A Second Application of Symmetry

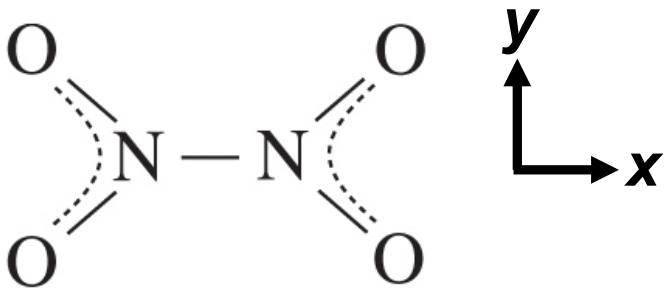
Chapter 4

Monday, October 5, 2015

Using Symmetry: Vibrational Spectroscopy

IR and Raman spectra can be interpreted using symmetry.

- **For nonlinear molecules, the number of vibrational modes is 3*N* - 6, where *N* is the number of atoms and 3*N* the number of *degrees of freedom***
- **Consider N_2O_4, which is D_{2h}**



- **Each atom can move in three dimensions**
  - **If all atoms move the same amount in the same direction the molecule moves, which is a translation, not a vibration (accounts for three degrees of freedom)**
  - **Molecule can also rotate around the three orthogonal axes (which accounts for three more degrees of freedom)**
- **So for N_2O_4 we predict that there will be 3*N* - 6 = 12 vibrational modes**

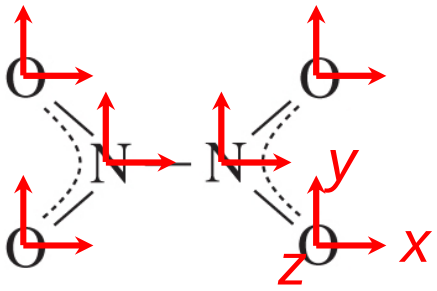
Using Symmetry: Vibrational Spectroscopy

We can use character tables to determine the symmetry of all 18 motions and then assign them to translation, rotation, or vibration.

We can also tell which vibrations are *IR* or *Raman active.*

Procedure:

1. **Assign *x,y,z* coordinates to each atom.**



2. **Determine how each axis transforms for every class of symmetry operation in the group.**
   - **If an atom moves, the character for all of its axes is 0**
   - **If an atom is stationary and the axis direction is unchanged, its character is 1**
   - **If an atom is stationary and the axis direction is reversed, its character is -1**

3. **Sum the characters in each class to determine the reducible representation Γ**

Using Symmetry: Vibrational Spectroscopy

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	18	0	0	-2	0	6	2	0

***E*: all 18 axes unchanged → $\chi = 18$**

***C*$_2$(*z*): all atoms move → $\chi = 0$**

***C*$_2$(*y*): all atoms move → $\chi = 0$**

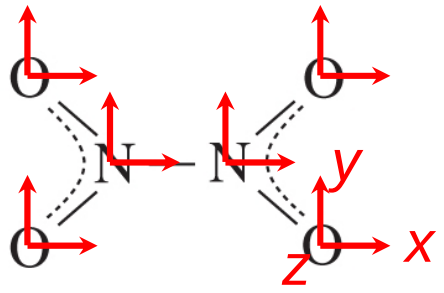
***C*$_2$(*x*): oxygens move**
N's *x* unchanged
N's *y*,*z* reversed → $\chi = -2$

***i*: all atoms move → $\chi = 0$**

σ(*xy*): *z* axes reversed
***x*,*y* axes unchanged → $\chi = 6$**

σ(*xz*): oxygens move
N's *x*,*z* unchanged
N's *y* reversed → $\chi = 2$

σ(*yz*): all atoms move → $\chi = 0$



Γ is the reducible representation for all motions of N_2O_4

Using Symmetry: Vibrational Spectroscopy

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	18	0	0	-2	0	6	2	0

4. **Now reduce Γ to its irreducible components using the character table and the following property of groups:**

$$\#\text{ of irreducible representations of a given type} = \frac{1}{\text{order}}\sum_{R}\left(\#\text{ of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation}\right)$$

$$\#\,A_g = 1/8*[18+0+0-2+0+6+2+0] = 3$$
$$\#\,B_{1g} = 1/8*[18+0+0+2+0+6-2+0] = 3$$
$$\#\,B_{2g} = 1/8*[18+0+0+2+0-6+2+0] = 2$$
$$\#\,B_{3g} = 1/8*[18+0+0-2+0-6-2+0] = 1$$
$$\#\,A_u = 1/8*[18+0+0-2+0-6-2+0] = 1$$
$$\#\,B_{1u} = 1/8*[18+0+0+2+0-6+2+0] = 2$$
$$\#\,B_{2u} = 1/8*[18+0+0+2+0+6-2+0] = 3$$
$$\#\,B_{3u} = 1/8*[18+0+0-2+0+6+2+0] = 3$$

