M.Sc. Semester-II
Compulsory Paper-7 (CP-7)
Group Theory and Spectroscopy

I. Symmetry and Group Theory in Chemistry

Lecture 5 : Determination of IR and Raman Active Vibrations in H_2O Molecule

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Symmetry and Group Theory in Chemistry : 25 Hrs

Symmetry elements and symmetry operation, Group and Subgroup, Point group, Classification and representation of groups, The defining property of a group, Sub group and Class, Group multiplication table for C_{2V}, C_{2h} and C_{3V} point group, Generators and Cyclic groups. Similarity Transformation, Table of conjugates for C_{2V}, C_{2h} and C_{3V} point group, Schonflies symbols.

Matrix notation for symmetry operation, Representations of groups by matrices (representation for the Cn, Cnv, Cnh and Dnh groups to be worked out explicitly). Character of a representation, Mulliken symbols for irreducible representations, Direct product relationship, Applications of group theory to quantum mechanics-identifying non-zero matrix elements.

The great orthogonal theorem (without proof) and rules derived from this theorem. Derivation of the orthonormalization condition. Character table. Construction of character table: C_{2V} and C_{3V} (only). Reducible representations and their reduction. Total character and their calculation. Application of character table in determination of IR and Raman active vibrations: H_2O, BF_3 and N_2F_2.

Coverage:

1. Molecular Vibrations of H20

2. Raman Active Molecular Vibrations

3. IR active Molecular Vibrations

4. Mutual Exclusion Rule

5. Summary

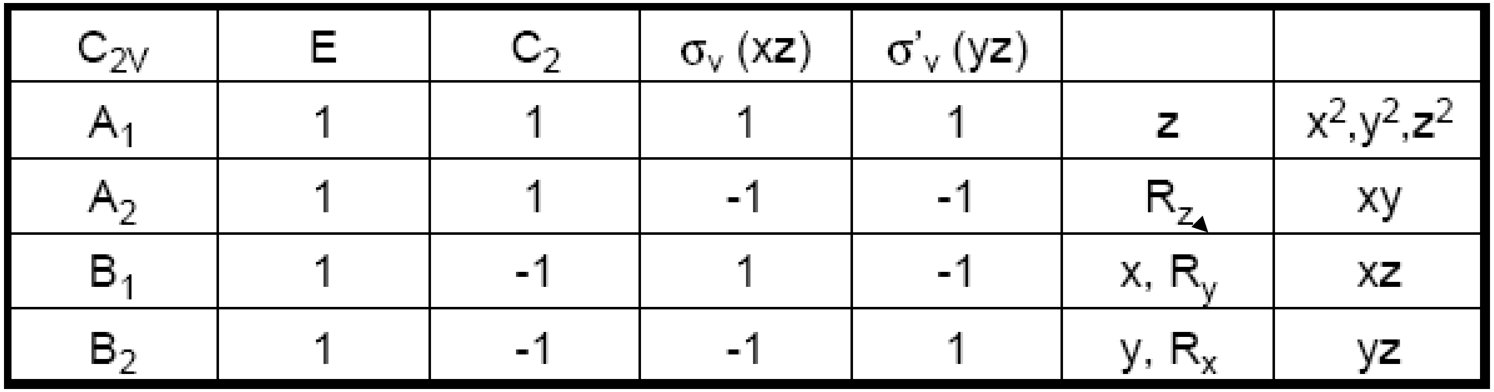
Molecular Vibrations of H_20 Molecule

$$\Gamma_{vib} = 2A_1 + B_1$$

The three vibrational modes remain. Two have A_1 symmetry, and one has B_1 symmetry.

Two vibrations are symmetric with respect to all symmetry operations of the group.

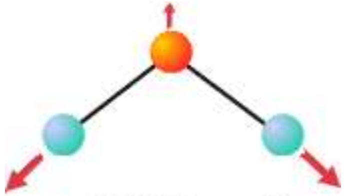
One vibration is asymmetric with respect to rotation and reflection perpendicular to the molecular plane.



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

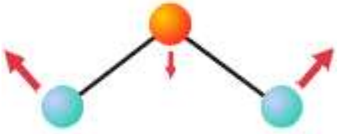
Molecular Vibrations

$$\Gamma_{vib} = 2A_1 + B_1$$



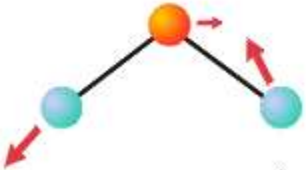
ν_1 (3652 cm^{-1})

A_1 symmetric stretch



ν_2 (1595 cm^{-1})

A_1 bend

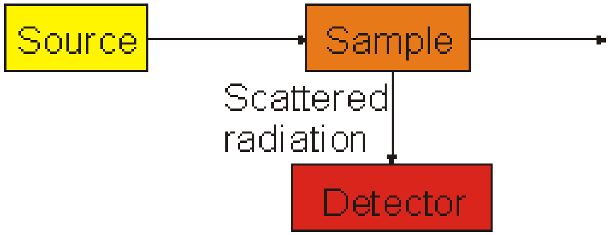


ν_3 (3756 cm^{-1})

B_1 asymmetric stretch

Raman Active Molecular Vibrations

Raman spectroscopy measures the wavelengths of light (in the IR range) scatted by a molecule. Certain molecular vibrations will cause the frequency of the scattered radiation to be less than the frequency of the incident radiation.



For a molecular vibration to be seen in the Raman spectrum (Raman active), it must change the polarizability of the molecule. The polarizability has the same symmetry properties as the quadratic functions:

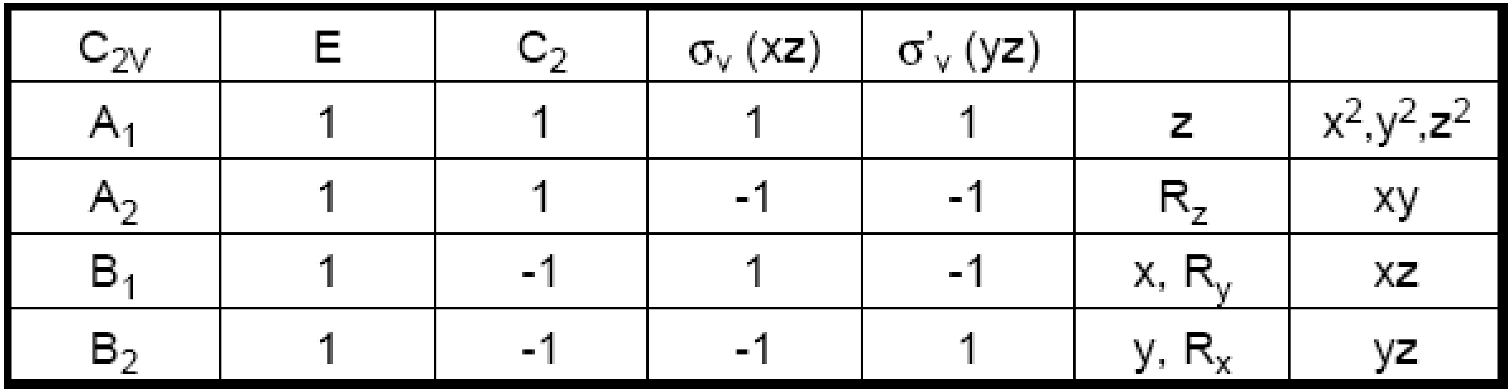
$$xy,\ yz,\ xz,\ x^2,\ y^2 \text{ and } z^2$$

IR active Molecular Vibrations

For a molecular vibration to be seen in the infrared spectrum (IR active), it must change the dipole moment of the molecule. The dipole moment vectors have the same symmetry properties as the cartesian coordinates x, y and z.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

