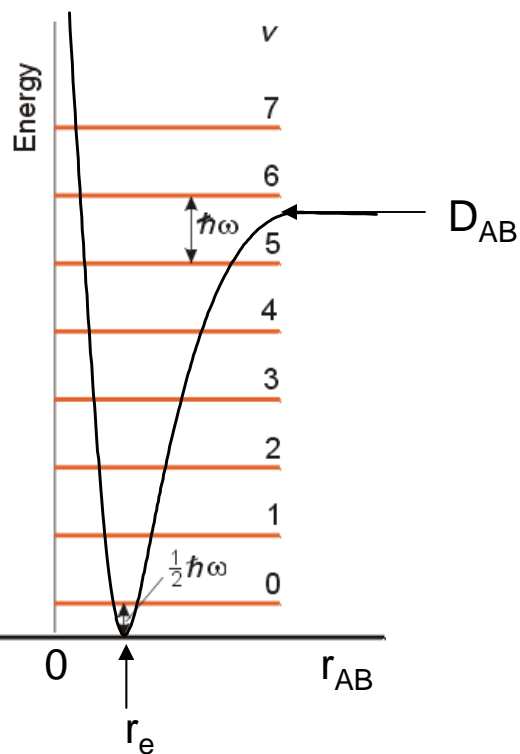


Chem 59-250 Vibrational Spectroscopy

A rough definition of *spectroscopy* is “the study of the interaction of matter with energy (radiation in the electromagnetic spectrum).” A molecular vibration is a periodic distortion of a molecule from its equilibrium geometry. The energy required for a molecule to vibrate is quantized (not continuous) and is generally in the infrared region of the electromagnetic spectrum.



For a diatomic molecule (A-B), the bond between the two atoms can be approximated by a spring that restores the distance between A and B to its equilibrium value. The bond can be assigned a force constant, k (in Nm^{-1} ; the stronger the bond, the larger k) and the relationship between the frequency of the vibration, ω , is given by the relationship:

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{or, more typically} \quad 2\pi c\bar{\nu} = \sqrt{\frac{k}{\mu}}$$

where, c is the speed of light, $\bar{\nu}$ is the frequency in “wave numbers” (cm^{-1}) and μ is the reduced mass (in amu) of A and B given by the equation:

$$\mu = \frac{m_A \times m_B}{m_A + m_B}$$

r_e = equilibrium distance between A and B D_{AB} = energy required to dissociate into A and B atoms

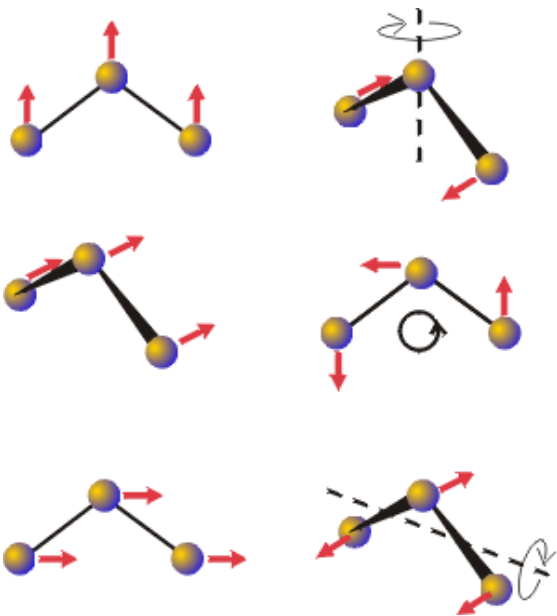
$$2\pi c\bar{\nu} = \sqrt{\frac{k}{\mu}} \quad \text{can be rearranged to solve for } k \text{ (in N/m): } k = 5.89 \times 10^{-5} \bar{\nu}^2 \mu$$

Molecule	$\bar{\nu}$ (cm ⁻¹)	k (N/m)	μ (amu)
HF	3962	878	19/20
HCl	2886	477	35/36 or 37/38
HBr	2558	390	79/80 or 81/82
HI	2230	290	127/128
Cl ₂	557	320	17.5
Br ₂	321	246	39.5
CO	2143	1855	6.9
NO	1876	1548	7.5
N ₂	2331	2240	7

For a vibration to be active (observable) in an infrared (IR) spectrum, the vibration must change the dipole moment of the molecule. (the vibrations for Cl₂, Br₂, and N₂ will not be observed in an IR experiment)

For a vibration to be active in a Raman spectrum, the vibration must change the polarizability of the molecule.

