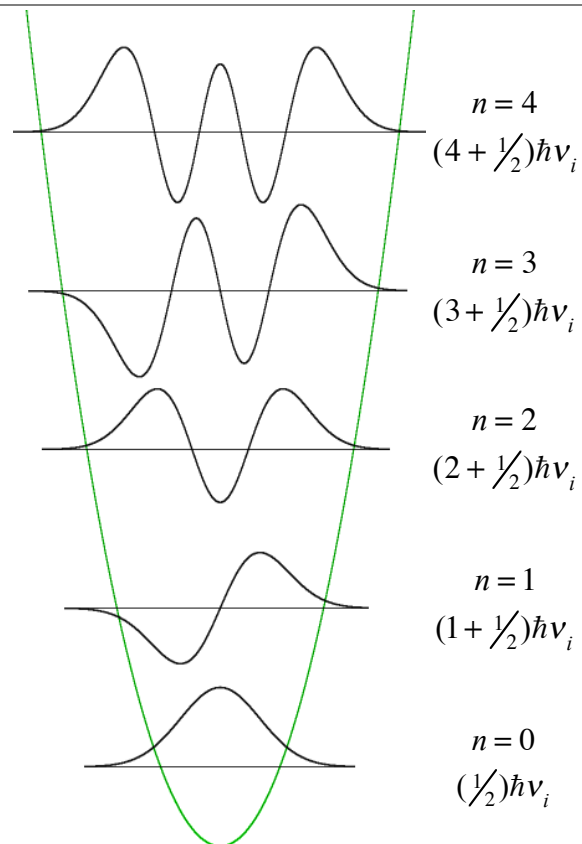
$$\text{frequency } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\lambda}$$

Harmonic Oscillator Wavefunctions

$$\psi_i(n) =$$

$$N_i e^{-(\alpha_i/2)Q_i^2} H_n(\sqrt{\alpha_i}Q_i)$$

$$\alpha_i = 2\pi n_i \mu / \hbar$$



Normal Coordinates

- Expressed in terms of normal coordinates, the vibrational potential energy function is diagonal (contains no cross terms):

$$U = U_{eq} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2$$

There are no terms involving $Q_i Q_j$

Normal Coordinates for Polyatomics

- For polyatomics, there exists a set of normal coordinates in which the vibrational Hamiltonian has a separable form

$$\mathcal{H}_{vib} = \sum_{k=1}^{3N-6} \mathcal{H}_k; \quad \mathcal{H}_k = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2$$

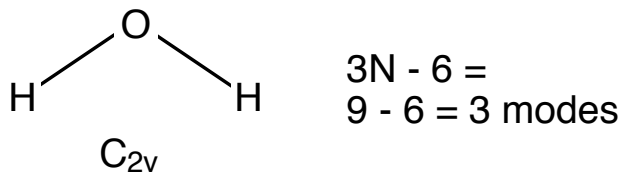
Q_k are mass-weighted coordinates

- Energies for each mode are given by:

$$E_i = (n_i + \frac{1}{2}) h \nu_i$$

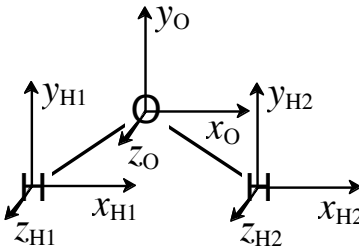
Normal Modes

The “normal modes” of vibration are those which correspond to motions along “normal coordinates”. Such normal coordinates transform as irreducible representations of the applicable point group, but are generally combinations of symmetry adapted internal coordinates. For example, consider H₂O. To what I.R.s do the normal modes belong?



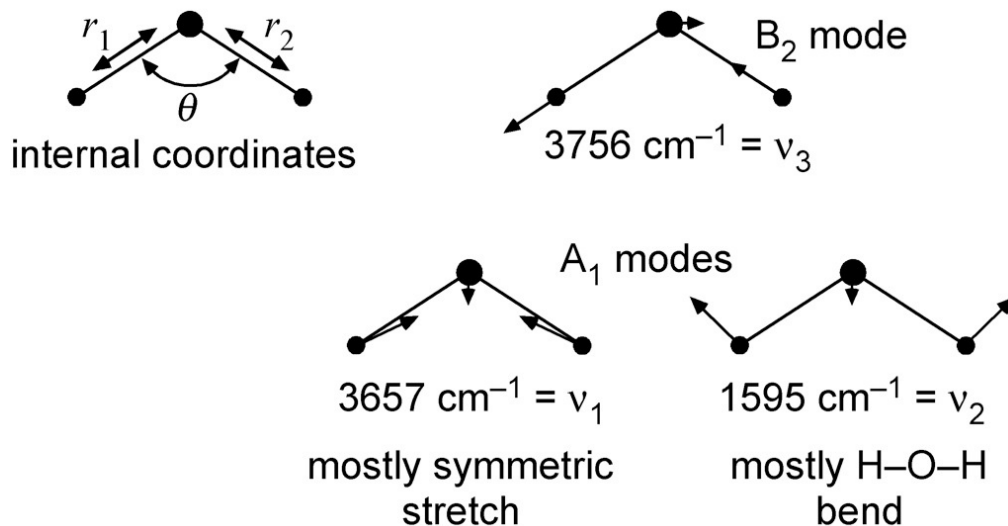
Determining Normal Mode Symmetries

- Find reducible rep. for all nuclear motions



- Eliminate translations and rotations (6 for nonlinear molecules, 5 for linear molecules). This guarantees that normal modes involve no net translation or rotation of center of mass.

