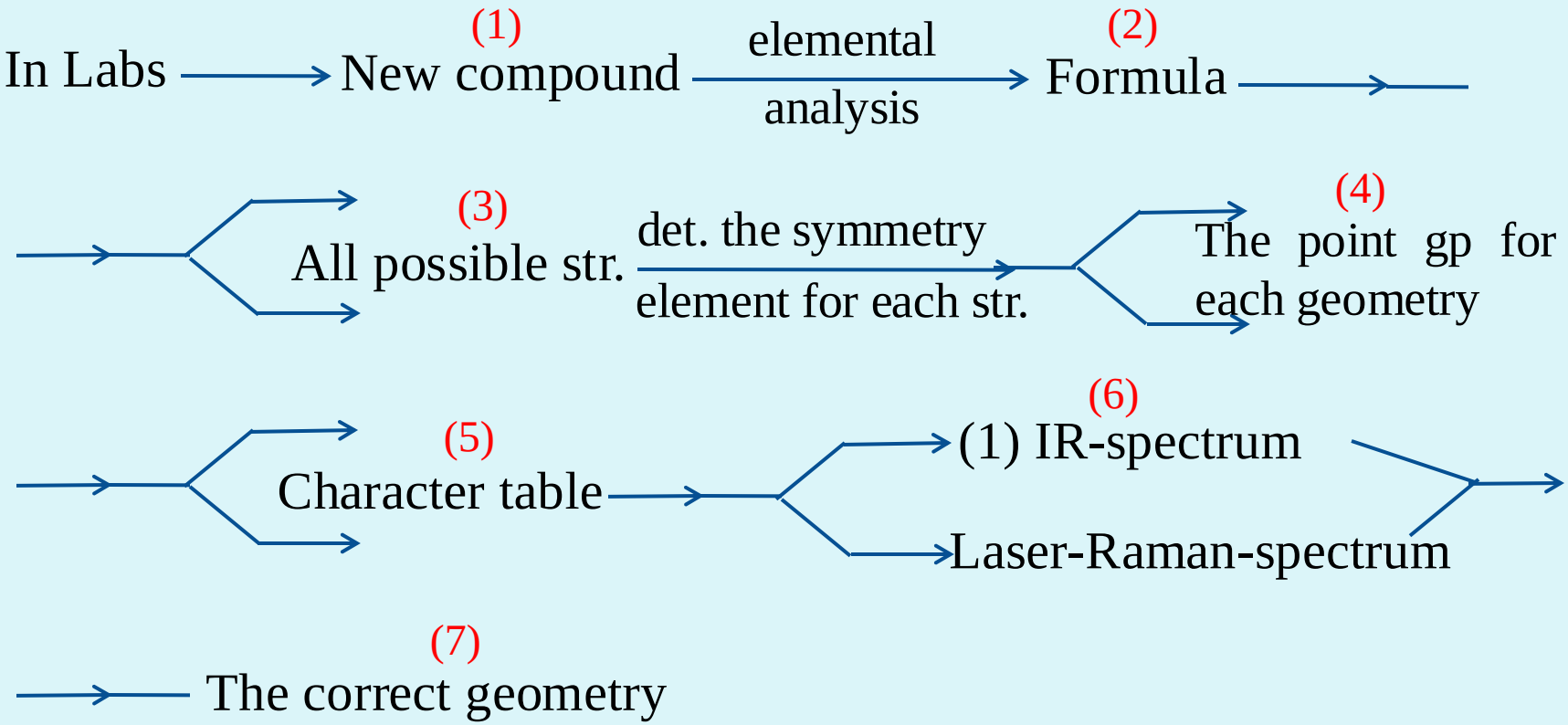
Group Theoretical Analysis

The character table:



* Character table:

Each point group has its character table.

Def.: The character table describe all the molecular motions ($T_{3N} = T_{Rot} + T_{trans.} + T_{vib}$) in terms of symmetry blocks (A, B, E, T … etc).

Example:

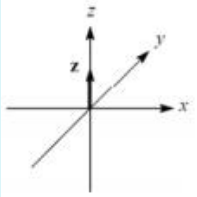
H_2O, SO_2 and many other molecules belong to C_2V P.G and therefore, the C_2V character table is used to describe their molecular motions.

