

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 μ , 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 α (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, α 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 Γ_{vib} can also be found by determining the reducible representation of the $3N$ degrees of freedom of H_2O , Γ_{tot} . By applying Group Theory it is straightforward to find $\Gamma_{\text{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where $3N = 9$, Γ_{tot} can be determined:

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

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

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

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

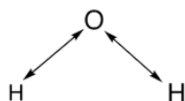
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

For H₂O, z transforms as a₁, x as b₁ and y as b₂. The modes a₁ and b₂ are IR active since Γ_{vib} contains 2a₁ + b₂.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z², x²-y², xy, xz and yz is used and again cross checked with Γ_{vib} . For H₂O, z² and x²-y² transform as a₁, xy as a₂, xz as b₁ and yz as b₂. The modes a₁ and b₂ are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H₂O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v₁ and v₂ occur at 3756 and 3657 cm⁻¹ whereas the bending v₃ motion occurs at 1595 cm⁻¹.

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_{2v} symmetry will yield the following results:

C _{2v}	E	C ₂	σ (xz)	σ (yz)	
Γ _{stretch}	2	0	0	2	= a ₁ + b ₂

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

H₂O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as PtCl₄²⁻. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for Γ_{stretch} has been worked out, Γ_{bend} 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 v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

References

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