Harmony, Photons, and the Shape of Molecules

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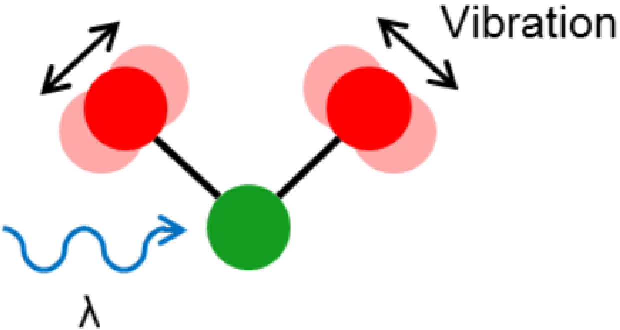
Introduction: shining light on molecules.

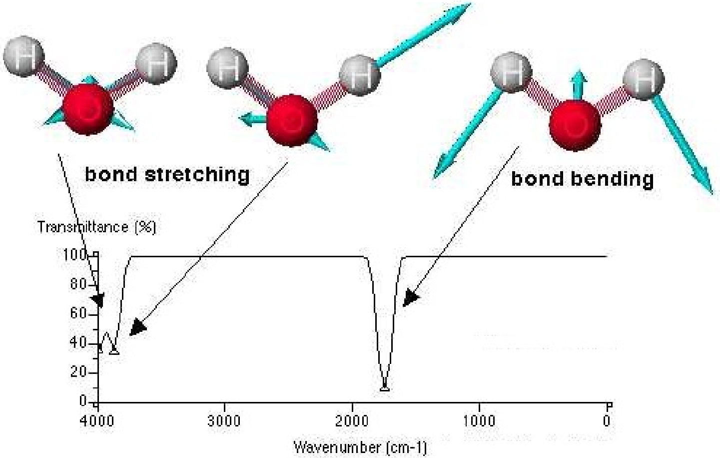
Takeaway: **symmetries make hard problems easier**.



We shine light with some wavelength λ on a molecule. What happens?

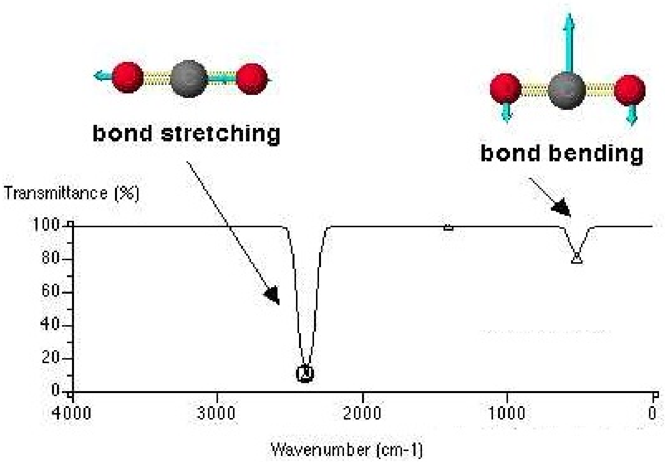
Some wavelengths excite vibrations.

H_2O has three special wavelengths that cause it to vibrate.



Linear molecules have two.

CO_2 has two special wavelengths which it absorbs. Why? The only difference from H_2O is shape.

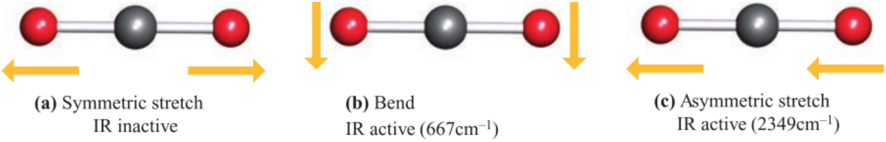


Shape and spectrum.

This problem is hard: it usually appears in a physical chemistry class.

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi.$$

However, we can predict how many special wavelengths a molecule will absorb (the *spectrum*) knowing only its *shape*.



Talk roadmap.

