

## 13.14: Group Theory Determines Infrared Activity

### Determining if a Normal Modes is IR or Raman Active

A transition from  $v \rightarrow v'$  is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment  $\mu$ , the integral is:

$$M(v \rightarrow v') = \langle \text{final wavefunction} | \vec{\mu} | \text{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode  $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \vec{\mu} | \phi(v = 0) \rangle \quad (13.14.1)$$

assuming the transition from the  $v = 0$  wavefunction to the  $v' \neq 0$  wavefunction.

Now, consider the case that  $\vec{\mu}$ , is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 13.14.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \quad (13.14.2)$$

Since  $|\phi(v = 0)\rangle$  and  $|\phi(v \neq 0)\rangle$  are mutually orthogonal to each other, the integral in Equation 13.14.1 will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the  $M$  to be nonzero,  $\vec{\mu}$  must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor  $\alpha$  (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \alpha | \phi(v = 0) \rangle \quad (13.14.3)$$

Following a similar argument as above,  $\alpha$  must be nonzero for the transition to be allowed and exhibits Raman scattering.

### Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation  $\Gamma_{\text{vib}}$  can also be found by determining the reducible representation of the  $3N$  degrees of freedom of  $\text{H}_2\text{O}$ ,  $\Gamma_{\text{tot}}$ . By applying Group Theory it is straightforward to find  $\Gamma_{x,y,z}$  as well as UMA (number of unmoved atoms). Again, using water as an example with  $C_{2v}$  symmetry where  $3N = 9$ ,  $\Gamma_{\text{tot}}$  can be determined:

$C_{2v}$	E	$C_2$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma_{x,y,z}$	3	-1	1	1	
UMA	3	1	1	3	
$\Gamma_{\text{tot}}$	9	-1	1	3	$=3a_1 + a_2 + 2b_1 + 3b_2$

Note that  $\Gamma_{\text{tot}}$  contains nine degrees of freedom consistent with  $3N = 9$ .

$\Gamma_{\text{tot}}$  contains  $\Gamma_{\text{translational}}$ ,  $\Gamma_{\text{rotational}}$  as well as  $\Gamma_{\text{vibrational}}$ .  $\Gamma_{\text{trans}}$  can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table,  $\Gamma_{\text{rot}}$  by finding the ones corresponding to  $R_x$ ,  $R_y$  and  $R_z$ .  $\Gamma_{\text{vib}}$  can be obtained by  $\Gamma_{\text{tot}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$ .

$$\Gamma_{\text{vib}}(\text{H}_2\text{O}) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

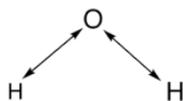
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation  $\Gamma_{\text{vib}}$  is necessary. If they contain the same irreducible representation, the mode is IR active.

For H<sub>2</sub>O, z transforms as a<sub>1</sub>, x as b<sub>1</sub> and y as b<sub>2</sub>. The modes a<sub>1</sub> and b<sub>2</sub> are IR active since  $\Gamma_{\text{vib}}$  contains 2a<sub>1</sub> + b<sub>2</sub>.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z<sup>2</sup>, x<sup>2</sup>-y<sup>2</sup>, xy, xz and yz is used and again cross checked with  $\Gamma_{\text{vib}}$ . For H<sub>2</sub>O, z<sup>2</sup> and x<sup>2</sup>-y<sup>2</sup> transform as a<sub>1</sub>, xy as a<sub>2</sub>, xz as b<sub>1</sub> and yz as b<sub>2</sub>. The modes a<sub>1</sub> and b<sub>2</sub> are also Raman active since  $\Gamma_{\text{vib}}$  contains both these modes.

The IR spectrum of H<sub>2</sub>O does indeed have three bands as predicted by Group Theory. The two symmetric stretches ν<sub>1</sub> and ν<sub>2</sub> occur at 3756 and 3657 cm<sup>-1</sup> whereas the bending ν<sub>3</sub> motion occurs at 1595 cm<sup>-1</sup>.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deduced from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C<sub>2v</sub> symmetry will yield the following results:

C <sub>2v</sub>	E	C <sub>2</sub>	σ(xz)	σ(yz)	
Γ <sub>stretch</sub>	2	0	0	2	= a <sub>1</sub> + b <sub>2</sub>

$$\Gamma_{\text{bend}} = \Gamma_{\text{vib}} - \Gamma_{\text{stretch}} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H<sub>2</sub>O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as PtCl<sub>4</sub>. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D<sub>4h</sub> symmetry. Once the irreducible representation for Γ<sub>stretch</sub> has been worked out, Γ<sub>bend</sub> can be determined by  $\Gamma_{\text{bend}} = \Gamma_{\text{vib}} - \Gamma_{\text{stretch}}$ .

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the ν=0 state. Some molecules do have a significant population of the ν=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

## References

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