C_2V-character table

C_2v	I	C_2	σ_v	σ_v'	IR	Raman
A_1	1	1	1	1	T_z	x^2-y^2,z^2
A2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	T_x, R_y	zx
B_2	1	-1	-1	1	T_y, R_x	yz

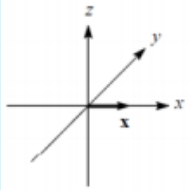
A_1, A_2, B_1 and B_2 are symmetry blocks, describe each of the molecular motions in relation to each symmetry element.

- The characters of the irreducible representations can describe the ways in which certain vector properties are transformed by the operations of the group



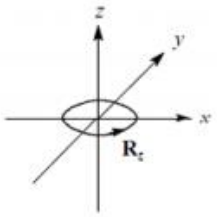
Operation	z becomes	In matrix notation
E	z	[+1]z
C_2	z	[+1]z
σ_v	z	[+1]z
σ_v'	z	[+1]z

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z



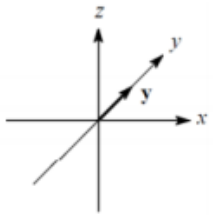
Operation	x becomes	In matrix notation
E	x	[+1]x
C_2	-x	[-1]x
σ_v	x	[+1]x
σ_v'	-x	[-1]x

C_{2v}	E	C_2	σ_v	σ_v'	
B_1	1	-1	1	-1	x



Operation	R_z becomes	In matrix notation
E	R_z	[+1]R_z
C_2	R_z	[+1]R_z
σ_v	$-R_z$	[-1]R_z
σ_v'	$-R_z$	[-1]R_z

C_{2v}	E	C_2	σ_v	σ_v'	
A_2	1	1	-1	-1	R_z



Operation	y becomes	In matrix notation
E	y	[+1]y
C_2	-y	[-1]y
σ_v	-y	[-1]y
σ_v'	y	[+1]y

C_{2v}	E	C_2	σ_v	σ_v'	
B_2	1	-1	-1	1	y

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

- **The character +1 and -1 indicate that:**

+1 keeps the symmetry element during the molecular motion while -1 breaks it.

So A_1 is totally symmetric motions where doesn't break any symmetry element during the motion, but A_2, B_1 and B_2 are anti-symmetric motions, they do break one or more of the symmetry elements during the motions.

Note that: A_1, A_2, B_1 and B_2 are monodegenerate motions.

- Tx, Ty, and Tz are the three translational motions for any C_2v molecule and they are expressed in terms of symmetry blocks as follow:

$$T_{trans} = A1 + B1 + B2$$

$$= 3 \text{ translational motion}$$

- Rx, Ry and Rz are the three rotational motions for any C2v molecule

$$T_{Rot} = A_2 + B_1 + B_2$$

$$= 3 \text{ rotational motion}$$

So all non-linear C_2v have $3T_{trans} + 3T_{Rot.}$

i.e $(T_t + T_R)$ are constant but T_{vib} depend on no. of motions (total no.) i.e $[3N-(T_t+T_R)]$.

- **In the table**

(T) means the motion is IR-active while x^2, y^2, z^2, xy, xz, yz is Raman-active vibrations.

to be IR-active, it must have dipole moment changes during vibrational.

but to be Raman active, it must have bond-polarizability changes

- Some motion have IR and Raman active

but some motion have IR inactive and Raman active or vise versa.

To determine this T_{vib} from character table of C_2v for H_2O

$$T_{vib} = T_{3N} - (T_t + T_{Rot})$$

$$\therefore T_{vib} = (3A_1 + A_2 + 2B_1 + 3B_2) - (A_1 + A_2 + 2B_1 + 2B_2)$$

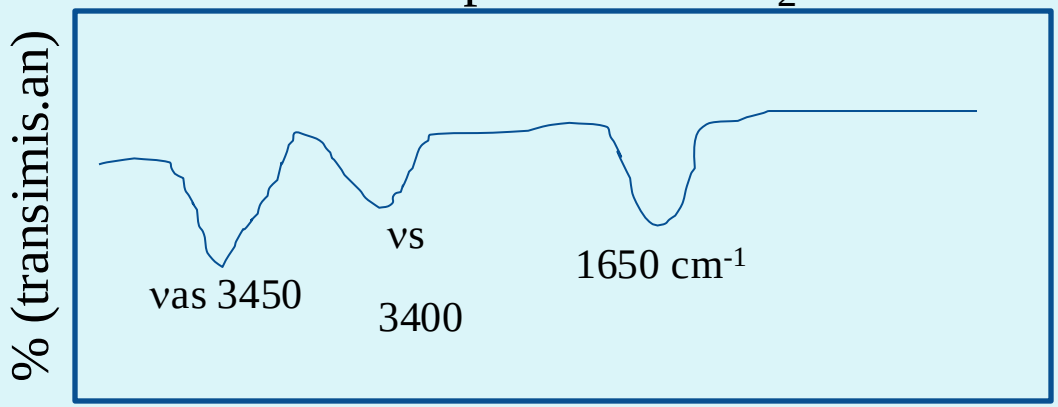
$$= 2A1 + B2 = 3 \text{ vibrational motion}$$