Here's the plan:

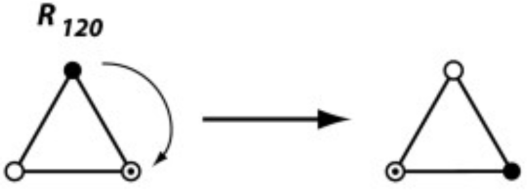
1. ~~Introduction: shining light on molecules.~~
2. Act 1: The symmetries of molecules.
3. Interlude: Throwing photons at things.
4. Act 2: Turning symmetries into matrices.
5. Act 3: Determining shape from spectrum.

Act 1: The symmetries of molecules.

The idea.

Symmetry is invariance under some change.

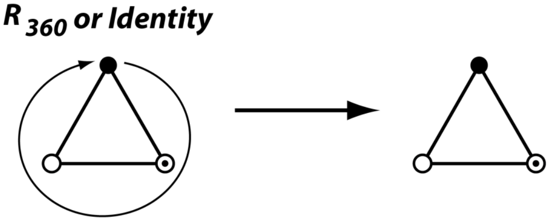
Symmetry operations are changes you can perform to a set of points, in particular the atoms of a molecule, that leave the shape unchanged.



Identity.

The identity symmetry, represented by E, is the act of doing nothing to the molecule of interest.

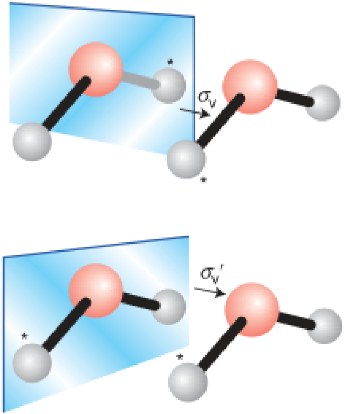
All moleculues possess this symmetry, but it is also the most important.



Mirror.

Another symmetry, given the tag σ by "professionals," reflects all atoms across some mirror plane.

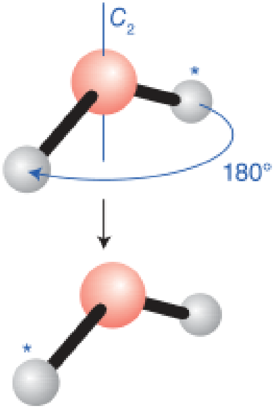
The water molecule has two planes of symmetry:



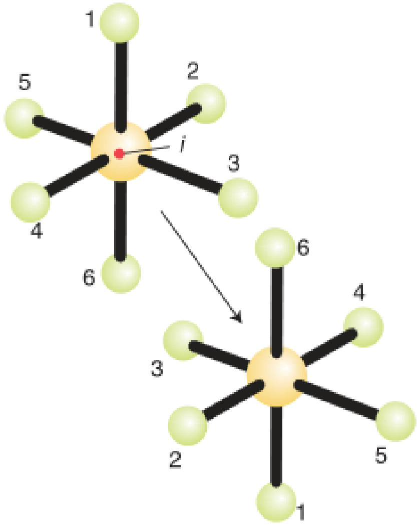
Rotation.

Rotation is yet another form of symmetry, written C_n, which represents the ability to rotate a molecule by $\frac{360}{n}$ degrees and have it be unchanged.

Consider rotating water by 180°:



Inversion.



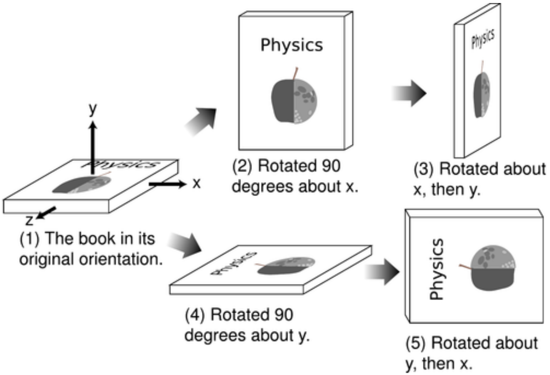
"Inversion involves passing each atom through the center of the molecule and placing it on the opposite side of the molecule."
- Daniel Harris, Michael Bertolucci

Inversion occurs through the center of the molecule, and is represented by the letter *i*.

