UNIT II: Infrared and Raman Spectroscopy

Vibrations in simple molecules (H_2O, CO_2) and their symmetry notation for molecular vibrations – group vibrations and the limitations – combined uses of IR and Raman spectroscopy in the structural elucidation of simple molecules like N_2O, ClF_3, NO_3^-, ClO_4^- effect of coordination on ligand vibrations – uses of groups vibrations in the structural elucidation of metal complexes of urea, thiourea, cyanide, thiocyanate and dimethyl sulfoxide.

Effect of isotopic substitution on the vibrational spectra of molecules – vibrational spectra of metal carbonyls with reference to the nature of bonding – geometry and number of C-O stretching vibrations (group theoretical treatment) – applications of Raman spectroscopy – resonance Raman spectroscopy.

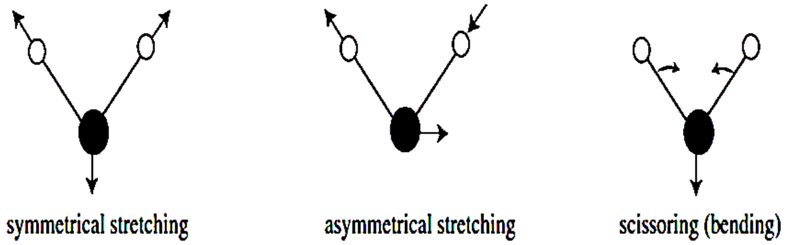
Vibrations in simple molecules (H_2O, CO_2)

Molecular Vibrations

There are two types of molecular vibrations, stretching and bending. A molecule consisting of n atoms has a total of 3n degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the remaining corresponds to fundamental vibrations; in a linear molecule, 2 degrees are rotational and 3 are translational. The net number of fundamental vibrations for nonlinear and linear molecules is therefore:

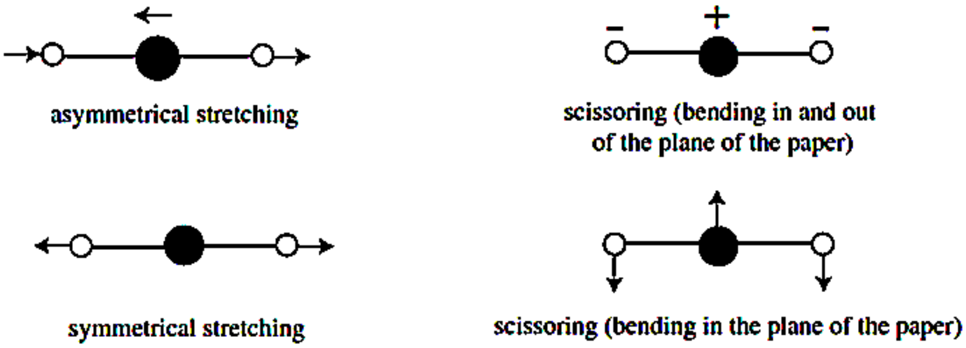
Molecule degrees of freedom:
(nonlinear 3n– 6)
(linear 3n– 5)

The fundamental vibrations for water, H_2O, are given in Figure. Water, which is nonlinear, has three fundamental vibrations.



Stretching and bending vibrational modes for H_2O.

Carbon dioxide, CO_2, is linear and hence has four fundamental vibrations (Figure). The two scissoring or bending vibrations are equivalent and therefore, have the same frequency and are said to be degenerate, appearing in an IR spectrum at 666 cm^{-1}.



asymmetrical stretching

scissoring (bending in and out of the plane of the paper)

symmetrical stretching

scissoring (bending in the plane of the paper)

Stretching and bending vibrational modes for CO_2.

Only two IR bands (2350 and 666 cm^{-1}) are seen for carbon dioxide, instead of four corresponding to the four fundamental vibrations. Carbon dioxide is an example of why one does not always see as many bands as implied by our simple calculation. In the case of CO_2, two bands are degenerate, and one vibration does not cause a change in dipole moment.

Symmetry Notation for Molecular Vibrations

Step 1, Use displacement coordinates.