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

So, $\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$

Using Symmetry: Vibrational Spectroscopy

The reducible representation is the sum of 18 irreducible reps:

$$\Gamma = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$$

5. **Now use the character table to subtract the translations and rotations, leaving the representations corresponding to the vibrations.**

Translations $(x,y,z) = B_{1u} + B_{2u} + B_{3u}$

Rotations $(R_x,R_y,R_z) = B_{1g} + B_{2g} + B_{3g}$

Vibrational modes (all that remain) =
$3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

These are the symmetries of the 12 vibrational modes of N_2O_4

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

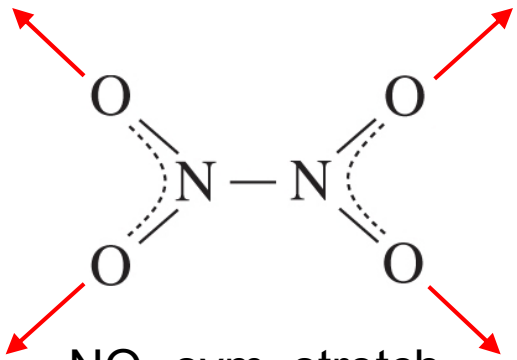
Using Symmetry: Vibrational Spectroscopy

Let's consider the vibrational modes of N_2O_4 in a little more detail.

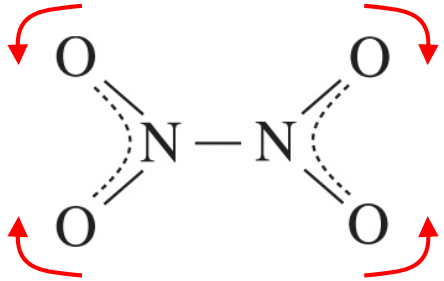
$$\text{Vibrations} = 3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$

Using the table, we can guess what these modes might look like.

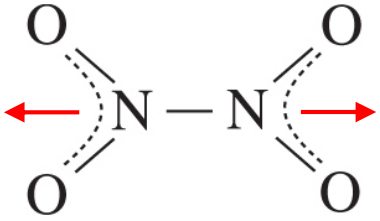
e.g., the three A_g modes are totally symmetric:



NO_2 sym. stretch

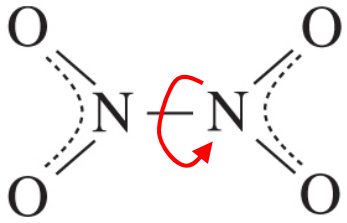


NO_2 sym. bend



N-N stretch

the A_u mode is symmetric w.r.t C_2 but antisymmetric w.r.t. σ and i:



torsion

Using Symmetry: Vibrational Spectroscopy

The character table tells us whether the vibrational modes are IR active and/or Raman active.

To be *IR active* (allowed), the vibration must change the dipole moment of the molecule.

- **Only irreducible representations with *x,y,z* symmetry do this**

N_2O_4 vibrations = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

IR active: $B_{1u} + 2B_{2u} + 2B_{3u}$

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Using Symmetry: Vibrational Spectroscopy

The character table tells us whether the vibrational modes are IR active and/or Raman active.

To be *Raman active* (allowed), the vibration must change the polarizability of the molecule.

- **Only irreducible representations that transform like the binary products of *x*,*y*, and *z* (i.e., *xy, xz, yz, x^2, y^2, z^2* or their linear combinations) do this**

N_2O_4 vibrations = $3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$

Raman active: $3A_g + 2B_{1g} + B_{2g}$

*Note that the A_u mode is IR and Raman *silent*.