Composing symmetries.

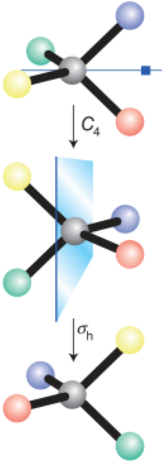
Applying one symmetry, and then another, is also a symmetry. Thus we can *compose* or *multiply* two symmetries to get another.

The order in which we compose two operations, like rotations, matters:



Improper rotation.

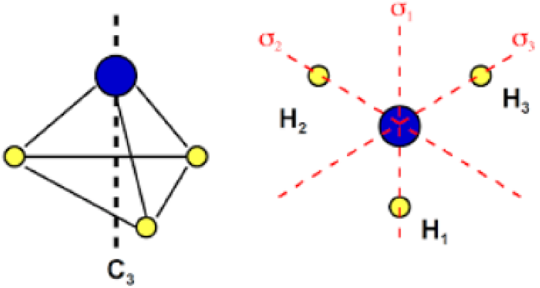
Improper rotation is simply rotation followed by a mirror, and is represented by S_n where n has the same meaning as in a normal rotation.



Point group.

The collection of all symmetry operations for a molecule, including the rule for composing them, is called the molecule's *symmetry group* or *point group*. The rule for composing symmetries is called the *group law*.

For example, ammonia, (NH_3) has a C_3 rotation axis (120°) and three mirror planes. This group is called C_{3v}.



Listing products.

Since we can multiply two symmetries to get another, we can construct a *multiplication table* that gives the product of any two symmetries.

Ammonia's point group C_{3v} has the multiplication table

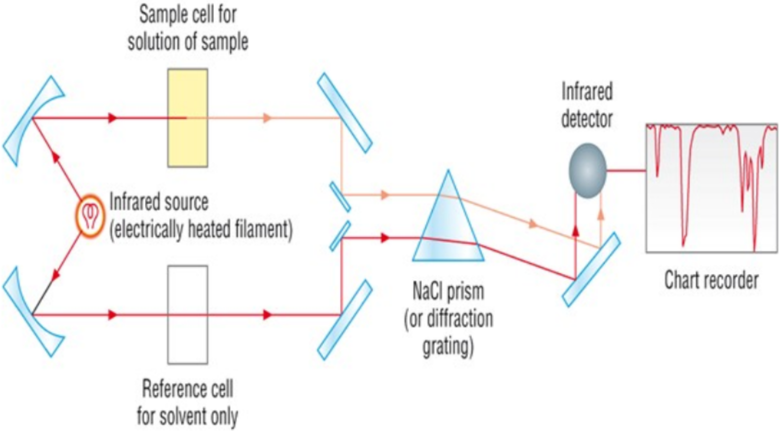
C_{3v}	E	C_3	C_3^2	σ_v^1	σ_v^2	σ_v^3
E	E	C_3	C_3^2	σ_v^1	σ_v^2	σ_v^3
C_3	C_3	C_3^2	E	σ_v^2	σ_v^3	σ_v^1
C_3^2	C_3^2	E	C_3	σ_v^3	σ_v^1	σ_v^2
σ_v^1	σ_v^1	σ_v^2	σ_v^3	E	C_3	C_3^2
σ_v^2	σ_v^2	σ_v^3	σ_v^1	C_3^2	E	C_3
σ_v^3	σ_v^3	σ_v^1	σ_v^2	C_3	C_3^2	E

.

Interlude: Throwing photons at things.

Intro to IR spectroscopy.