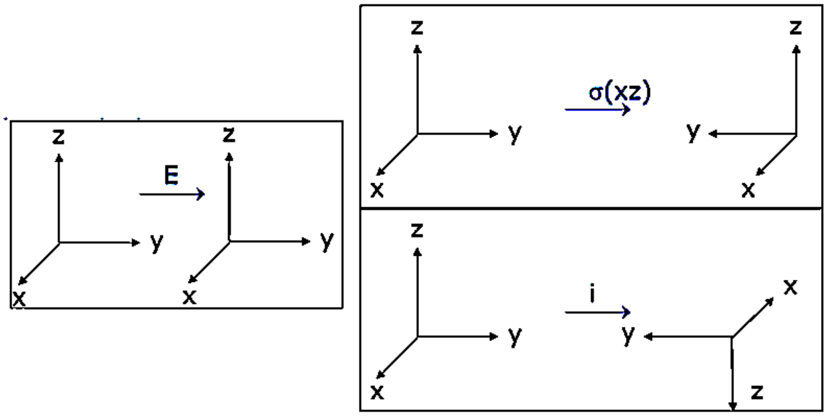
Step 2, What is the point group of H_2O

Step 3, Generate a reducible representation

Step 4, Reducing the representation

Step 5, Examining the irreducible representations (Determine Γ_{vib})

The characters of the reducible representation can be determined by considering the combined effect of each symmetry operation on the atomic vectors.



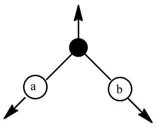
Operation		Contribution per atom*
E	→	3
C_2	→	-1
C_3	→	0
C_4	→	1
C_6	→	2
σ	→	1
i	→	-3
S_3	→	-2
S_4	→	-1
S_6	→	0

*$C_n = 1 + 2\cos(360/n)$; $Sn = -1 + 2\cos(360/n)$

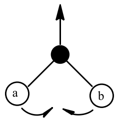
1. Water Molecule (H_2O)

   If the symmetry label (e.g. A_1, B_1, E) of a normal mode of vibration is associated with x, y, or z in the character table, then the mode is IR active.

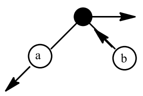
   If the symmetry label (e.g. A_1, B_1, E) of a normal mode of vibration is associated with a product term (x^2, xy) in the character table, then the mode is Raman active.



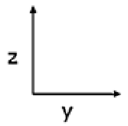
ν_1 A_1 symmetruc stretch; IR-active; 3657 cm^{-1}



ν_3 A_1 symmetruc bend (scissoring); IR-active; 1595 cm^{-1}

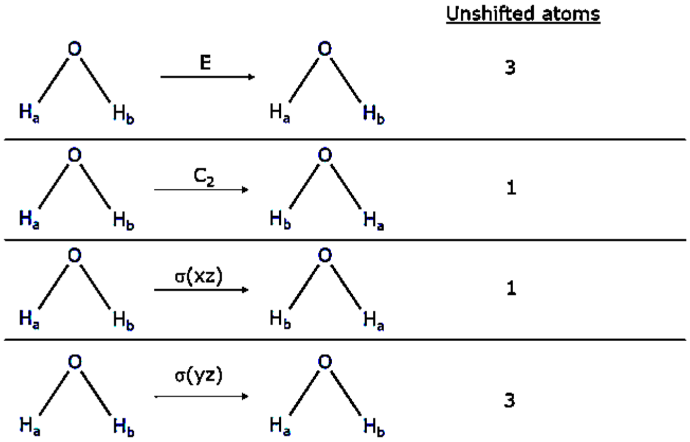


ν_2 B_2 αsymmetruc stretch; IR-active; 3756 cm^{-1}



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

Derivation of reducible representation for degrees of freedom in H_2O



The reducible representation for the displacement coordinates is the multiplication of the number of unshifted atoms and the contribution to character

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Unshifted Atoms	3	1	1	3
Contribution per atom	3	-1	1	1
Γ_{tot}	9	-1	1	3

The reduction can be achieved using the reduction formula:

$$N = \frac{1}{h}\sum_x \chi_r^x \chi_i^x n^x$$

A_1: (1/4)[(9)(1)(1) + (-1)(1)(1) + (1)(1)(1) + (3)(1)(1)] = 3

A_2: (1/4)[(9)(1)(1) + (-1)(1)(1) + (1)(-1)(1) + (3)(-1)(1) = 1

B_1: (1/4)[(9)(1)(1) + (-1)(-1)(1) + (1)(1)(1) + (3)(-1)(1) = 2

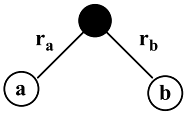
B_2: (1/4)[(9)(1)(1) + (-1)(-1)(1) + (1)(-1)(1) + (3)(1)(1) = 3

$$\begin{array}{ll} \Gamma_{tot} & = 3A_1 + A_2 + 2B_1 + 3B_2 \\ -[\Gamma_{trans} & = A_1 + B_1 + B_2] \\ -[\Gamma_{rot} & = A_2 + B_1 + B_2] \\ \hline \Gamma_{vib} & = 2A_1 + B_2 \end{array}$$