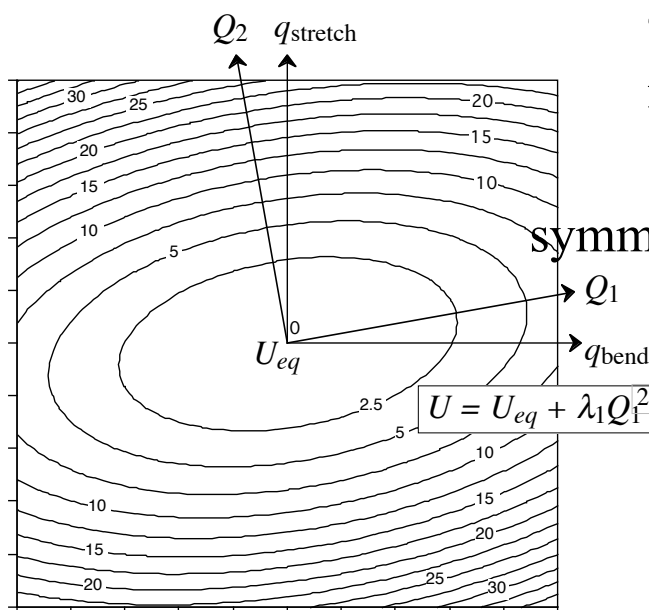
Normal Coordinates and Symmetry Coordinates



Frequencies are for H_2^{16}O .

For D_2^{16}O , $(\nu_1, \nu_2, \nu_3) = (2669, 1178, 2788 \text{ cm}^{-1})$

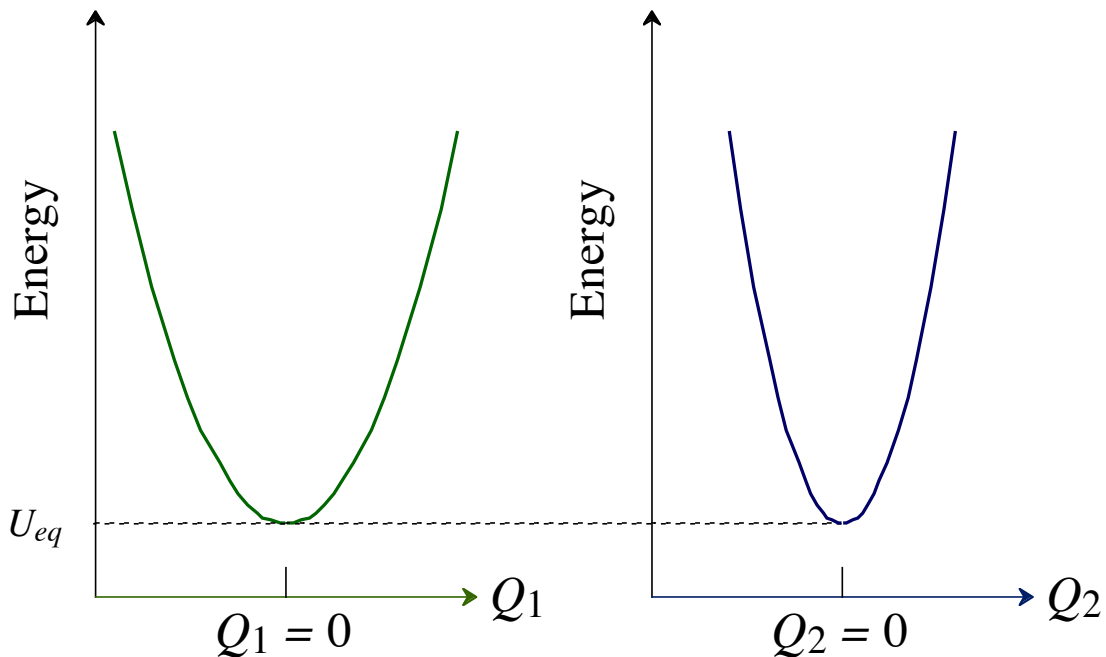
For the two A_1 modes of H_2O , the potential energy surface in terms of internal coordinates,



q_{stretch} & q_{bend} , and
normal coordinates,
 Q_1 & Q_2 . (only A_1
symmetry coordinates
shown)

$$U = U_{eq} + \lambda_1 Q_1^2 + \lambda_2 Q_2^2$$

1-D Slices Through 2-D Potential Surface



Harmonic Oscillator Wavefunctions

- For each mode, i , ψ_i has the form

$$\psi_i(n) = N_i e^{-(\alpha_i/2)Q_i^2} H_n(\sqrt{\alpha_i}Q_i); \quad \alpha_i = 2\pi n_i \mu / \hbar$$

$$H_0(x) = 1; \quad H_1(x) = 2x; \quad H_2(x) = 4x^2 - 2;$$

$$H_3(x) = 8x^3 - 12x; \quad H_4(x) = 16x^4 - 48x^2 + 12$$

For even(odd) n , $H_n(x)$ is an even(odd) function.