Character table for D_{2h} point group

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

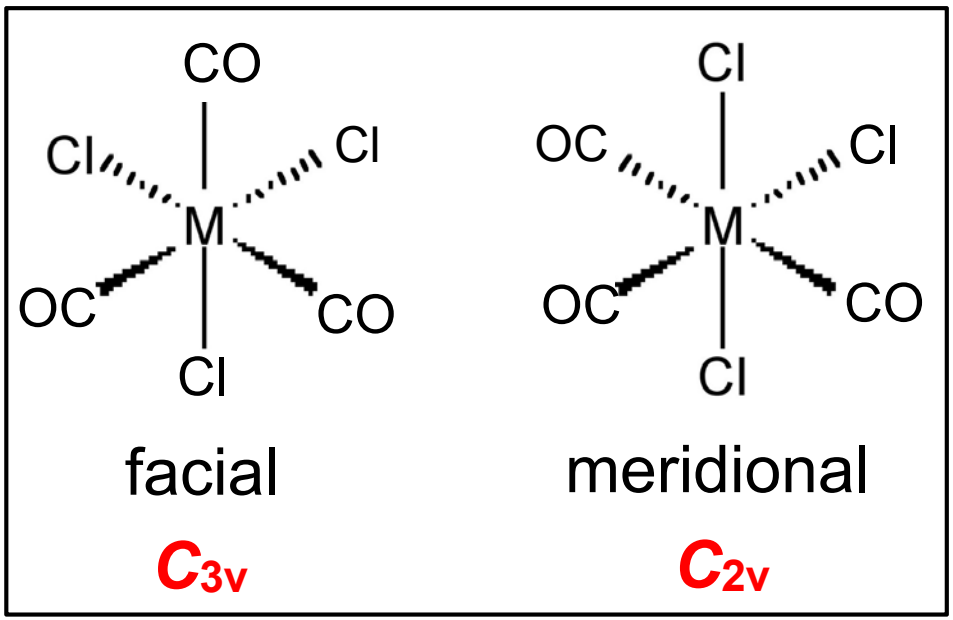
Using Symmetry: Selected Vibrational Modes

We may be interested in the vibrations of specific groups in a molecule rather than all possible motions of the molecule.

e.g., C-O stretching in metal carbonyl complexes

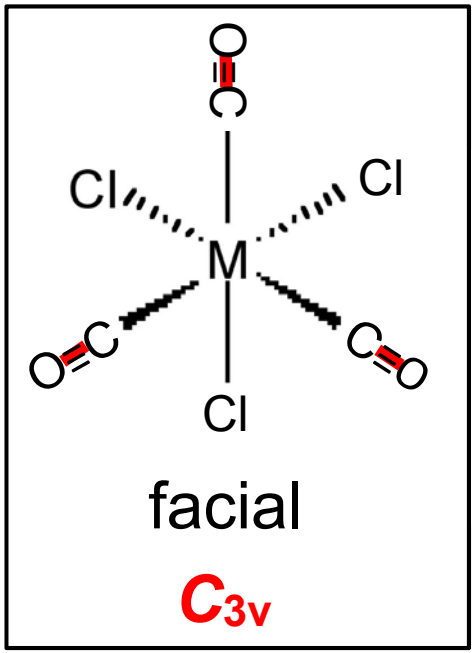
In this case, we can create reducible representations of the bond vectors of interest, determine their irreducible components, and find the active modes.

Example: can we use IR/Raman spectroscopy to distinguish between *fac*-$ML_3(CO)_3$ and *mer*-$ML_3(CO)_3$ isomers?



Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
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)

χ = 1 if unchanged

χ = 0 if changed

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	3	0	1

Reduce to irreducible representations:

$$\#\text{ of irreducible representations of a given type} = \frac{1}{\text{order}}\sum_R \left[\#\text{ of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation}\right]$$

A_1 = 1/6*[3+0+3] = 1

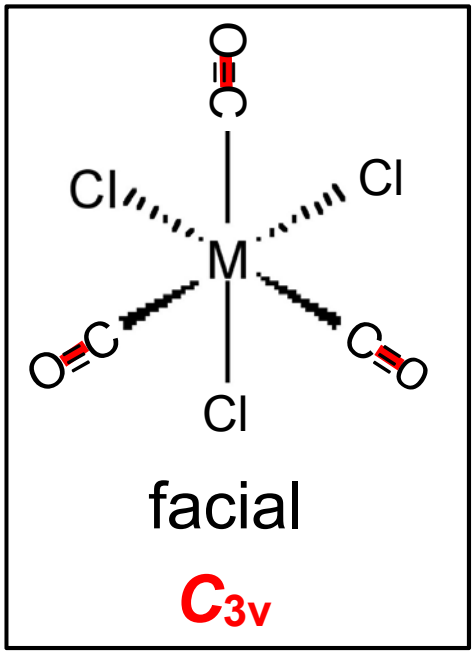
A_2 = 1/6*[3+0-3] = 0

E = 1/6*[6+0+0] = 1

So, $\Gamma = A_1 + E$

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
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)