Using Internal Coordinates to analyze vibrations

$$\hat{P}^{\Gamma_i}(f_j) = \frac{l_i}{h}\sum_{\hat{R}} \chi_{\hat{R}}(\Gamma i)\,(\hat{R}f_j)$$

- l_i →dimension of the i^th irreducible representation
- h →order of the group
- $\hat{P}^{\Gamma_i}$ →projection operator
- f_j →arbitrary function
- Γi →IR under consideration
- χ →character of IR for the element $\hat{R}$



r_a,r_b - internal coordinates

Internal Coordinates

Vibration of water molecule: $\Gamma_{vib} = 2A_1 + B_2$

Which are bond-stretching vibrations & which are bending vibrations? Internal coordinate

	E	C_2	σ_{xz}	σ_{yz}
# of unshifted coordinates	2	0	0	2
Γ_{red}	2	0	0	2

a_{A1} = 1/4 [(2×1×1) + (2×1×1)] = 1

a_{A2} = 1/4 [(2×1×1) + (2×(-1)×1)] = 0

a_{B1} = 1/4 [(2×1×1) + (2×(-1)×1)] = 0

a_{B2} = 1/4 [(2×1×1) + (2×1×1)] = 1

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

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

$\Gamma_{ben} = (2A_1 + B_2) - \Gamma_{str} = (2A_1 + B_2) - (A_1 + B_2) = A_1$

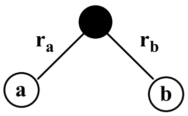
$\Gamma_{str} + \Gamma_{ben} = A_1 + A_1$ (both symmetric)

$\Gamma_{str} = B_2$ (asymmetric)

Using Projection Operator to analyse two possible stretching vibration, A_1 and B_2

$$\hat{P}^{\Gamma_i}(f_j) = \frac{l_i}{h}\sum_{\hat{R}} \chi_{\hat{R}}(\Gamma i)\,(\hat{R}f_j)$$

- l_i →dimension of the i^th irreducible representation
- h →order of the group
- $\hat{P}^{\Gamma_i}$ →projection operator
- f_j →arbitrary function
- Γi →IR under consideration
- χ →character of IR for the element $\hat{R}$



$r_{a,}r_b$ - internal coordinates

The linear combinations of the coordinates also have A_1 and B_2 symmetry

Consider the internal coordinates r_1 and r_2

Take r_1 as the generating function

C_{2v}	E	C_2	σ_{xz}	σ_{xz}	
P^{A_1}	$1x1xr_1$	$1x1xr_2$	$1x1xr_2$	$1x1xr_1$	$2r_1+2r_2$
P^{A_2}	$1x1xr_1$	$1x1xr_2$	$1x\text{-}1xr_2$	$1x\text{-}1xr_1$	0
P^{B_1}	$1x1xr_1$	$1x\text{-}1xr_2$	$1x1xr_2$	$1x\text{-}1xr_1$	0
P^{B_2}	$1x1xr_1$	$1x\text{-}1xr_2$	$1x\text{-}1xr_2$	$1x1xr_1$	$2r_1-2r_2$

$$P\bar{r}_1 = 1\times\bar{r}_1 + 1\times\bar{r}_2 + 1\times\bar{r}_2 + 1\times\bar{r}_1 \;= 2r_1 + 2r_2 \;\Rightarrow \text{normalized}\; \frac{1}{\sqrt{2}}(\bar{r}_1+\bar{r}_2)$$

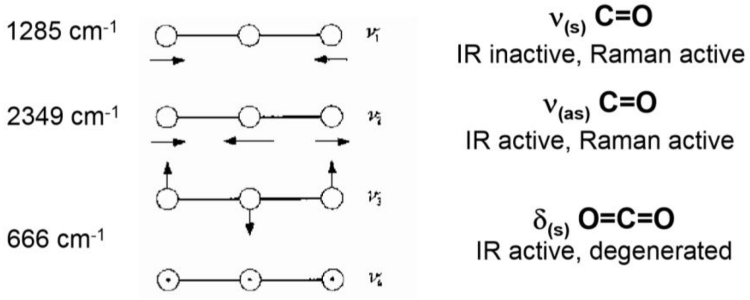
- A_1 representation has $\bar{r}_1$ + $\bar{r}_2$ as a basis
- A_1 stretch has $\bar{r}_1$ and $\bar{r}_2$ increasing or decreasing at the same time.

$$P\bar{r}_1 = \bar{r}_1 - \bar{r}_2 - \bar{r}_2 + \bar{r}_1 \;= 2\bar{r}_2 \;- 2\bar{r}_2 \rightarrow \text{normalize}\frac{1}{\sqrt{2}}(\bar{r}_1 - \bar{r}_2)$$

B_2 vibration in water is the one where the $\bar{r}_1$ coordinates is reducing whilst the $\bar{r}_2$ coordinates increase, and vice versa.