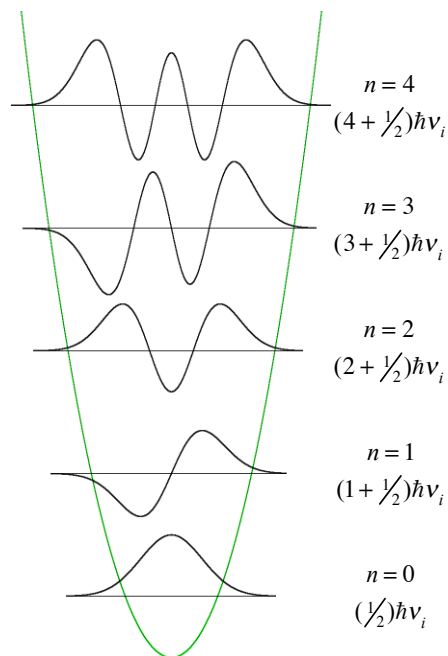
$$H_n(\sqrt{\alpha_i}Q_i) \xrightarrow{\hat{R}} +H_n(\sqrt{\alpha_i}Q_i) \text{ for even } n.$$

and $H_n(\sqrt{\alpha_i}Q_i)$ transforms like Q_i for odd n .

Fundamentals, Overtones, Combinations

A molecule may be excited with multiple vibrational quanta. e.g., for H₂O three numbers specify the number of quanta in each mode.

- Fundamentals: 100 010 001
A₁ A₁ B₂
- Overtones: 200 020 002
A₁ A₁ A₁
- Combinations: 110 101 011
A₁ B₂ B₂



If two modes, i & j , form a basis for a degenerate representation, then λ_i and λ_j are equal (i.e., the modes have the same frequency). Then,

$$\hat{R}Q_i = aQ_i + bQ_j ; \hat{R}Q_j = cQ_i + dQ_j$$

$$\Gamma(R) = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \text{ is an orthogonal matrix}$$

$$\therefore a^2 + b^2 = c^2 + d^2 = a^2 + c^2 = c^2 + d^2 = 1;$$

$$ac + bd = ab + cd = 0.$$

$$\lambda_i (\hat{R}Q_i)^2 + \lambda_i (\hat{R}Q_j)^2 = \lambda_i \left[a^2 Q_i^2 + b^2 Q_j^2 + 2ab Q_i Q_j + c^2 Q_i^2 + d^2 Q_j^2 + 2cd Q_i Q_j \right]$$

$$= \lambda_i (Q_i^2 + Q_j^2)$$

\swarrow
 $2(ab + cd)Q_i Q_j = 0$

The Result:

The total potential, U , is not changed under the action of a symmetry operation

when $\alpha_i = \alpha_j$,

$$e^{-\frac{\alpha_i}{2}Q_i^2} e^{-\frac{\alpha_j}{2}Q_j^2} \xrightarrow{\hat{R}} e^{-\frac{\alpha_i}{2}Q_i^2} e^{-\frac{\alpha_j}{2}Q_j^2}$$

$\psi_{\text{vib.}}$ is therefore unchanged in the ground state

(At the bottom p. 325 in Cotton, this is not at all clear.)

- Conclusion: All molecules' vibrational wavefunctions belong to the totally symmetric representation for the appropriate point group when the molecule is in its vibrational ground state (no excited modes).
- Fundamentals: One vibrational quantum is created

$$\prod_{i=1}^{3N-6} \psi_i(0) \rightarrow \left\{ \prod_{i \neq j}^{3N-6} \psi_i(0) \right\} \psi_j(1)$$

— symmetry of vibrational wavefunction determined by the j^{th} mode.

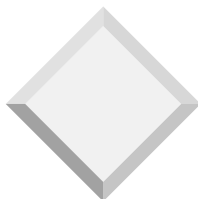
Example: CO stretching modes for Cr(CO)₆ (Mn(CO)₆⁺, V(CO)₆⁻)

O_h	E	$8C_3$	$3C_2$ ($=C_4^2$)	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_u	2	-1	2	0	0	-2	1	-2	0	0		
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(x, y, z)	
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

Cr(CO)₆: $A_1 \sim 2100 \text{ cm}^{-1}$, $T_{1u} \sim 2000 \text{ cm}^{-1}$, $E_g \sim 1985 \text{ cm}^{-1}$

Mn(CO)₆⁺: $T_{1u} \sim 2100 \text{ cm}^{-1}$, V(CO)₆⁻: $T_{1u} \sim 1860 \text{ cm}^{-1}$

Question: What combination and overtone bands are possible?