$\Gamma = A_1 + E$

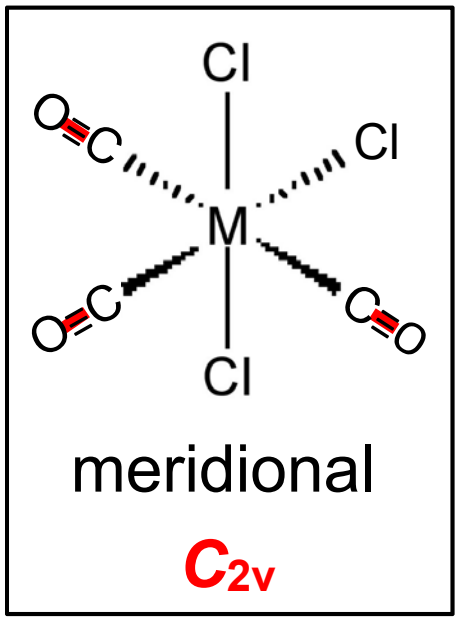
IR active (*x*,*y*,*z*): A_1 and E (2 peaks predicted)

Raman active (quadratic): A_1 and E (2 peaks predicted)

→ The *fac* isomer is expected to have 2 peaks in both its IR and Raman spectra.

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
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

χ = 1 if unchanged

χ = 0 if changed

C_{2v}	*E*	C_2(z)	σ_v(xz)	σ_v(yz)
Γ	3	1	3	1

Reduce to irreducible representations:

$$\#\text{ of irreducible representations of a given type} = \frac{1}{\text{order}}\sum_R \left[\#\text{ of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation}\right]$$

A_1 = 1/4*[3+1+3+1] = 2

A_2 = 1/4*[3+1-3-1] = 0

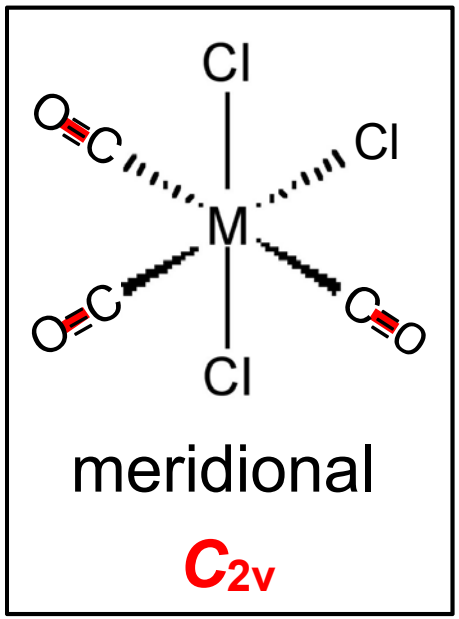
B_1 = 1/4*[3-1+3-1] = 1

B_2 = 1/4*[3-1-3+1] = 0

So, $\Gamma = 2A_1 + B_1$

Using Symmetry: Selected Vibrational Modes

Let's create reducible representations of the C-O bonds in each molecule:



Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
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

$\Gamma = 2A_1 + B_1$

IR active (*x*,*y*,*z*): A_1 and B_1 (3 peaks predicted)

Raman active (quadratic): A_1 and B_1 (3 peaks predicted)

→ The *mer* isomer is expected to have 3 peaks in both its IR and Raman spectra.

Summary

Group theory can tell us which molecules are chiral, possess dipole moments, possess chemically identical groups, and other symmetry-related properties

We can use group theory to determine the vibrational modes of molecules. Procedure:

- **Determine point group of molecule**
- **Determine reducible representation for vectors of interest**
- **Reduce this representation to its irreducible components (modes)**
- **If desired, assign the modes to the different motions (rotations, translations, stretches, bends, wags, twists, etc.)**
- **If desired, read off which modes are IR/Raman active**

To dig deeper, check out: Cotton, F. A. *Chemical Applications of Group Theory*.