1. Carbon dioxide Molecule (CO_2)

   Linear molecules, such as CO2, have 3N-5 vibrational modes because 3 of all the modes result in a translation and 2 in a rotation.



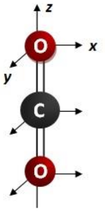
Carbon Dioxide, CO_2

$D_{\infty h}$	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratics
$A_{1g}=\Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	2cos(φ)	...	0	2	-2cos(φ)	...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$	2	2cos(2φ)	...	0	2	2cos(2φ)	...	0		(x^2-y^2, xy)
$E_{3g}=\Phi_g$	2	2cos(3φ)	...	0	2	-2cos(3φ)	...	0		
...	...	...	...	...	...	...	...	...		
$A_{1u}=\Sigma^+_u$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u}=\Sigma^-_u$	1	1	...	-1	-1	-1	...	1		
$E_{1u}=\Pi_u$	2	2cos(φ)	...	0	-2	2cos(φ)	...	0	(x, y)	
$E_{2u}=\Delta_u$	2	2cos(2φ)	...	0	-2	-2cos(2φ)	...	0		
$E_{3u}=\Phi_u$	2	2cos(3φ)	...	0	-2	2cos(2φ)	...	0		
...	...	...	...	...	...	...	...	...		

Vibrational spectroscopy

A vibration will be active in the IR if there is a change in the dipole moment of the molecule and if it has the same symmetry as one of the x, y, z coordinates. To determine which modes are IR active, the irreducible representation corresponding to x, y, and z are checked with the reducible representation of Γ_{vib}. IR mode is active if the same irreducible representation is present in both.

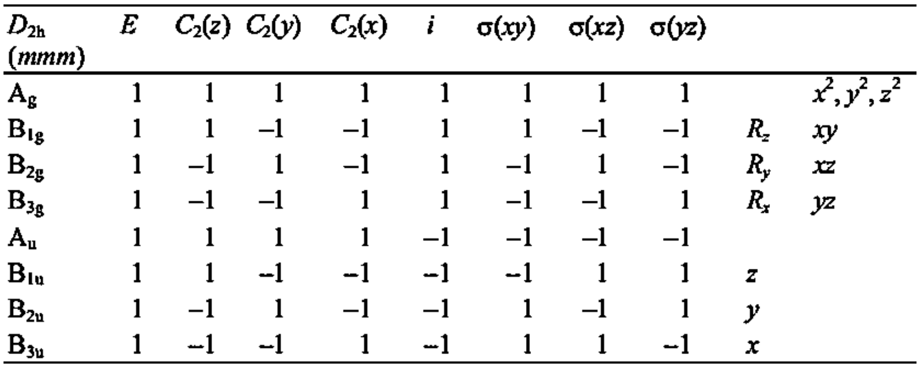
Furthermore, a vibration will be active in the Raman if there is a change in the polarizability of the molecule and if it has the same symmetry as one of the direct products of the x, y, z coordinates. To determine which modes are Raman active, the irreducible representation corresponding to xy, xz, yz, x^2, y^2, and z^2 are checked with the reducible representation of Γ_{vib}. Raman mode is active if the same irreducible representation is present in both.



Carbon dioxide molecule on a Cartesian coordinate

1. Assign point group: $D_{\infty h}$
2. Determine group-subgroup point group: D_{2h}
3. Find the number of normal (vibrational) modes or degrees of freedom using the equation: $3n - 5 = 3(3) - 5 = 4$

2. Derive reducible representation Γ_{3N}:



D_{2h} (*mmm*)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ(xy)	σ(xz)	σ(yz)
Γ_{3N}	9	-3	-1	-1	-3	1	3	3

3. Decompose the reducible representation into irreducible components using the reduction formula:

$\Gamma_{3N} = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$

4. Solve for the irreducible representation corresponding to the normal modes with the subgroup character table:

$\Gamma_{3N} = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$

$\Gamma_{rot} = B_{2g} + B_{3g}$

$\Gamma_{trans} = B_{1u} + B_{2u} + B_{3u}$

$\Gamma_{vib} = \Gamma_{3N} - \Gamma_{rot} - \Gamma_{trans}$

$\Gamma_{vib} = A_g + B_{1u} + B_{2u} + B_{3u}$

5. Use the correlation table to find the normal modes for the original point group:

   $v_1 = A_g = \Sigma^+_g$

   $v_2 = B_{1u} = \Sigma^+_u$

   $v_3 = B_{2u} = \Pi_u$

   $v_4 = B_{3u} = \Pi_u$

6. Label whether the modes are either IR active or Raman active:

   v_1 = Raman active

   v_2 = IR active

   v_3 = IR active

   v_4 = IR active

Group Vibrations and the Limitations

These group frequencies are to a first approximation independent of the remaining structure of the molecule. This often makes it possible to identify the structure of a molecule by visually examining its vibrational spectrum.