O_h	E	$8C_3$	$3C_2$ ($=C_4^2$)	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_u	2	-1	2	0	0	-2	1	-2	0	0		
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(x, y, z)	
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

Infrared Spectroscopy

Consider $\int \varphi_j^{gnd} \hat{d} \varphi_j^{exc} d\tau,$

where \hat{d} transforms as $x, y,$ or z

This task is straightforward

\Rightarrow evaluate $\Gamma_x \otimes \Gamma_y \otimes \Gamma_z \otimes \Gamma_j = \Gamma_1$ (totally sym. IR)

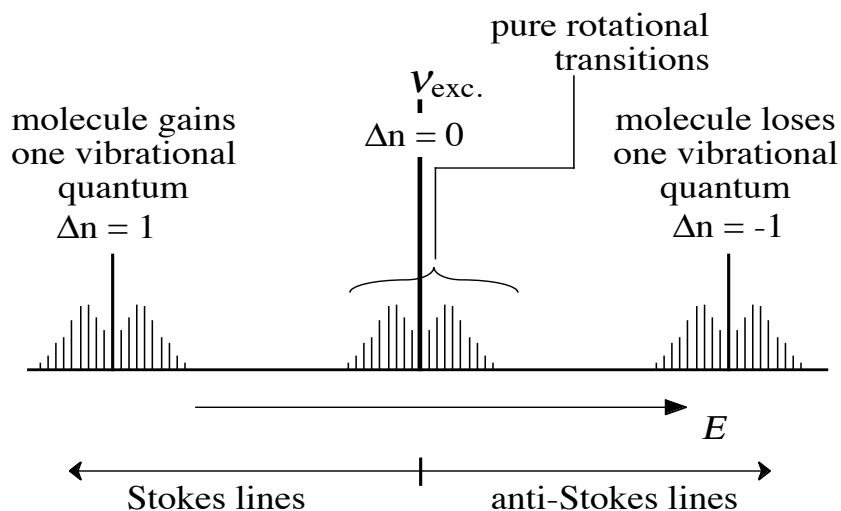
we know this occurs iff $\Gamma_x = \Gamma_j$
 Γ_y
 Γ_z

A Fundamental is infrared active when the excited mode transforms as $x, y,$ or z .

Raman Spectroscopy

- Inelastic scattering of photon (not a resonant absorption spectroscopy)

Example (schematic) - a diatomic molecule in the gas phase





Chandrashekhara
Venkata RAMAN
1888-1970

C. V. Raman

Nobel Prize in Physics 1930

"for his work on the scattering of light and for the discovery of the effect named after him"

In 1922, Raman published "Molecular Diffraction of Light", first of a series of investigations with his collaborators which ultimately led to his discovery, on the Feb. 28th, 1928, of the radiation effect which bears his name ("A new radiation", *Indian J. Phys.*, **2** (1928) 387.)

Infrared (IR) and Raman Spectroscopy	
<p>Infrared spectra originate in the transitions between two vibrational levels in a single electronic state.</p> <p>Rayleigh Raman</p> <p>Raman spectra originate in the electronic polarization caused by UV or visible light.</p>	
<p>(b) Infrared Spectrum</p> <p>Vibrational frequencies are observed as absorption peaks in the IR region.</p>	<p>(d) Raman Spectrum</p> <p>Vibrational frequencies are observed as Raman shifts from the incident frequency in the UV or visible region.</p>
<p>(c) An Infrared Experiment</p> <p>$A = -\log(\Phi_s / \Phi_r) \propto dc$</p> <p>A comparative measurement of transmitted light.</p>	<p>(e) A Raman Experiment</p> <p>$I_{sc} \propto \nu_{sc}^4 E_0 c$</p> <p>Measurement of scattered light at 90°.</p>

IR-Raman Comparison

- (a) IR = absorption; Raman = inelastic scattering
- (b) IR spectrum shows absorption peaks; in Raman vibrational frequencies are observed as shifts from the incident frequency
- (c) in IR an external reference is used for comparison
- (d) in Raman, an intense Rayleigh (elastic scattering) peak is observed with Raman (inelastic) peaks displaced from it - energy difference is absorbed by the molecule
- (e) The exciting radiation must be monochromatic, the signal is proportional to the incident light intensity.

Polarizability Tensor

$$\begin{bmatrix} d_{x,\text{ind.}} \\ d_{y,\text{ind.}} \\ d_{z,\text{ind.}} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Components of the induced dipole created by **E**-field of photon. Molecular polarizability tensor. **E**-field of scattering photon.

Raman Spectroscopy

- Became much more important after development of lasers because only about one thousandth of the scattered radiation is Raman, the rest is scattered elastically (with conservation of energy)
- Selection rules — scattering amplitudes involve the elements of the polarizability tensor (which must be nonzero):

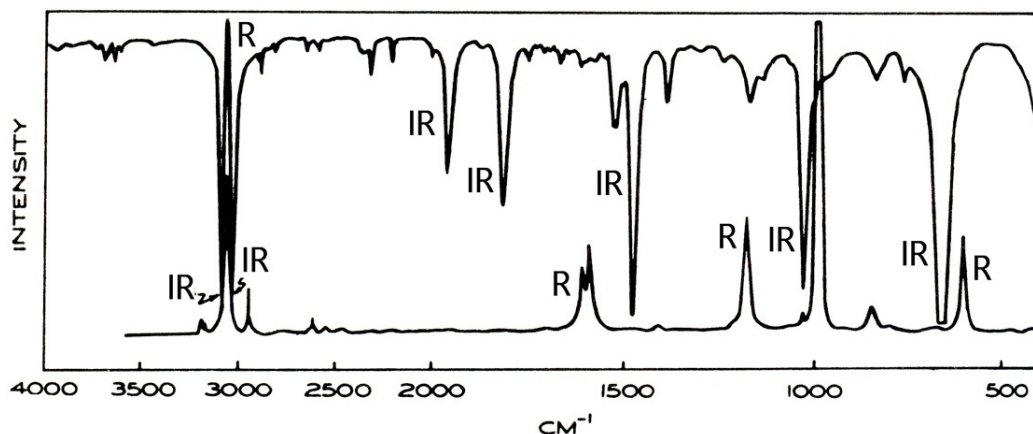
$$\int \psi_j^{\text{gnd}} \alpha_{mn} \psi_j^{\text{exc}} d\tau \sim \Gamma_{mn} \otimes \Gamma_j \quad m, n = x, y, \text{ or } z$$

i.e., Γ_j must transform as $x^2, y^2, z^2, xy, xz, yz$

Exclusion Rule

- If a molecule is centrosymmetric, then allowed infrared transitions are forbidden in the Raman spectrum and allowed Raman transitions are forbidden in the IR. (Why?)
- If an inversion center is present, then x , y , and z belong to u representations and α_{mn} belong to g representations.