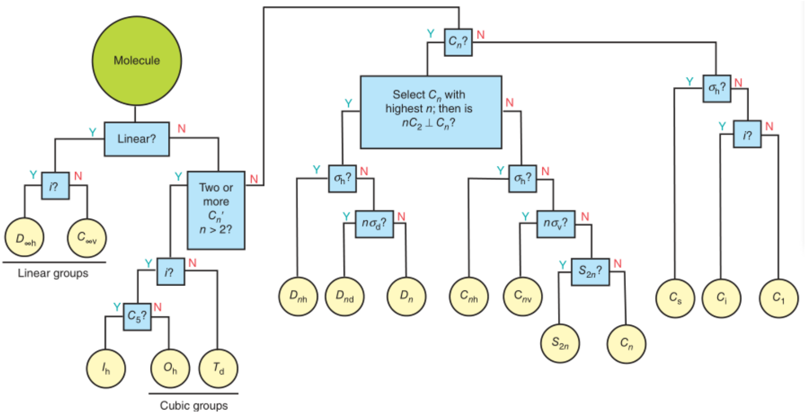
Infrared spectroscopy is the primary physical tool of our entire discussion about relating symmetry to light. The layout of an IR spectrometer is seen below:



Act 2: Turning symmetries into matrices.

Turning the crank.

There is a straightforward way to find the point group for any molecule.



Once we know the point group, how do we use it?

Turn symmetries into matrices.

The structure of a group is captured by its group law: what happens when you compose two elements $g_1 \circ g_2$? For instance, usually $g_1 \circ g_2 \neq g_2 \circ g_1$.

Order also matters in the rule for matrix multiplication:

$$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix},$$
$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}.$$

You might think there is a connection, and look for a machine – called a *representation* – which turns symmetry operations into matrices.

$$\text{symmetry} \longrightarrow \boxed{\text{representation}} \longrightarrow \text{matrix}$$

Group law $\longrightarrow$ matrix multiplication.

We want our representation to *respect* the group law.

If we turn group elements g_1 and g_2 into matrices M_1 and M_2, then the matrix product $M_1 \cdot M_2$ had better be the same thing we'd get by feeding $g_1 \cdot g_2$ into the machine.

$$\begin{aligned} g_1 &\longrightarrow \boxed{\text{ rep }} \longrightarrow M_1, \\ g_2 &\longrightarrow \boxed{\text{ rep }} \longrightarrow M_2, \\ g_1 \circ g_2 &\longrightarrow \boxed{\text{ rep }} \longrightarrow M_1 \cdot M_2. \end{aligned}$$

Said differently: if R is a representation, we want

$$R(g_1 \circ g_2) = R(g_1) \cdot R(g_2),$$

where $\cdot$ is matrix multiplication.

Characterizing machines.

We can imagine that there might be many ways to turn group elements into matrices while respecting the group law. Can we classify them?

One trick for *characterizing* different machines is called the *character*. Turn a group element into a matrix and add the numbers on the diagonal.

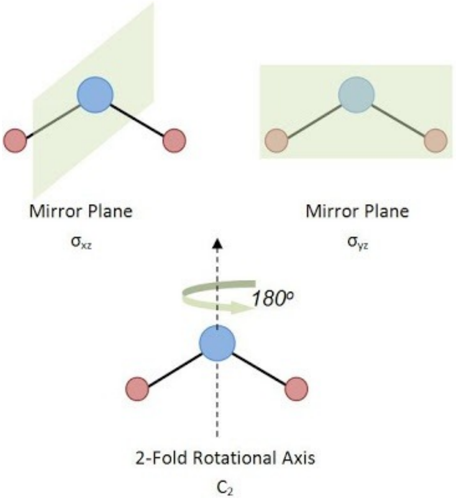
$$\sigma_v \longrightarrow \boxed{\text{rep 1}} \longrightarrow \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \longrightarrow \boxed{\text{character}} \longrightarrow 0,$$

$$\sigma_v \longrightarrow \boxed{\text{rep 2}} \longrightarrow \begin{bmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 2 \end{bmatrix} \longrightarrow \boxed{\text{character}} \longrightarrow 1.$$

With "rep" and "character" we can turn group elements into *numbers*.

A water example.

Recall the point group of water is $C_{2v} = \{E, C_2, \sigma_v(xz), \sigma_v'(yz)\}$:



Reps for water.