i.e. T_{vib} of H_2O = $2A_1 + B_2$ of all C_2V

and A_1 are (IR and R) active

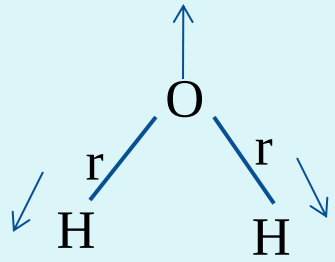
B_2 are (IR and R) active

IR-spectrum of H_2O



To drawing these three T_{vib}.

(i)



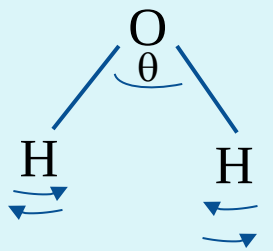
νs (O-H); A_1
(IR, R)

$r \longrightarrow r + \Delta r$

$r \longrightarrow r - \Delta r$

Symmetric stretching motion, where keeps all symmetry element.

(ii)



$\theta \longrightarrow (\theta + \Delta\theta)$

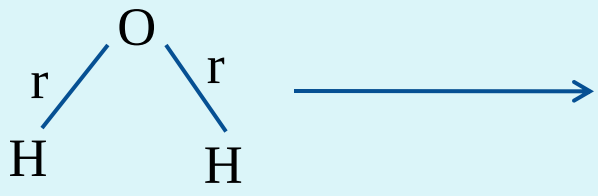
$\longrightarrow (\theta - \Delta\theta)$

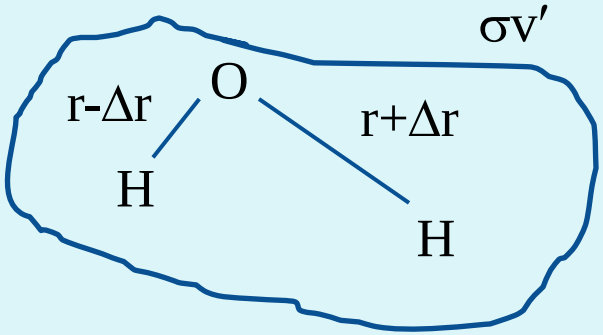
Symmetric bending motion, keeps all symmetry element

δs (HOH); A_1

(IR, R)

(iii)





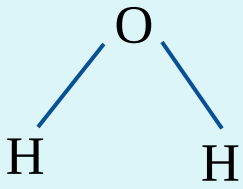
Loss C_2, σ_v

ν_{as} (O-H); B_2

(IR, R)

Since theoretical calculation identical with experimental

So the H_2O molecule present in the following and is C_2V



The Character table of C_3v

NH_3, PCl_3 and many other molecules belong to C_3v P.G. and therefore, the C_3v character table is used to describe their molecular motions.

C_3v-character table

C_3v	I	$2C_3$	$3\sigma_v$	IR	Raman
A_1	1	1	1	T_Z	x^2+y^2, z^2
A2	1	1	-1	R_Z	------
E	2	-1	0	(T_x, T_y) & (R_x, R_y)	(x^2-y^2, xy) & (yz, zx)

A_1: is monodegenerate motion, symmetric and IR and Raman active.

A_2: is monodegenerate motion, antisymmetric and IR and Raman inactive.

E: is doubly degenerate motion (each E represent two motions), antisymmetric and IR and Raman active.

$T_{trans} = A_1 + E = 3$ translation motion.

$T_{Rot} = A_2 + E = 3$ Rotational motion.

but calculation indicate that,

$T_3N = 3A_1 + 4E + A_2 = 12$ motions

$\therefore T_{vib} = 2A_1 + 2E = 6$ vibrational motions

IR and Raman active

Both the infrared and Raman spectra should display the same 4 bands.