The following is a list of frequency regions (in cm^{-1}) and associated functional groups for organic compounds.
3,700 - 3,100: OH, NH and ≡CH
3,180 - 2,980: aryl, olefinic, and three-membered ring CH
3,000 - 2,700: aliphatic CH
3,100 - 2,400: acidic and strongly bonded hydrogens
2,300 - 1,900: C≡C and C=C=C
2,000 - 1,700: aryl and olefinic overtones
1,900 - 1,550: C=O
1,700 - 1,550: C=C and C=N
1,660 - 1,450: N=O
1,660 - 1,500: NH2, CNH
1,620 - 1,420: aromatic and heteroaromatic rings
1,500 - 1,250: CH3 and CH2
1,350 - 1,150: CH2 and CH wag
1,300 - 1,000: C–O
1,000 - 600: olefinic and acetylenic wag
900 - 700: aromatic wag
900 - 500: OH, NH and NH2 wag
830 - 500: CCl, CBr and CI

Generally, the infrared bands for inorganic materials are broader, fewer in number and appear at lower wavenumbers than those observed for organic materials. If an inorganic compound forms covalent bonds within an ion, it can produce a characteristic infrared spectrum.

Main infrared bands of some common inorganic ions:

- CO_3^{2-} 1450-1410, 880-800 cm^{-1}
- SO_4^{2-} 1130-1080, 680-610 cm^{-1}
- NO_3^- 1410-1340, 860-800 cm^{-1}
- PO_4^{3-} 1100-950 cm^{-1}
- SiO_{42}- 1100-900 cm^{-1}
- NH_4^+ 3335-3030, 1485-1390 cm^{-1}
- MnO_4^- 920-890, 850-840c m^{-1}

Diatomic molecules produce one vibration along the chemical bond. Monatomic ligand, where metal s coordinate with atoms such as halogens, H, N or O, produce characteristic bands. These bands are summarized in below.

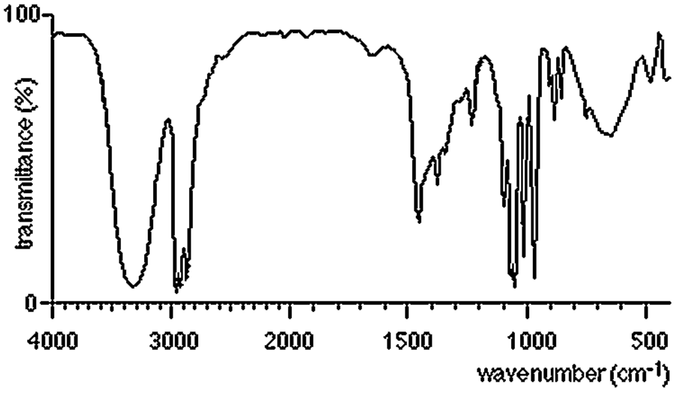
Chracteristic infrared bands of diatomic inorganic molecules: M(metal), X(halogen)

- M-H stretching 2250-1700 cm^{-1}
- M-H bending 800-600 cm^{-1}
- M-X stretching 750-100 cm^{-1}
- M=O stretching 1010-850 cm^{-1}
- M=N stretching 1020-875 cm$_{-1-}$

Fingerprint Region

The region to the right-hand side of the diagram (from about 1500 to 500 cm^{-1}) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. This is called the **fingerprint region**.

infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$



It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.

- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The absence of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample’s IR spectrum confirms the identity of the compound.