Say we look for some reps that respect the C_{2v} group law, then write down the characters for each element in a table.

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

The first miracle.

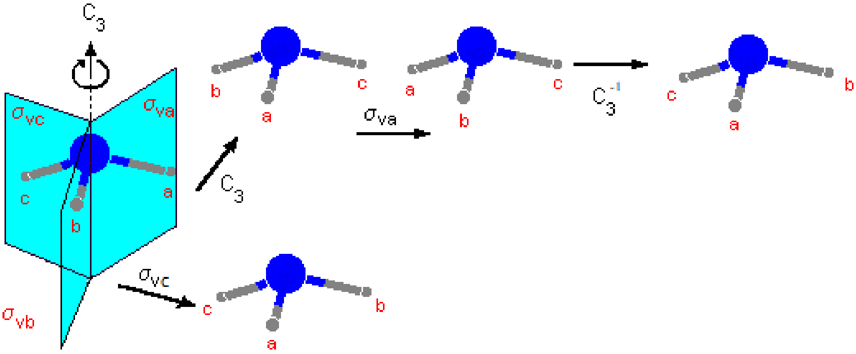
You might think we could find reps of C_{2v} that spit out bigger matrices.

But **every rep** can be built out of the four *irreducible reps* on the previous slide by "stacking" on the diagonal:

$$D(g) = \left(\begin{array}{c|c|c|c|c} \ddots & 0 & 0 & 0 & 0 \\ \hline 0 & D^{(r)}(g) & 0 & 0 & 0 \\ \hline 0 & 0 & \ddots & 0 & 0 \\ \hline 0 & 0 & 0 & D^{(s)}(g) & 0 \\ \hline 0 & 0 & 0 & 0 & \ddots \end{array}\right) \quad \text{for all } g \in G$$

The second miracle.

Symmetries split into *conjugacy classes* with the same characters.



Character is a function of class.

The C_{3v} point group has 6 elements, but all rotations have the same character and all mirrors have the same character.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x, y) (R_x, R_y)

Character tables.

Miracles:

1. Every rep can be built out of a small number of *irreducible reps*.
2. Group elements split into *conjugacy classes* with the same characters.
3. If you take two different irreps, multiply their characters for each group element, and add them up, you always get zero.

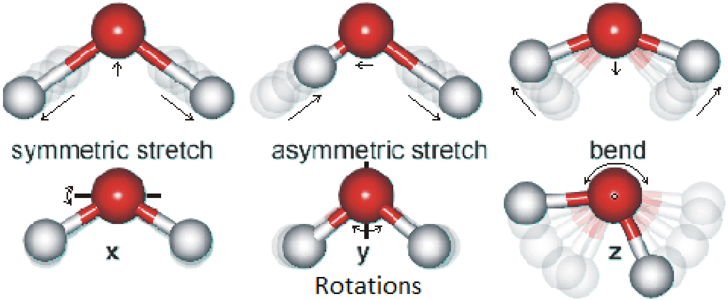
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$h=24$
A_1	1	1	1	1	1	
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)
T_2	3	0	−1	−1	1	(x, y, z)

Act 3: Determining shape from spectrum.

The recipe.

With the character table, we will

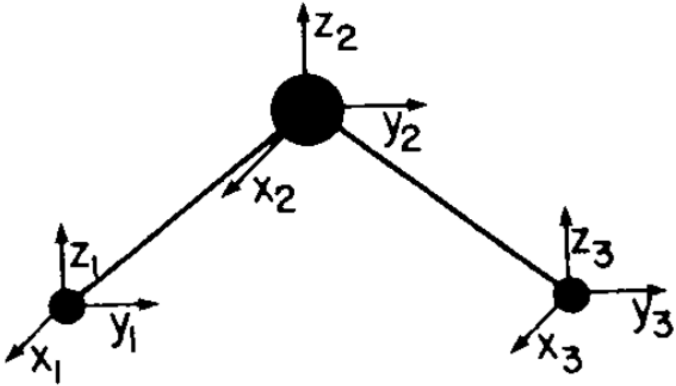
1. Represent all possible ways a molecule can move,
2. Remove translations and rotations, then
3. Apply “selection rules” to see how many motions are IR active.