These 4 bands are

two for $2A_1$, and two for 2E

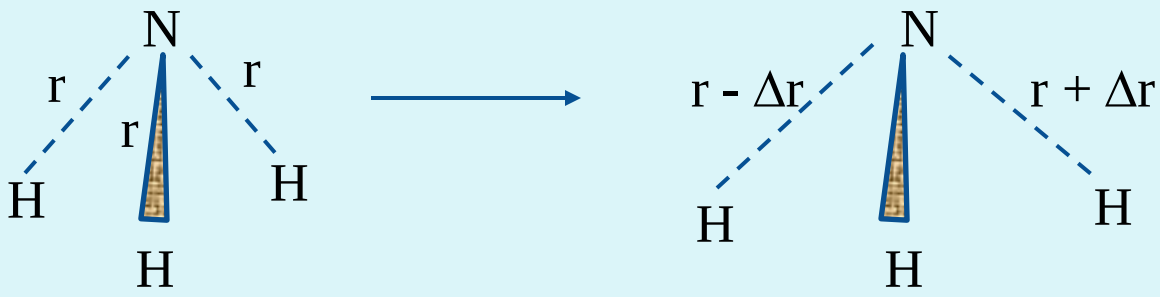
i.e. one peak for one E

where each E appear in one peak (this one peak; present in real two peak supper imposed).

Doubly degenerate two vibrations are resolved components (at 90^o to one another) in all possible planes around the bond axis, the two vibration are identical in energy, thus produce but one peak.

To draw the vibrational motion NO_3^- (C_3v) or NH_3 (C_3v).

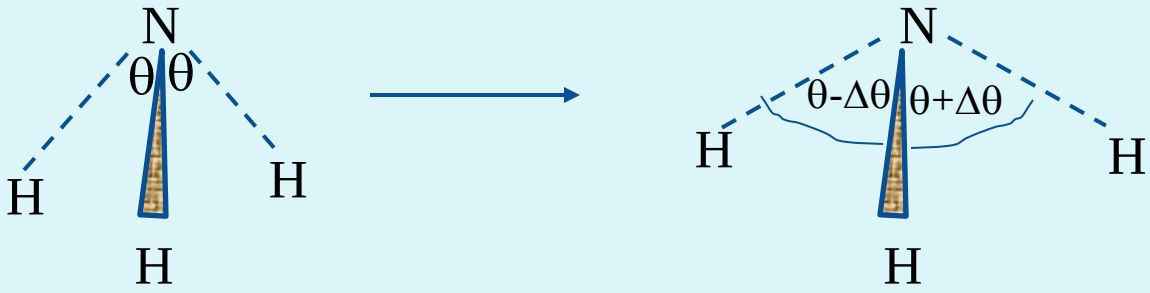
(i)



ν_s (N-H); A_1

Keeps the symmetry element

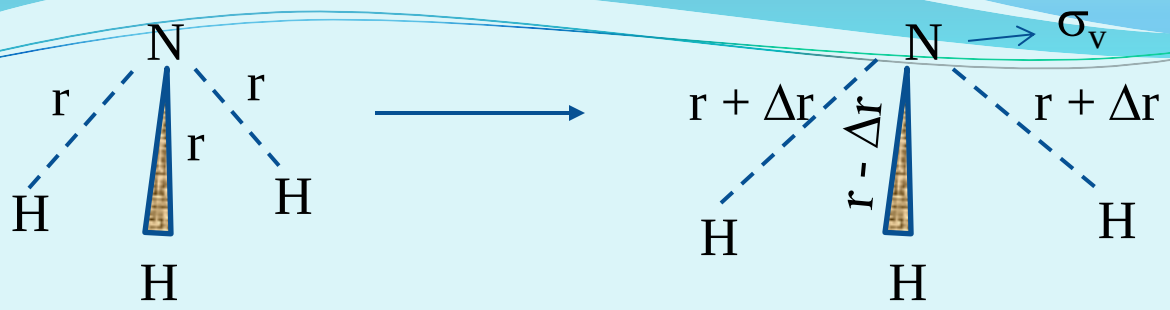
(ii)



δ_s (HNH); A_1

Keeps the symmetry element

(iii)



ν_{as} (N-H); E

(iv)