Combined uses of IR and Raman Spectroscopy in the Structural Elucidation of Simple Molecules

1. **N_2O (Nitrous oxide)** $N \equiv N^{+} - O^{-}$

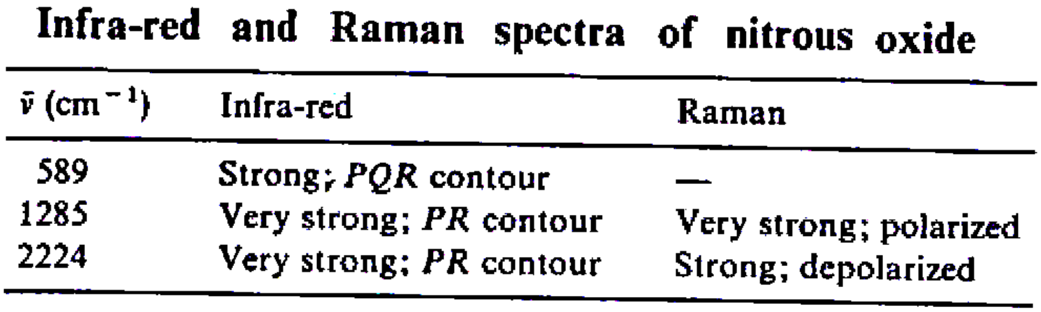
No. of atoms : 3
Total No.freedoms : 3 x 3 = 9
Structure : Linear
Vibrational deg. of freedom : 3 x 3 – 5 = 42 modes degenerate

- N_2O is isoelectronic with CO_2. It is linear but not symmetrical. It as three intense IR absorptions at (bending) 598, (symmetric)1285 , and (assymmetric) 2224 cm^{-1}.

- Two of these (symmetric)1285 , and (asymmetric) 2224 cm^{-1} appear in Raman spectrum; the (bending) 598 is not observed due to weak intensity. Thus according to rule of mutual exclusion, the molecule has no center of symmetry, i.e., it does not have the symmetric structure N – O – N because two bands are common to its IR and Raman spectra. Hence N_2O has a unsymmetrical structure N – N – O, confirmed by its rotational spectrum.