Degrees of freedom.

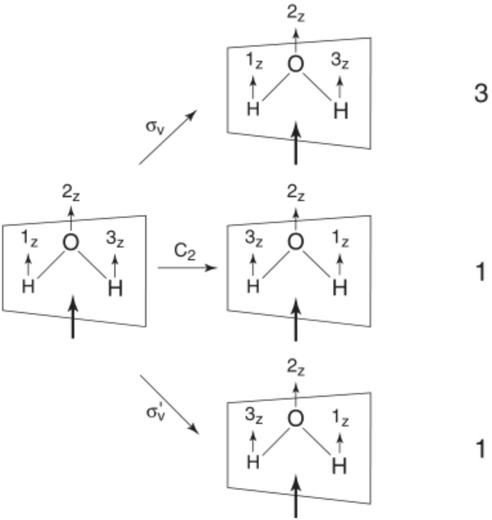
We'll list all "degrees of freedom" or ways that a molecule can move.

Imaging gluing (x, y, z) axes to each of N atoms. This gives $3N$ independent motions.



Symmetries mix up motions.

A symmetry leaves the stationary molecule unchanged, but can change one kind of motion into another.



Symmetries act like *matrices*.

Think of C_2 as a matrix acting on the (x, y, z) arrows for each atom.

$$C_2 \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix}$$

We turned the symmetry C_2 into a matrix using a **representation** R_{tot}.

Reducing the rep.

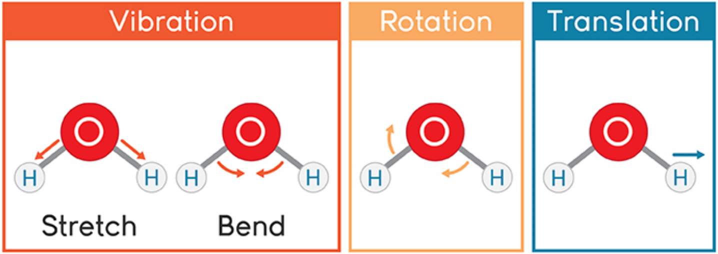
There is a trick for reducing big reps into smaller ones using "miracle 3," that multiplying and adding characters for different irreps gives zero.

C_{2v}	E	C_2	σ_v	σ'_v	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x
R_{tot}	9	-1	1	3	

We find $R_{\text{tot}} = 3A_1 + A_2 + 2B_1 + 3B_2$.

Subtractions.

This R_{tot} contains all motions – vibrations, translations, and rotations.



We subtract off one copy of the reps associated with translations x, y, z and rotations R_x, R_y, R_z, as marked in the table, leaving

$$R_{\mathrm{vib}} = 2A_1 + B_2.$$

Selections.

Last, we take $R_{\text{vib}} = 2A_1 + B_2$ and apply the *selection rule*: count how many irreps transform like x, y, or z in the character table.

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

This comes from quantum mechanics: a photon absorption must change the molecule's *dipole moment*, which is associated with irreps labeled x, y, z in the table.

We see both A_1 and B_2 count, so water has **three special wavelengths**.

The full recipe.

Given any molecule, we can determine the number of IR peaks as follows:

1. Determine the molecule's point group and look up its character table.
2. Find the character for each class of symmetries, giving the reducible R_{tot} for all $3N$ degrees of freedom.
3. Reduce R_{tot} to write it as a sum of irreps.
4. Subtract the characters for translations and rotations to get R_{vib}
5. Apply the *selection rule*: of the remaining irreps, count how many transform like x, y, or z.

The result of the count in step (5) gives the number of IR absorptions.

Minute paper.

Thanks for coming! Please write responses on an index card and hand it to us on your way out:

1. Could you list one thing we discussed today which you found especially memorable or interesting?

2. Can you mention one topic which you found confusing, or that you might read more about to clarify on your own?