For polyatomic molecules, the situation is more complicated because there are more possible types of motion. Each set of possible atomic motions is known as a *mode*. There are a total of $3N$ possible motions for a molecule containing N atoms because each atom can move in one of the three orthogonal directions (i.e. in the x, y, or z direction).



A mode in which all the atoms are moving in the same direction is called a *translational mode* because it is equivalent to moving the molecule - there are three translational modes for any molecule.

A mode in which the atoms move to rotate (change the orientation) the molecule called a *rotational mode* - there are three rotational modes for any non-linear molecule and only two for linear molecules.

Translational modes

Rotational modes

The other $3N-6$ modes (or $3N-5$ modes for a linear molecule) for a molecule correspond to vibrations that we might be able to observe experimentally. We must use symmetry to figure out what how many signals we expect to see and what atomic motions contribute to the particular *vibrational modes*.

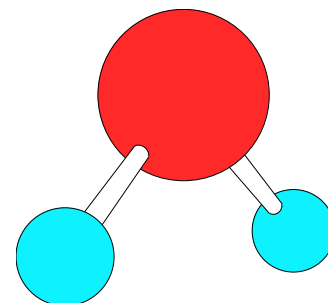
We must use character tables to determine how many signals we will see in a vibrational spectrum (IR or Raman) of a molecule. This process is done a few easy steps that are similar to those used to determine the bonding in molecules.

1. Determine the point group of the molecule.
2. Determine the Reducible Representation, Γ_{tot} , for all possible motions of the atoms in the molecule.
3. Identify the Irreducible Representation that provides the Reducible Representation.
4. Identify the representations corresponding to translation (3) and rotation (2 if linear, 3 otherwise) of the molecule. Those that are left correspond to the *vibrational modes* of the molecule.
5. Determine which of the vibrational modes will be visible in an IR or Raman experiment.

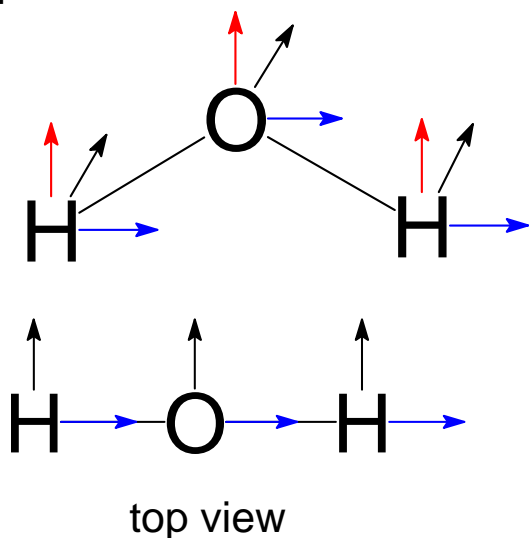
Chem 59-250 Vibrational Spectroscopy and Symmetry

Example, the vibrational modes in water.

The point group is C_{2v} so we must use the appropriate character table for the reducible representation of all possible atomic motions, Γ_{tot} . To determine Γ_{tot} we have to determine how each symmetry operation affects the displacement of each atom the molecule – this is done by placing vectors parallel to the x, y and z axes on each atom and applying the symmetry operations. As with the bonds in the previous examples, if an atom changes position, each of its vectors is given a value of 0; if an atom stays in the same place, we have to determine the effect of the symmetry operation of the signs of all three vectors.



