Vibrational Spectroscopy - Infrared and Raman

The number of normal modes of vibration of a molecule with N atoms can be determined from the displacements of each atom in the x, y, and z directions. There are obviously 3N such displacements, but 3 of these result in translation of the whole molecule in the x, y, and z directions, and 3 result in molecular rotations. Thus the molecule has 3N-6 normal modes of vibration. [3N-5 if the molecule is linear, since there is no rotation possible about the molecular axis.]

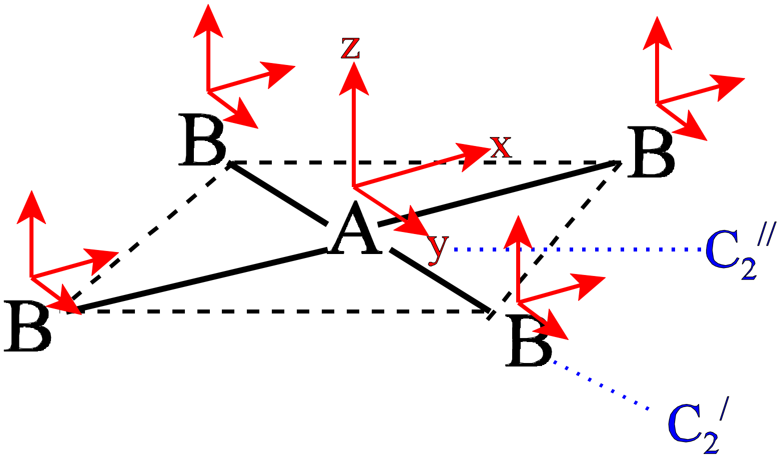
The symmetry of each of the normal modes can easily be determined by Group Theory since the matrices that describe the atomic displacements have characters that form the basis for irreducible representations of the molecular point group.

We use a square planar molecule (point group D_{4h}) as an example

We represent the three degrees of freedom of each atom by 15 unit vectors, 3 on each stom.
We then determine the character of the 15 x 15 matrix that describes the motions of the atoms corresponding to the symmetry operations of the molecular point group

Each atomic x,y,z vector contributes to the character by
+1 (if it remains in place after the symmetry operation),
-1 (if it is inverted),
cos θ (if it is rotated by θ°; note that cos 90° = 0)
0 (if it is moved out of position),

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$ (xz, yz)	$2\sigma_d$
Γ_{xyz}	15	1	-1	-3	-1	-3	-1	5	3	1



Γ_{xyz} can be reduced to $A_{1g}+A_{2g}+B_{1g}+B_{2g}+E_g+2A_{2u}+B_{2u}+3E_u$

The Character Table shows us that A_{2g} and E_g are *rotations* and A_{2u} and E_u are *translations*

Therefore thr symmetries of the normal modes are

$A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

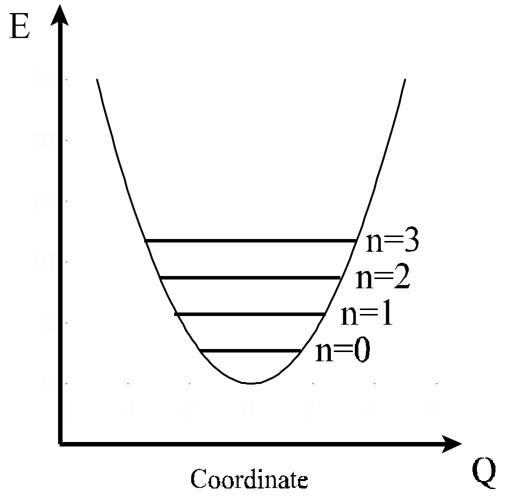
We can also discover which of these involve pure bond stretches by using the four bonds as a basis set

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$ (xz, yz)	$2\sigma_d$
Γ_{bond}	4	0	0	2	0	0	0	4	2	0

Γ_{bond} reduces to $A_{1g} + B_{1g} + E_u$

Selection Rules

Consider a particular vibration



Transition from
n=0 to n=1 Fundamental
n=0 to n=2 First overtone
n=0 to n=3 Second overtone
etc

Assuming normal harmonic oscillation, the wave function for the i-th normal mode of order n (vibrational quantum number 0,1,2....) can be written as

$$\Psi_i(n) = N_i e^{-(\alpha_i/2)\xi_i^2} H_n(\sqrt{\alpha_i}\xi_i)$$

where N_i is a normalization factor
H_n is a Hermite polynomial of order n
$H_0(x) = 1$
$H_1(x) = 2x$
$H_2(x) = 4x^2 - 2$
$H_3(x) = 8x^3 - 12x$
ξ_i is the i-th normal coordinate
$\alpha_i = 2\pi\nu_i/h$

So the ground state wave-function is

$$\psi_i(0) = N_i e^{-(\alpha_i/2)\xi_i^2}$$

Since normal coordinates are normalized, $\psi_i(0)$ is invariant under all symmetry operations and forms a basis for the totally symmetric representation.

For the excited states the wave functions take the symmetry of the n-th Hermite polynomial.

Fundamental transitions (n=0 to n=1) give rise to IR and Raman absorption bands that are at least an order of magnitude greater than any other kind, and are of greatest practical interest.

For the case of the square-planar molecule AB_4 we found the normal vibrational modes to be

$A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

These are the symmetries of the n=1 vibrational wave-functions

Since the ground state vibrational wave-function has A_{1g} symmetry, infrared-active transitions must be to those excited states that belong to the same representation as one or more of the Cartesian coordinates. This for D_{4h} the allowed transitions are to A_{2u} and E_u only – i.e. there are three observable fundamental bands (one of which, an E_u mode, corresponds to pure bond stretching, see Γ_{bond} above)

What about Raman spectroscopy?