Exclusion Rule - Benzene



Vibrational spectra of benzene reproduced from S.K. Freeman, *Applications of Laser Raman Spectroscopy*, John Wiley & Sons, N.Y. 1974.

Examples

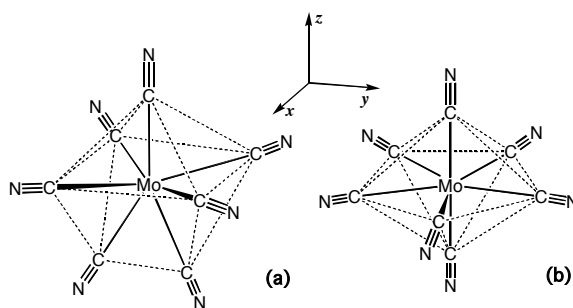
- Describe the number and character of the IR and Raman transitions observed for BrF_5 if the molecule has D_{3h} symmetry. C_{4v} symmetry?
- How can IR and Raman spectra allow one to distinguish between syn- and anti-planar structures of N_2F_2 ?
- For BF_3 , Raman and IR active modes. B-F stretching modes can be observed in both the IR and Raman spectra — which are affected by the presence of two B isotopes (^{10}B and ^{11}B)?

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

C_{4v}	E	$2C_4$	$C_2(C_4^2)$	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

Example

The seven-coordinate complex $\text{Mo}(\text{CN})_7^{4-}$ has been studied both as solid $\text{K}_4\text{Mo}(\text{CN})_7 \cdot 2\text{H}_2\text{O}$ and in aqueous solution. In the C—N stretching region the IR spectrum has bands at 2119, 2115, 2090, 2080, 2074, and 2059 cm^{-1} for the solid and at 2080 and 2040 cm^{-1} for solutions. How many Raman and infrared bands would you expect for (a) the monocapped trigonal prism and (b) the pentagonal bipyramid and how many coincidences (bands present in both the IR and Raman spectra) should there be for each geometry? How do you interpret these data?



CoL_6 modes in $[\textit{trans}\text{-CoCl}_2(\text{en})_2]^+$

- To understand the electronic spectra of transition metal complexes, it turns out that the vibrational modes have to be considered.
 - Electronic spectrum of $[\textit{trans}\text{-CoCl}_2(\text{en})_4]^+$ is shown in Fig. 9.13 in Cotton
- Determine the vibrational modes of the $[\textit{trans}\text{-CoCl}_2\text{N}_4]$ grouping.

Vibrations of the *trans*-[CoCl₂N₄] group

- On p. 293 of Cotton's text *and* on p. 343 of Harris & Bertolucci, the vibrational modes are given as $2A_{1g}, B_{1g}, B_{2g}, E_g, 2A_{2u}, B_{1u}, 3E_u$

This should be

$2A_{1g}, B_{1g}, B_{2g}, E_g, 2A_{2u}, B_{2u}, 3E_u$

D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		$x^2 - y^2$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	(R_x, R_y)	(xz, yz)
E_g	2	0	-2	0	0	2	0	-2	0	0		
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	z	
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	(x, y)	

Combination Bands – Nondegenerate Modes

- When a molecule is vibrationally excited with an *odd* number of quanta in more than one nondegenerate mode, a simple direct product is used to determine the symmetry of the total vibrational state.
- H₂O example:

Fundamentals:	100	010	001	Recall,
	A ₁	A ₁	B ₂	v ₁ , v ₂ both A ₁
				v ₃ is B ₂
Combinations:	110	101	011	
	A ₁	B ₂	B ₂	

Overtones - Degenerate Modes; Symmetric Direct Products

- With two quanta in a degenerate mode, the symmetries of ψ_{vib} are given by*:

$$\chi^+(R) = \frac{1}{2}(\chi^2(R) + \chi(R^2))$$

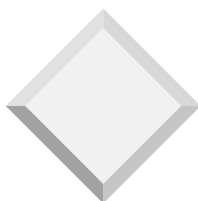
- With three quanta the formula is

$$\chi^+(R) = \frac{1}{6}(\chi^3(R) + 3\chi(R)\chi(R^2) + 2\chi(R^3))$$

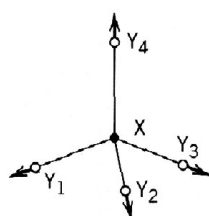
(*See Wilson, Decius, & Cross, “Molecular Vibrations...”, Section 7.3. Also see the *Antisymmetry* handout for proof for the two and three quanta cases. Note: Carter does overtones wrong for CH₄ on p. 194.)