The sum for the vectors on all atoms is placed into the reducible representation.

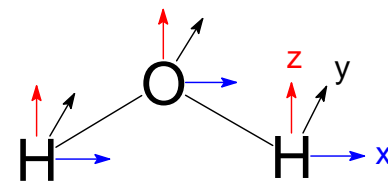


Make a drawing of the molecule and add in vectors on each of the atoms. Make the vectors point in the same direction as the x (shown in blue), the y (shown in black) and the z (shown in red) axes. We will treat all vectors at the same time when we are analyzing for molecular motions.

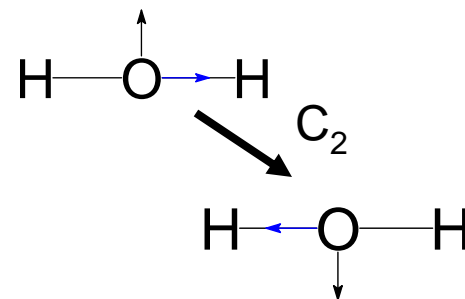
Chem 59-250 Vibrational Spectroscopy and Symmetry

Example, the vibrational modes in water.

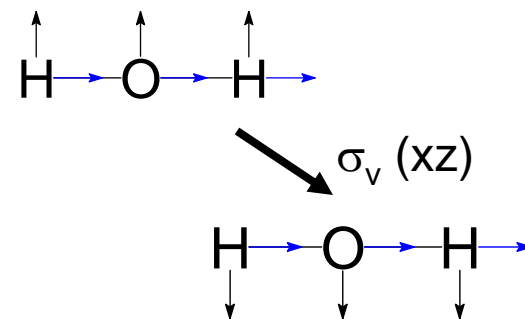
The E operation leaves everything where it is so all nine vectors stay in the same place and the character is 9.



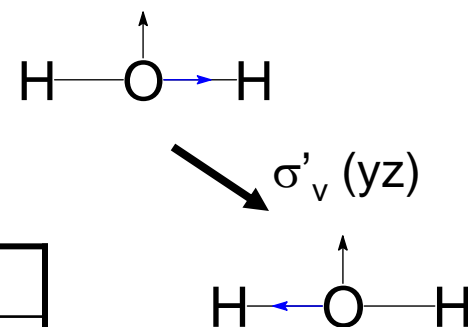
The C_2 operation moves both H atoms so we can ignore the vectors on those atoms, but we have to look at the vectors on the oxygen atom, because it is still in the same place. The vector in the z direction does not change (+1) but the vectors in the x, and y directions are reversed (-1 and -1) so the character for C_2 is -1.



The σ_v (xz) operation leaves each atom where it was so we have to look at the vectors on each atom. The vectors in the z and x directions do not move (+3 and +3) but the vectors in the y direction are reversed (-3) so the character is 3.



The σ'_v (yz) operation moves both H atoms so we can ignore the vectors on those atoms, but we have to look at the vectors on the oxygen atom, because it is still in the same place. The vectors in the z and y directions do not move (+1 and +1) but the vectors in the x direction is reversed (-1) so the character is 1.



C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_{tot}	9	-1	3	1

C_{2V}	E	C_2	$\sigma_v (xz)$	$\sigma'_v (yz)$
Γ_{tot}	9	-1	3	1

C_{2V}	E	C_2	$\sigma_v (xz)$	$\sigma'_v (yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

From the Γ_{tot} and the character table, we can figure out the number and types of modes using the same equation that we used for bonding:

$$n_x = \frac{1}{\text{order}} \sum [(\# \text{ of operations in class}) \times (\text{character of RR}) \times (\text{character of X})]$$