The Raman Effect

The oscillating electric field of the radiation induces a dipole in the molecule

$$\vec{M} = \alpha\vec{E}$$

where α is the polarizability

For radiation of frequency ν_0

$$M = \alpha E_0 \cos(2\pi\nu_0 t) \tag{1}$$

For a vibrating molecule α is time-dependent

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial Q_1}\right)_0 Q_1 + \ldots.. \tag{2}$$

where Q_1 is a displacement coordinate

For a molecular vibration of frequency ν_1

$$Q_1 = Q_1^0 \cos(2\pi\nu_1 t) \tag{3}$$

where Q_1^0 is the vibrational amplitude

Combining equations (1), (2), and (3)....

$$M = E_0 \cos(2\pi\nu_0 t)\left[\alpha_0 + \left(\frac{\partial\alpha}{\partial Q_1}\right)_0 Q_1^0 \cos(2\pi\nu_1 t)\right]$$

$$= E_0\alpha_0\cos(2\pi\nu_0 t) + E_0Q_1^0\left(\frac{\partial\alpha}{\partial Q_1}\right)_0\cos(2\pi\nu_0 t)\cos(2\pi\nu_1 t)$$

$$= E_0\alpha_0\cos(2\pi\nu_0 t)$$
$$+\frac{1}{2}E_0Q_1^0\left(\frac{\partial\alpha}{\partial Q_1}\right)_0\left\{\cos[2\pi(\nu_0+\nu_1)t]+\cos[2\pi(\nu_0-\nu_1)t]\right\}$$

The first term is the Rayleigh Scattering (no frequency change) and the second term describes the Antistokes ($\nu_0+\nu_1$) and Stokes ($\nu_0-\nu_1$) regions of the Raman Scattering. A quantum mechanical treatment correctly predicts that the antistokes lines are much less intense than the stokes lines.

Since $\vec{M}$ and $\vec{E}$ are both vector quantities, α_0 is a second rank tensor.

$$\begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} = \begin{bmatrix} \alpha_{0xx} & \alpha_{0xy} & \alpha_{0xz} \\ \alpha_{0yx} & \alpha_{0yy} & \alpha_{0yz} \\ \alpha_{0zx} & \alpha_{0zy} & \alpha_{0zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

For non-chiral molecules $\alpha_{0yx} = \alpha_{0xy}$, etc and with the proper choice of axes the tensor can be diagonalized, so that α_0 can be represented by three principal components α_{0xx} , α_{0yy} , and α_{0zz}

Thus the polarizability operator has the symmetry of *quadratic and binary functions of x, y, and z.*

For D_{4h} the Raman-allowed transitions are A_{1g}, B_{1g}, and B_{2g} Again, checking with Γ_{bond}, the A_{1g} and B_{1g} modes correspond to pure bond stretches.

So for a D_{4h} AB_4 molecule there are three IR and three Raman allowed fundamental transitions. Note that, for a centrosymmetric molecule, no Raman-active vibration is also IR-active, and vice-versa. (Exclusion Rule)

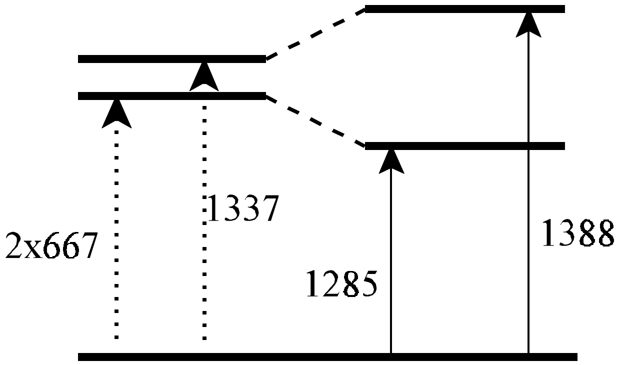
Complications...

Configuration Interaction (Fermi Resonance) will occur if
ν_a (fundamental) ≈ ν_b (combination or overtone), *and* the symmetries of both are the same

Original example. CO_2.
The three fundamental transitions have frequencies
667 (bend, IR-active),
1337 (symmetric stretch, Raman-active) and
2350 cm^{-1} (antisymmetric stretch, IR-active)

The Raman spectrum of CO_2 shows two bands of similar intensity at 1285 and 1388 cm^{-1}.

The 1337-cm^{-1} vibration has Σ_g^+ symmetry (in $D_{\infty h}$) and the first overtone of the bending mode (expected at 2 x 667 = 1334 cm^{-1}) contains a component of Σ_g^+ symmetry.



The overtone band should be very weak, but "steals" intensity from the allowed fundamental band since the new excited states are linear combinations of the original excited states.

Many IR spectra are recorded on solids (as KBr pellets or hydrocarbon mulls). The site symmetry of a particular molecule in the crystal may alter the selection rules.

For example CO_3^{2-} has D_{3h} symmetry in solution. The totally symmetric A_{1g} stretching mode is IR-inactive, but Raman-active.

In $CaCO_3$ (calcite) the site-symmetry of CO_3^{2-} is D_3, but the totally-symmetric mode (nowA_1)is still IR-inactive.

In $CaCO_3$ (aragonite) the site-symmetry is C_s and the totally-symmetric mode (now A') is allowed and can be observed weakly.

Degenerate modes may be split in solids, e.g. the bending mode of SCN^- has E symmetry, but in solid KSCN two bands are seen at 470 and 484 cm^{-1}.