Fundamentals and Overtones and Combination bands for XY_4 molecules

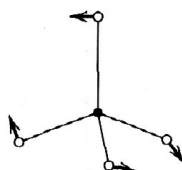
- On p. 194 of Carter, overtones of CH_4 are treated incorrectly. Cotton leaves out their treatment entirely.
- Let's work out the normal modes, look at the fundamentals - then discuss how the overtone and combination bands are handled differently



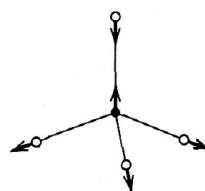
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)



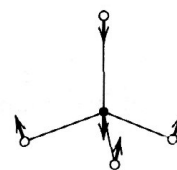
$\nu_1(A_1)$



$\nu_2(E)$



$\nu_3(T_2)$



$\nu_4(T_2)$

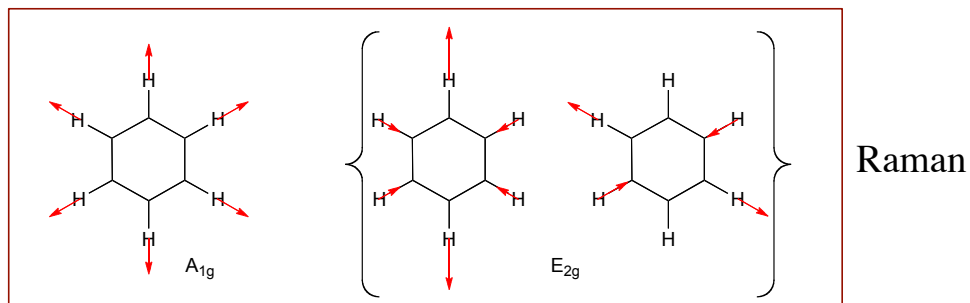
Tetrahedral XY_4 molecules.

Fermi Resonance

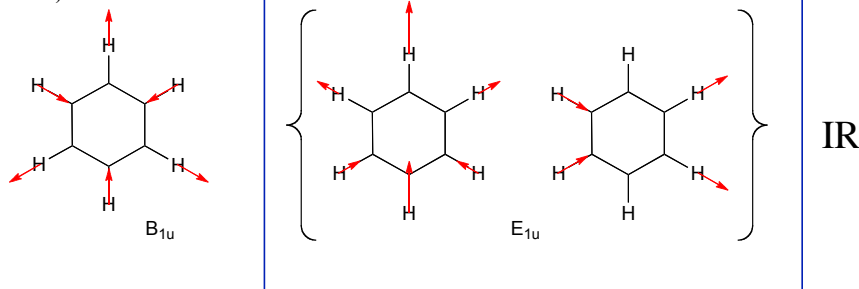
- Just as “configuration interaction” occurs in electronic spectra, mixing between fundamentals and combination or overtone bands can occur in vibrational spectra.
- ‘Weak’ combination/overtone bands can ‘borrow’ intensity from fundamentals if the sum of the frequencies in the combination/overtone band is close to the frequency of the fundamental.
- CO₂ example from Cotton: fundamental frequencies are 668, 1337 (Raman), 2349 cm⁻¹ (what are they?). 200 mixes with 010.