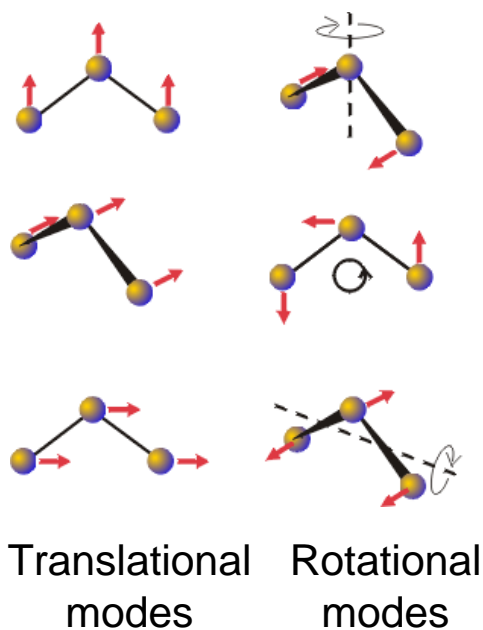
This gives:

$$n_{A_1} = \frac{1}{4} [(1)(9)(1) + (1)(-1)(1) + (1)(3)(1) + (1)(1)(1)] \quad n_{B_1} = \frac{1}{4} [(1)(9)(1) + (1)(-1)(-1) + (1)(3)(1) + (1)(1)(-1)]$$

$$n_{A_2} = \frac{1}{4} [(1)(9)(1) + (1)(-1)(1) + (1)(3)(-1) + (1)(1)(-1)] \quad n_{B_2} = \frac{1}{4} [(1)(9)(1) + (1)(-1)(-1) + (1)(3)(-1) + (1)(1)(1)]$$

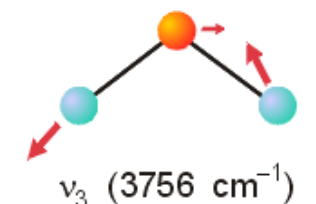
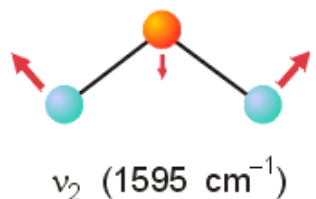
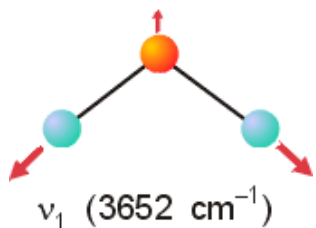
Which gives: 3 A_1 's, 1 A_2 , 3 B_1 's and 2 B_2 's or a total of 9 modes, which is what we needed to find because water has three atoms so $3N = 3(3) = 9$.

Now that we have found that the irreducible representation for Γ_{tot} is $(3A_1 + A_2 + 3B_1 + 2B_2)$, the next step is to identify the translational and rotational modes - this can be done by reading them off the character table! The three translational modes have the symmetry of the functions x , y , and z (B_1 , B_2 , A_1) and the three rotational modes have the symmetry of the functions R_x , R_y and R_z (B_2 , B_1 , A_2).



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The other three modes $(3(3)-6 = 3)$ that are left over for water ($2A_1 + B_1$) are the vibrational modes that we might be able to observe experimentally. Next we have to figure out if we should expect to see these modes in an IR or Raman vibrational spectrum.



The three vibrational modes for water. Each mode is listed with a ν (Greek letter 'nu') and a subscript and the energy of the vibration is given in parentheses. ν_1 is called the "symmetric stretch", ν_3 is called the "anti-symmetric stretch" and ν_2 is called the "symmetric bend".

Remember that for a vibration to be observable in an IR spectrum, the vibration must change the dipole moment of the molecule. In the character table, representations that change the dipole of the molecule are those that have the same symmetry as translations. Since the irreducible representation of the vibrational modes is $(2A_1 + B_1)$ all three vibrations for water will be **IR active (in red)** and we expect to see three signals in the spectrum.

For a vibration to be active in a Raman spectrum, the vibration must change the polarizability of the molecule. In the character table, representations that change the polarizability of the molecule are those that have the same symmetry as the second order functions (**with squared and multiplied variables**). Thus all three modes will also be **Raman active (in blue)** and we will see three signals in the Raman spectrum.

C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz