

Paper 201-Sec A

**Application of Group Theory in Infrared and
Raman Spectroscopy**

Dr Sandeep Kaur, March-April, 2020

A vibrational transition in the IR spectra occurs because of an interaction between the incident radiation and the molecular dipole moment, μ .

The probability of any such dipole-induced transition is proportional to the transition moment : $\int \Psi_i^* \mu \Psi_f d\tau$

As the vibrational ground state wave function is always real, $\Psi_i^* = \Psi_i$ and so the transition moment can be written as $\int \Psi_i \mu \Psi_f d\tau$.

The vector, μ , can be divided into 3 components, μ_x, μ_y, μ_z along the 3 cartesian coordinate axes, and only one of the 3 integrals given below needs to be non-zero.

$$\int \Psi_i \mu_x \Psi_f d\tau$$

$$\int \Psi_i \mu_y \Psi_f d\tau$$

$$\int \Psi_i \mu_z \Psi_f d\tau$$

$$\int \Psi_i \mu_k \Psi_f d\tau (k = x, y, z)$$

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
Unshifted atoms	3	1	1	3
Γ_{3N}	9	-1	1	3

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$		
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

Eg of C_{2v} SO_2
Also H_2O

$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$$

$$\Gamma_{T+R} = A_1 + A_2 + 2B_1 + 2B_2$$

$$\Gamma_{vib} = 2A_1 + B_2$$

$2A_1$ Symmetric

B_2 Anti-symmetric, can be seen from the character table with respect to C_2 and $\sigma(xz)$

What are the symmetries of the 3 components of the integral ?

All wave functions for normal vibrations in their ground states, Ψ_i , are bases for the totally symmetric representation of the point group of the molecule.

μ_k has the same symmetry properties as that of a translation vector along the same axis, T_k .

Ψ_f has the symmetry of the vector that describes the vibrational mode involved.

In C_{2v} , $\Gamma_{\text{vib}} = 2A_1 + B_2$ ie vibrations are of A_1 or B_2 symmetries. Will they occur in the IR spectrum of the molecule ?

Ψ_i A_1 symmetry

From the character table we see -

T_x	B_1
T_y	B_2
T_z	A_1

Hence, $\Gamma(\Psi_i) \times \begin{matrix} \Gamma(T_x) \\ \Gamma(T_y) \\ \Gamma(T_z) \end{matrix} \times \Gamma(\Psi_f)$

For A_1 vibrations, we get

$$A_1 \quad \times \quad \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix} \quad \times \quad A_1$$

which is :

$$\begin{array}{rclclcl} A_1 & \times & B_1 & \times & A_1 & = B_1 \\ A_1 & \times & B_2 & \times & A_1 & = B_2 \\ \mathbf{A_1} & \times & \mathbf{A_1} & \times & \mathbf{A_1} & = \mathbf{A_1} \end{array}$$

This third product includes the totally symmetric A_1 irreducible representation, and hence A_1 modes are IR active.

Similarly for B_2 mode, we get

$$A_1 \quad \times \quad \begin{matrix} B_1 \\ B_2 \\ A_1 \end{matrix} \quad \times \quad B_2$$

which is :

$$\begin{array}{rclclcl} A_1 & \times & B_1 & \times & B_2 & = A_2 \\ A_1 & \times & B_2 & \times & B_2 & = A_1 \\ A_1 & \times & A_1 & \times & B_2 & = B_2 \end{array}$$

Thus A_1 is again present and so the B_2 mode is also IR active.

Rules for Raman spectra

The probability of a vibrational transition occurring in Raman scattering is proportional to : $\int \Psi_i \alpha \Psi_f d\tau$, where α is the *polarisability* of the molecule.

$$\int \Psi_i \alpha_{jk} \Psi_f d\tau \quad (j, k = x, y \text{ or } z)$$

In C_{2v} , $\Gamma_{\text{vib}} = 2A_1 + B_2$ ie vibrations are of A_1 or B_2 symmetries. Will they occur in the IR spectrum of the molecule ?

Ψ_i A_1 symmetry

From the character table we see -

x^2, y^2, z^2 A_1

xy A_2

zx B_1

yz B_1

Hence,

$$\Gamma(\Psi_i) \quad \times \quad \Gamma(\alpha_{jk}) \quad \times \quad \Gamma(\Psi_f)$$

$(\alpha_{jk} = jk)$

For A_1 vibrations, we get

$$A_1 \quad \times \quad A_1 \quad \times \quad A_1$$

A_2

B_1

B_2

which is :

$$A_1 \quad \times \quad A_1 \quad \times \quad A_1 \quad = \quad A_1$$

$$A_1 \quad \times \quad A_2 \quad \times \quad A_1 \quad = \quad A_2$$

$$A_1 \quad \times \quad B_1 \quad \times \quad A_1 \quad = \quad B_1$$

$$A_1 \quad \times \quad B_2 \quad \times \quad A_1 \quad = \quad B_2$$

Similarly for B_2 mode,

we get $A_1 \times \begin{matrix} A_1 \\ A_2 \\ B_1 \\ B_2 \end{matrix} \times B_2$

which is :

$$A_1 \times A_1 \times B_2 = B_2$$

$$A_1 \times A_2 \times B_2 = B_1$$

$$A_1 \times B_1 \times B_2 = A_2$$

$$A_1 \times B_2 \times B_2 = A_1$$

An IR active mode may or may not be Raman active and vice versa. Some modes may be active in both.

The more symmetrical a molecule, the fewer the number of modes that are active in both spectra.

For any molecule with a centre of symmetry, a mutual exclusion rule exists.

For such a molecule, no vibration mode will be active in both IR and Raman spectra ie *In a centrosymmetric molecule no Raman-active vibration is also IR-active and no IR-active vibration is also Raman active.*

This is because, T_x , T_y , T_z are antisymmetric with respect to inversion (ungerade, u) while x^2 , etc are symmetric (gerade, g).

Hence modes of u-symmetry cannot be Raman active while ones of g-symmetry cannot show IR absorption.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Eg of T_d RuO_4

$$\Gamma_{3N} = A_1 + E + T_1 + 3T_2$$

$$\Gamma_{T+R} = T_1 + T_2$$

$$\Gamma_{vib} = A_1 + E + 2T_2$$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Unshifted atoms	5	2	1	1	3
Γ_{3N}	15	0	-1	-1	3

Important:

If the vibrational mode has the same symmetry as one or more of the translation vectors (T_x, T_y, T_z) for a particular point group, then A_1 representation is present and a transition from the ground state to that mode will be IR active.

Eg : Tetrahedral molecule, point group, T_d

$$\Gamma_{\text{vib}} = A_1 + E + 2T_2$$

From the character table we see -

(T_x, T_y, T_z) together have T_2 symmetry

Hence,

$$\text{For } A_1 \text{ vibrations} \quad A_1 \times T_2 \times A_1 = T_2$$

$$\text{For } E \text{ vibration} \quad A_1 \times T_2 \times E = T_2 \times E = T_1 + T_2$$

$$\text{For } T_2 \text{ vibrations} \quad A_1 \times T_2 \times T_2 = T_2 \times T_2 = A_1 + E + T_1 + T_2$$

Thus, T_2 vibrations are IR active as A_1 is present but A_1 and E are not IR active.

Eg : Tetrahedral molecule, point group, T_d , $\Gamma_{\text{vib}} = A_1 + E + 2T_2$

From the character table we see – the components of the polarisability have symmetries A_1 ($x^2 + y^2 + z^2$), E ($2z^2 - x^2 - y^2$, $x^2 - y^2$) and T_2 (xy , yz , zx)

For A_1 vibrations

A_1	\times	A_1	\times	A_1	$= A_1$
A_1	\times	E	\times	A_1	$= E$
A_1	\times	T_2	\times	A_1	$= T_2$

For E vibration

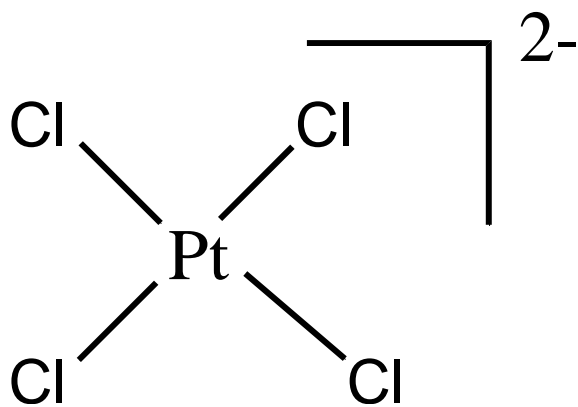
A_1	\times	A_1	\times	E	$= E$
A_1	\times	E	\times	E	$= A_1 + A_2 + E$
A_1	\times	T_2	\times	E	$= T_1 + T_2$

For T_2 vibrations

A_1	\times	A_1	\times	T_2	$= T_2$
A_1	\times	E	\times	T_2	$= T_1 + T_2$
A_1	\times	T_2	\times	T_2	$= A_1 + E + T_1 + T_2$

Thus, all the vibrations of a tetrahedral molecule are Raman active.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	



Eg of D_{4h} $PtCl_4^{2-}$

$$\Gamma_{3N} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

$$\Gamma_{T+R} = A_{2g} + E_g + A_{2u} + E_u$$

$$\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$



$$\Gamma_{\text{vib}} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$

A_{1g} $x^2 + y^2, z^2$ Raman only

B_{1g} $x^2 - y^2$ Raman only

B_{2g} xy Raman only

A_{2u} T_z IR only

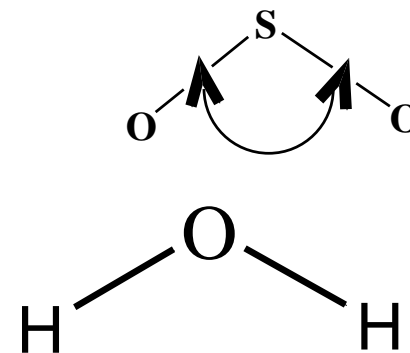
B_{2u} Totally inactive

$2E_u$ (T_x, T_y) IR only

PtCl_4^{2-} has a centre of symmetry, hence mutual exclusion rule applies.

Classification of vibrational modes

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
Γ_{str}	2	0	0	2



$$\therefore \Gamma_{str} = A_1 + B_2$$

There are 2 S–O stretching frequencies, both active in IR and Raman, with one Raman band being polarized ie A_1 .

The remaining vibration is the deformation of the O–S–O angle. The vector is Γ_{bend} and it is regarded as a 'double-ended' arrow.

Effects of SOs on this vector –

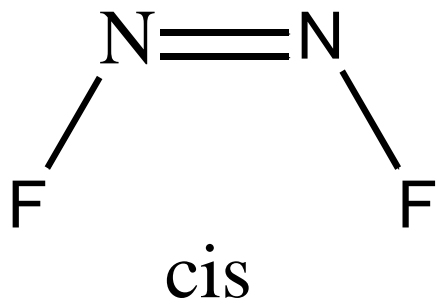
E +1

C_2 +1 one half of the angle is taken into the other, the final angle is unchanged as for C_2

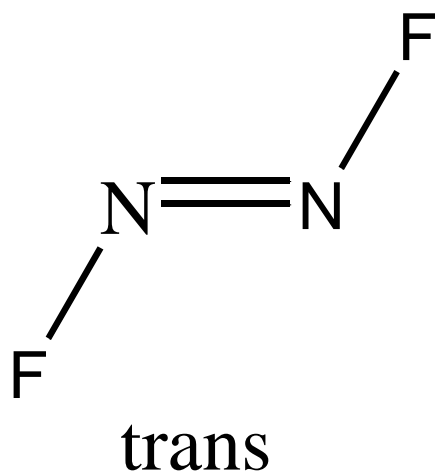
$\sigma(xz)$ +1

$\sigma(yz)$ +1

Example : *cis-N₂F₂* is C_{2v} and *trans-N₂F₂* is C_{2h} shown below



C _{2h}	E	C ₂	i	σ _h		
A _g	1	1	1	1	R _z	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	R _x , R _y	xz, yz
A _u	1	1	-1	-1	z	
B _u	1	-1	-1	1	x, y	



C _{2h}	E	C ₂	i	σ _h
Unshifted atoms	4	0	0	4
Γ _{3N}	12	0	0	4

$$\Gamma_{3N} = 4A_g + 2B_g + 2A_u + 4B_u$$

From the character table we see that $\Gamma_{T+R} = A_g + 2B_g + A_u + 2B_u$

$\Gamma_{\text{vib}} = 3A_g + A_u + 2B_u$ (so there are total six vibrations)

IR active are A_u, B_u

Raman active is A_g

It is found that the two N–F distances form the basis for Γ_{NF} , the two NNF angles for Γ_{NNF} and the N=N distance for Γ_{NN} , given below-

C_{2h}	E	C_2	i	σ_h
Γ_{NF}	2	0	0	2
Γ_{NNF}	2	0	0	2
Γ_{NN}	1	1	1	1

$$\Gamma_{\text{NF}} = A_g + B_u$$

$$\Gamma_{\text{NNF}} = A_g + B_u$$

$$\Gamma_{\text{NN}} = A_g$$

A_g and B_u vibrations involve only motions within the molecular plane, since their characters with respect to σ_h are positive. But A_u vibration will involve out-of-plane deformation as the character with respect to σ_h is negative. So one out-of-plane mode, A_u and five in-plane modes.

The three Raman active vibrations A_g , consist of symmetric N–F stretching, symmetric NNF bending and N=N stretching, the relative amounts of each depend on the actual values of the force constants and atomic masses. The two B_u vibrations in IR involve asymmetric N–F stretching and NNF angle bending.