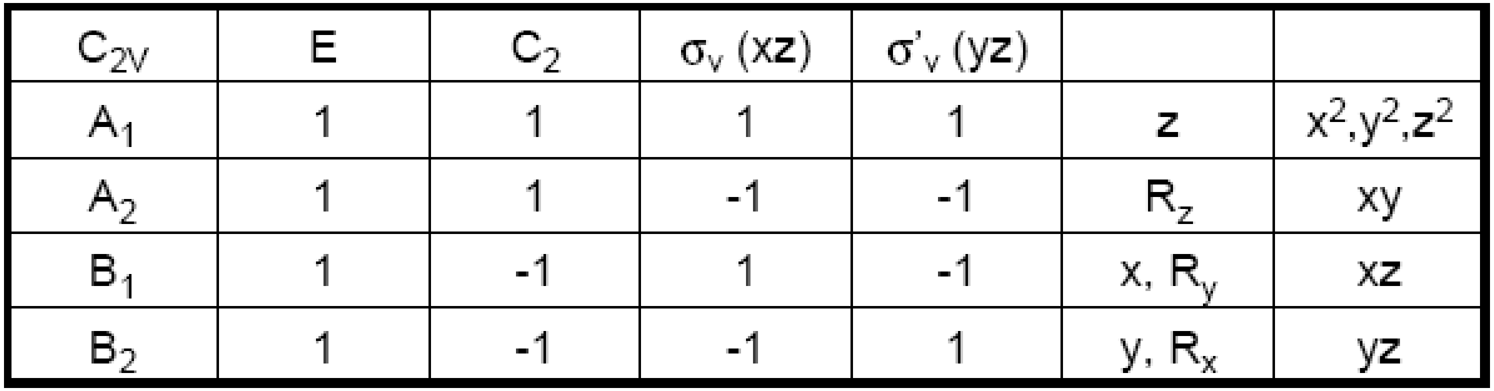


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry have z as a basis function, so they will be seen in the infrared spectrum of water. This will result in two peaks (at different frequencies) in the IR spectrum of water.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

The two vibrations with A_1 symmetry also have quadratic basis functions, so they will be seen in the Raman spectrum of water as well.

The two vibrations with A_1 symmetry will appear as two peaks in both the IR and Raman spectra. The two frequencies observed in the IR and Raman for these vibrations will be the same in both spectra.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

The two vibrations with A_1 symmetry will appear as two peaks in both the IR and Raman spectra. The two frequencies observed in the IR and Raman for these vibrations will be the same in both spectra.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

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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

The vibration with B_1 symmetry has x and xz as basis functions. This vibration will be both IR active and Raman active. This vibration will appear as a peak (at the same frequency) in both spectra.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

C_{2V}	E	C_2	$\sigma_v\ (xz)$	$\sigma'_v\ (yz)$		
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

Both the IR and Raman spectra should show three different peaks.

Mutual Exclusion Rule

If a molecule has a center of symmetry, none of its modes of vibration can be both infrared and Raman active.

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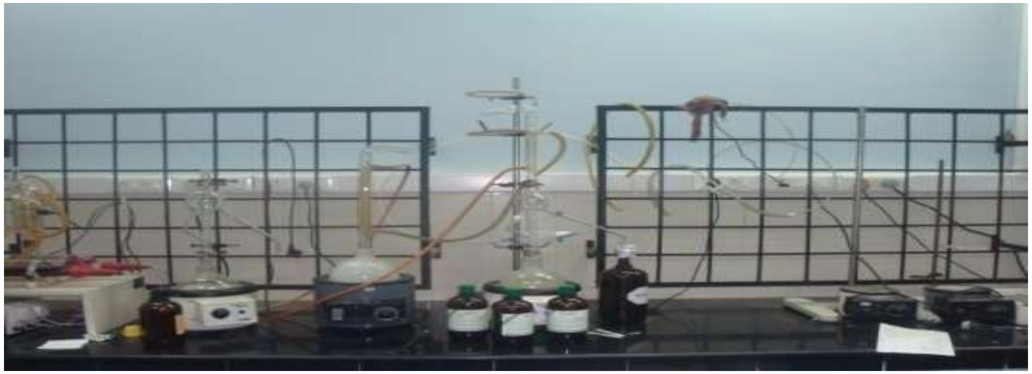
The cis and trans isomers of square planar ***$ML_2(CO)_2$, can be easily distinguished using spectroscopy. The cis isomer has absorptions that are seen in both the IR and Raman spectra, whereas the trans isomer does not.***

Summary

1. Obtain the point group of the molecule.
2. Obtain Γ_{3N} by considering the three cartesian coordinates on all atoms that aren't moved by the symmetry operation.
3. Reduce Γ_{3N} .
4. Eliminate translations and rotations.
5. Determine if remaining vibrations are IR and/or Raman active.

Thank You



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