Example: C-H region of benzene

<http://home.arcor.de/rothw/gauss/varsanyi/molekuele/Bz/>

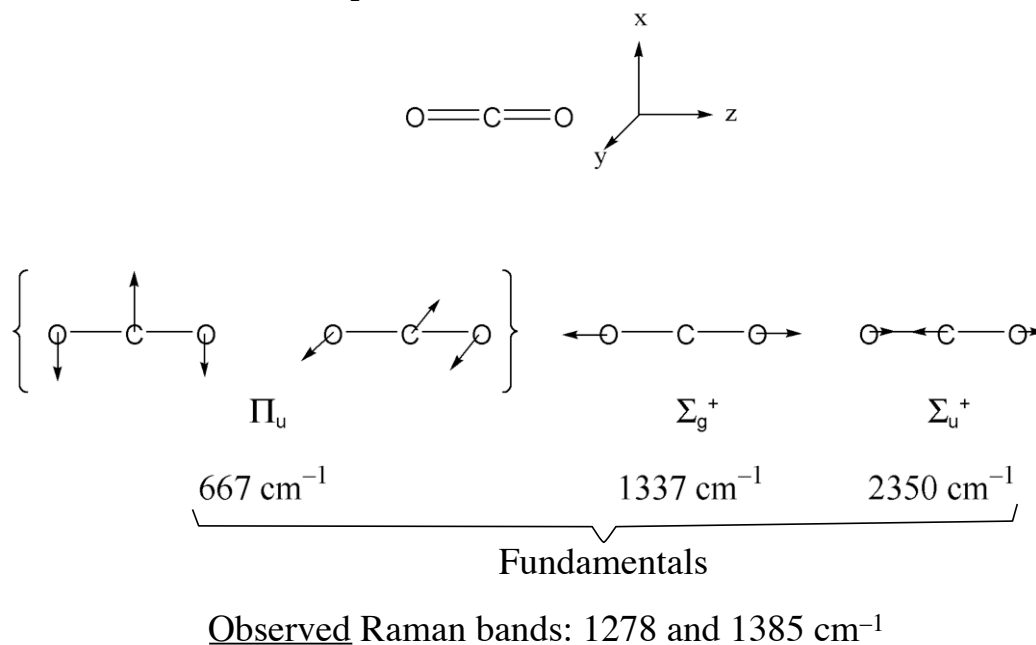


see Wilson, Decius, and Cross

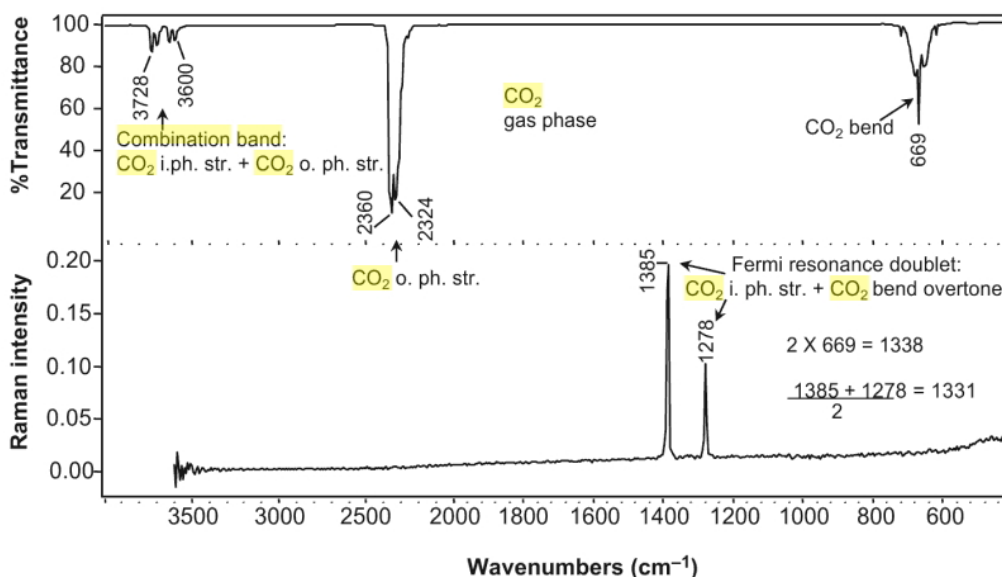


C₆H₆: three IR bands at 3045, 3073, 3099 cm⁻¹; C₆D₆: one IR band at 2293 cm⁻¹

Normal Modes and Vibrational Frequencies for CO₂



Vibrational Spectra for CO₂



Observed Raman bands: 1278 and 1385 cm^{-1}

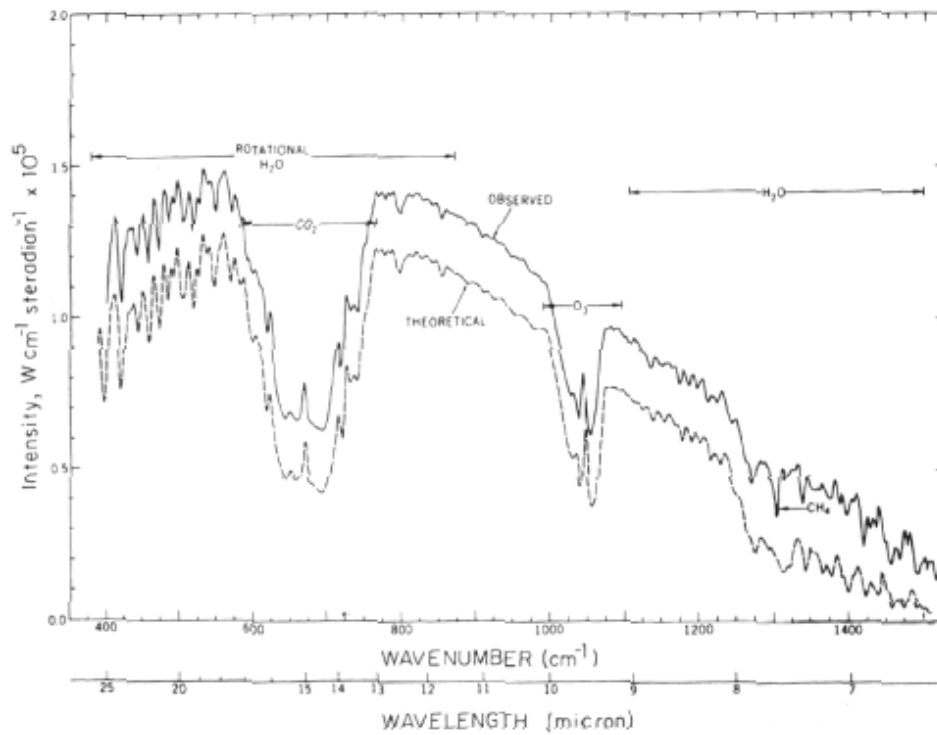


FIG. 6.1. Observed and theoretical spectra for clear skies over the Gulf of Mexico, April 23, 1969. The observed spectrum is displaced upward by $0.2 \times 10^{-3} \text{ W cm}^{-2} \text{ steradian}^{-1} \text{ wave number}^{-1}$. After Conrath et al. (1970).