- IR lines with PR structure: linear molecule

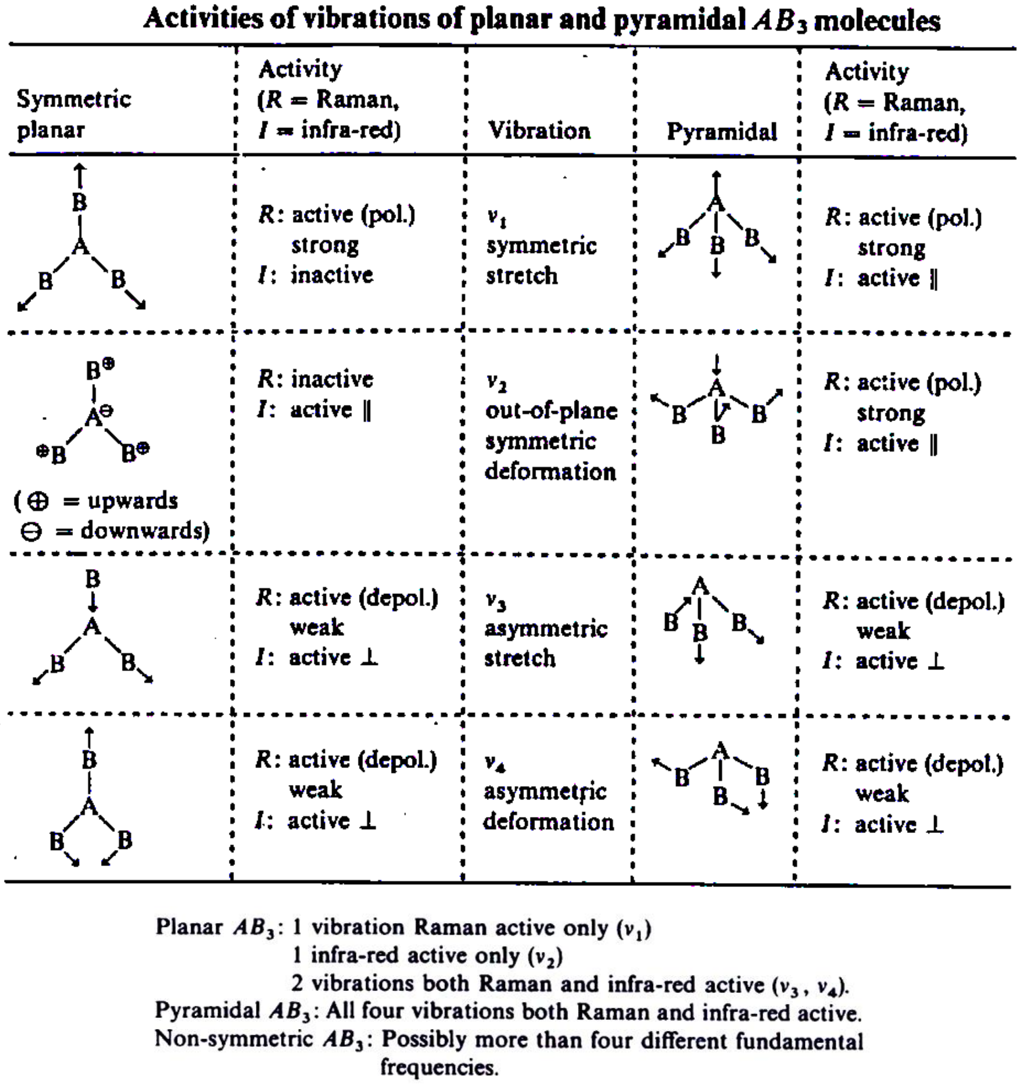
- No center of symmetry: N-N-O



Infra-red and Raman spectra of nitrous oxide

$\bar{\nu}$ (cm^{-1})	Infra-red	Raman
589	Strong; *PQR* contour	—
1285	Very strong; *PR* contour	Very strong; polarized
2224	Very strong; *PR* contour	Strong; depolarized

AB_3: This type molecule is expected to have 3N-6 = 6 fundamental vibrations. However if the shape of the molecule has some symmetry this number will be reduced by degeneracy. For symmetric planar and symmetric pyramidal shape one stretching mode and one angle deformation mode are each doubly degenerate. So four different fundamental frequencies would be observed. These are shown in the table. The main symmetry axis passes through atom A and is perpendicular to B_3 plane. The vibrations types are classified based on this axis.



Activities of vibrations of planar and pyramidal AB_3 molecules

Symmetric planar	Activity (R = Raman, I = infra-red)	Vibration	Pyramidal	Activity (R = Raman, I = infra-red)
	R: active (pol.) strong I: inactive	ν_1 symmetric stretch		R: active (pol.) strong I: active ∥
(⊕ = upwards ⊖ = downwards)	R: inactive I: active ∥	ν_2 out-of-plane symmetric deformation		R: active (pol.) strong I: active ∥
	R: active (depol.) weak I: active ⊥	ν_3 asymmetric stretch		R: active (depol.) weak I: active ⊥
	R: active (depol.) weak I: active ⊥	ν_4 asymmetric deformation		R: active (depol.) weak I: active ⊥

Planar AB_3: 1 vibration Raman active only (ν_1)
1 infra-red active only (ν_2)
2 vibrations both Raman and infra-red active (ν_3, ν_4).
Pyramidal AB_3: All four vibrations both Raman and infra-red active.
Non-symmetric AB_3: Possibly more than four different fundamental frequencies.

2. **ClF_3 (chlorine trifluoride)**

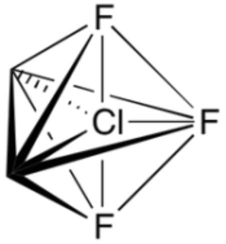
No. of atoms : 4
Total No.freedoms : 3 x 4 = 12
Structure : non-linear
Vibrational deg. of freedom : 3 x 4 – 6 = 6 normal nondegenerate vibration modes,

The infrared and Raman spectra of the interhalogen ClF_3 has been studied in the vapor phase. Frequencies for the six fundamental vibrations of the molecule been assigned based on C_{2v} symmetry. All are Raman and IR active.

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

326(al)	434(bl)	364(b2)
528(al)	703(bl)	
752(al)		

The F–Cl–F angle involving the axial F atoms is 175°



The red lines outline a trigonal bipyramid. Black lines show the electron pairs

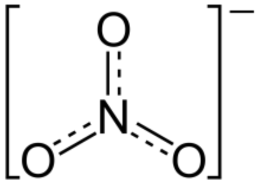
These are arranged in a trigonal bipyramidal shape with a 175° F(axial)-Cl-F(axial) bond angle.

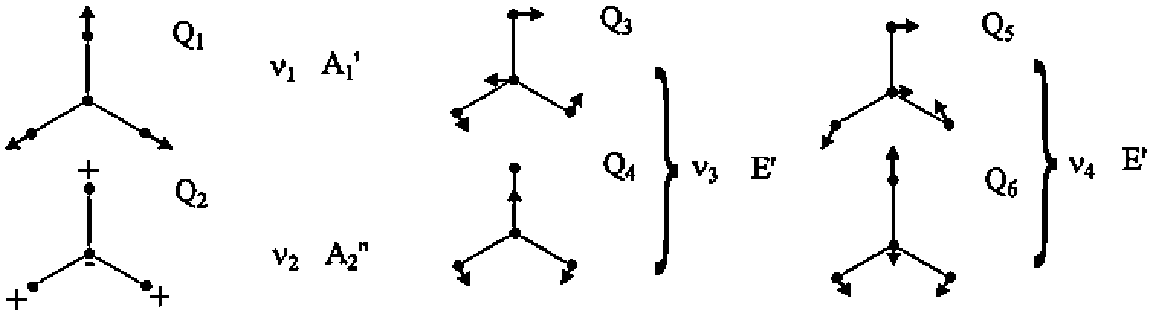
3. NO_3^- (Nitrate ion)

