

# Structure Determination Using IR and Raman Spectroscopy

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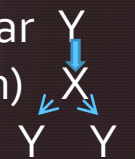

# Molecules of Type $XY_3$

- $XY_3$  type molecules will have 6 fundamentals
- Depending on **symmetry** it degenerates.
- **Simplest**: The planar  $D_{3h}$  point group and the pyramidal  $C_{3v}$  point group.
- No of **distinct fundamentals** is 4 for both of them.
- **Planar  $D_{3h}$  point group**
  - Symmetric stretching vibration is forbidden in **IR**
  - Intense polarized band in **Raman**.

- Pyramidal  $C_{3v}$

- Symmetric stretching and bending modes are polarized in Raman.

## PREDICTIONS OF FUNDAMENTALS OF SYMMETRIC $XY_3$ MOLECULES

MODEL	No. Of distinct fundamentals	No. of fundamentals permitted in IR	No. permitted in Raman	No. of coincidences	No. of polarized Raman lines
Planar $(D_{3h})$ 	4	3	3	2	1
Pyramidal $(C_{3v})$ 	4	4	4	4	2

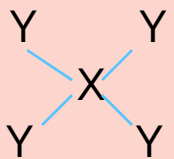
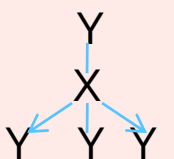
# IR and Raman Spectral Data of $\text{NO}_3^-$

$\text{NO}_3^-$ (planar $D_{3h}$ )		$\text{PCL}_3$ (pyramidal $C_{3v}$ )		Assignment
IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	
—	1.049 (polarized)	504 (11)	514 (polarized)	Symmetric Stretching
830 (11)	—	252 (11)	256 (polarized)	Symmetric deforming
1.350 (⊥)	1.355 (depolarized)	482 (⊥)	482 (depolarized)	Asymmetric stretching
680 (⊥)	690 (depolarized)	198 (⊥)	184 (depolarized)	Asymmetric deformation

- Based on **selection rule** and **polarization** both the case allow determination of their structure.
- Among molecule type  $XY_3$ , special interest is **chlorine trifluoride**,  $ClF_3$ .
- Observed IR spectrum of this molecule showed **6** lines: **326, 364, 434, 528, 703 and 752  $cm^{-1}$** .
- Molecule must have **symmetry lower than  $D_{3h}$  and  $C_{3v}$** .
- The **point group** of such a molecule is  **$C_{2v}$** , **Six distinct no. of fundamental frequencies active in both IR and Raman.**

# Molecules of Type XY<sub>4</sub>

- Common model- **Square planar** (point group D<sub>4h</sub>) and **Tetrahedral** (point group T<sub>d</sub>) ones.
- Predictions based on selection rules and polarizations for given two types :

Model	No. of distinct fundamentals	No. of fundamentals active in IR	No. of fundamentals active in Raman	No. of coincidences	No. of polarized Raman lines
Square Planar (D <sub>3h</sub> ) 	7	3	3	0	1
Tetrahedral (T <sub>d</sub> ) 	4	2	4	2	1

- Hybridization led to **trigonal-bipyramidal structure** with **three** equatorial position or **two** axial positions.
- SF<sub>4</sub> molecules illustrate **difficulties** in determining molecular structure.
- **Fermi resonance, overtones** and **combinations** create difficulties in fixing the fundamentals.
- Based on **symmetry , vibrational selection rules, polarization & group frequency** make IR and Raman spectroscopy , powerful tool for structure determination.

THANK YOU