Planck's Blackbody Radiation Law

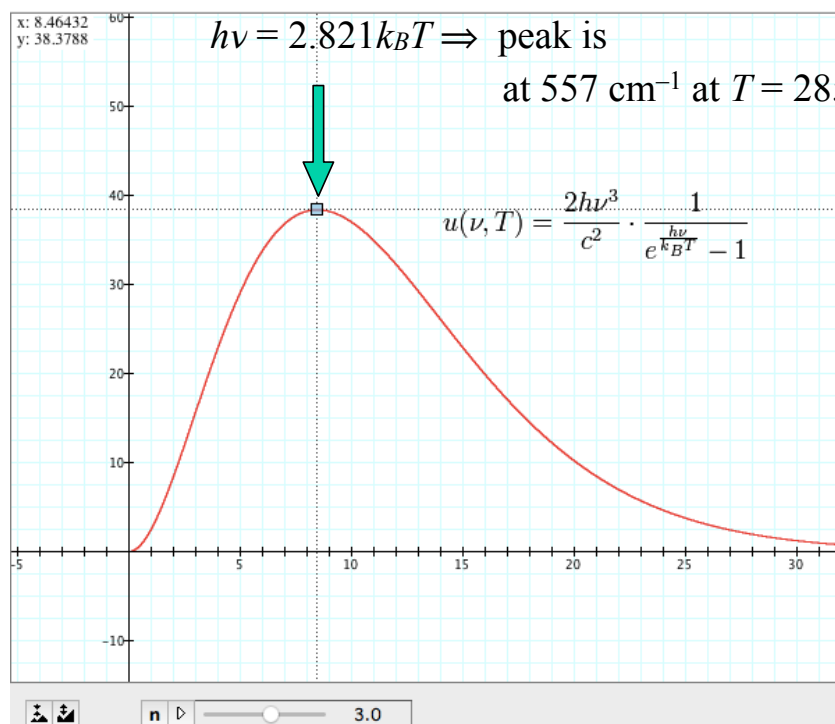


TABLE 4.1 Selected Groups that Display Fermi Resonance Bands in their Vibrational Spectrum.

Group	Bands (cm ⁻¹)	Assignment	Active	
			IR	Raman
CO ₂	1385, 1278	CO ₂ i. ph. str + 2x CO ₂ bend	No	Yes
R-C(=O)-H	~2820, ~2710	CH str. + 2x CH i.ph. bend	Yes	Yes
N=C=O ⁻	~1300, ~1200	NCO i.ph. str. + 2x NCO bend	Yes	Yes
R-COOH	~3000-2650	OH str. + 2x OH i. pl bend	Yes	Yes
	~3000-2550	OH str. + 2x C-O str.	Yes	Yes
CH ₂	~2920-2890	CH ₂ str. + 2 x CH ₂ bend	Yes	Yes
Aryl-C(=O)-Cl	~1780, ~1730	C=O str. + 2x 880 aryl-C str.	Yes	Yes
N≡C-N=C(NH ₂) ₂	2200, 2170	C≡N str. + (1250 +925 cm ⁻¹) Combination band	Yes	-
R-C≡C-R	2300, 2235	C≡C str + C-C≡C bend	No	Yes
C=O	1810, 1780	C=O str. + 2x ~900 ring bend	Yes	-
Aryl-NH ₂	3355, 3205	NH ₂ i. ph. str. + 2x NH ₂ bend	Yes	Yes
NH ₄ Cl	2825	NH ₄ i. ph. str. + 2x NH ₄ bend	Yes	Yes
-C(=O)-NH-C	3300 (s), 3100(m)	MH str. + 2x CNH str.-bend	Yes	Yes

$D_{\infty h}$	E	$2C_{\infty}^{\Phi}$	\dots	$\infty\sigma_v$	i	$2S_{\infty}^{\Phi}$	\dots	∞C_2		
Σ_g^+	1	1	\dots	1	1	1	\dots	1		x^2, y^2, z^2
Σ_g^-	1	1	\dots	-1	1	1	\dots	-1		
Π_g	2	$2\cos\Phi$	\dots	0	2	$-2\cos\Phi$	\dots	0	R_z	(xz, yz)
Δ_g	2	$2\cos 2\Phi$	\dots	0	2	$2\cos 2\Phi$	\dots	0	(R_x, R_y)	$(x^2 - y^2, xy)$
\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots		
Σ_u^+	1	1	\dots	-1	-1	-1	\dots	1	z	
Σ_u^-	1	-1	\dots	-1	-1	1	\dots	1		
Π_u	2	$2\cos\Phi$	\dots	0	-2	$2\cos\Phi$	\dots	0	(x, y)	
Δ_u	2	$2\cos 2\Phi$	\dots	0	-2	$-2\cos 2\Phi$	\dots	0		
\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots	\dots		

$$\frac{1}{2}(\chi^2(C^{\Phi}) + \chi(C^{2\Phi})) = \frac{1}{2}(4\cos^2\Phi + 2\cos 2\Phi) = (1 + \cos 2\Phi) + \cos 2\Phi = 1 + 2\cos 2\Phi$$

$$[\Pi_u \otimes \Pi_u]^+ \left| \begin{array}{ccc|ccc} 3 & 1+ & \dots & 1 & 3 & 1+ & \dots & 1 \\ & 2\cos 2\Phi & & & & 2\cos 2\Phi & & \end{array} \right| \Rightarrow \Sigma_g^+ + \Delta_g$$