No. of atoms : 4
Total No.freedoms : 3 x 4 = 12
Structure : non-linear
Vibrational deg. of freedom : 3 x 4 – 6 = 6 normal degenerate vibration modes,

The infrared and Raman spectra of powdered ionic nitrates have detected several low intensity vibrational bands on the low frequency side of $\nu_1(A'_1)$'), $\nu_2(A''_2$, $\nu_3(E')$ and $\nu_4(E')$. NO_3^- belongs to D_{3h} point group.

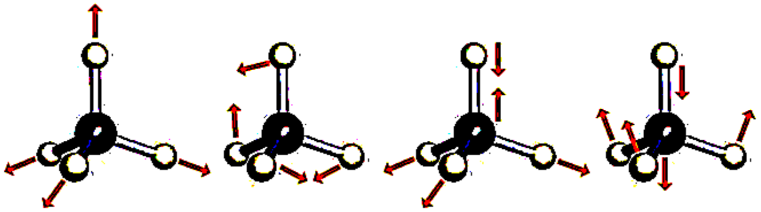
Nitrate ion fits the planar spectra: v1 is 1049 cm(-1) since it only Raman active. Since usually stretching mode are larger than bending v3 and v4 are assigned

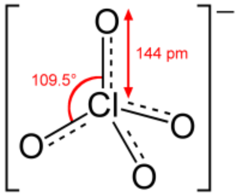




4. ClO_4^- (perchlorate ion)

No. of atoms : 5
Total No.freedoms : 3 x 5 = 15
Structure : non-linear
Vibrational deg. of freedom : 3 x 5 – 6 = 9 normal degenerate vibration modes)


Symmetric stretch IR inactive
Deformation (doubly degenerate) IR inactive
Stretch (triply degenerate) IR active (3019 cm^{-1})
Deformation (triply degenerate) IR active (1306 cm^{-1})



~1102 cm^{-1} IR & Raman (stretch triply degenerate)
~935 cm^{-1} Raman (symmetric stretch)
~628 cm^{-1} IR & Raman (stretch triply degenerate)
~462 cm^{-1} Raman (deformation doubly degenerate)

In the free state the perchlorate ion has Td symmetry with its vibrational modes distributed as

$$\Gamma_{vib} = A_1 + E + 2F_2$$

where the A_1 and E_2 species are Raman active only while the two F_2 species are both IR and Raman active.

These modes are expected to occur at 928, 459, 1119 and 625 cm^{-1} respectively for the perchlorate ion.

ν1(A) is the stretching totally symmetrical vibration (935 cm–1); ν2(E) (462 cm–1) is the twice degenerate vibration; ν3(F) is the thrice degenerate vibration (1102 cm–1); ν3(F) is the thrice degenerate vibration (628 cm–1).

Effect of coordination on Ligand Vibrations

- Complex formation leads to several changes in the ligand. These may manifest through changes in the electronic structure, the state of energy or symmetry of the ligand. These changes affect the vibrations of the ligand and this in turn will cause a change in its vibrational spectrum compared to that of the free ligand.

- The vibrational spectrum of a complex compound is influenced by the structure, the symmetry of the complex, the strength of its co-ordination bonds and its interaction with the environment. Based on the changes in the spectrum of the complex (compared to the free ligand) many properties of the compound may be deduced.

- Coordination of the donor atom of the ligand to the central atom lowers the symmetry of the ligand. This decreases in symmetry gives rise to bands in the infrared spectrum which were not infrared-active in the free ligand, in accord with the selection rules. Bonds which are equivalent in the free ligand are not equivalent in the coordinated state; this may cause the splitting of certain bonds. This change can be readily seen in the spectra of simple ions, such as carbonate, sulphate or nitrate, and in the spectra of their complexes.

Uses of groups vibrations in the structural elucidation of metal complexes of

1. Urea:

Urea has ***C_{2v}*** point group symmetry if the four hydrogen atoms are in the plane of the molecule. The symmetry analysis is given below.

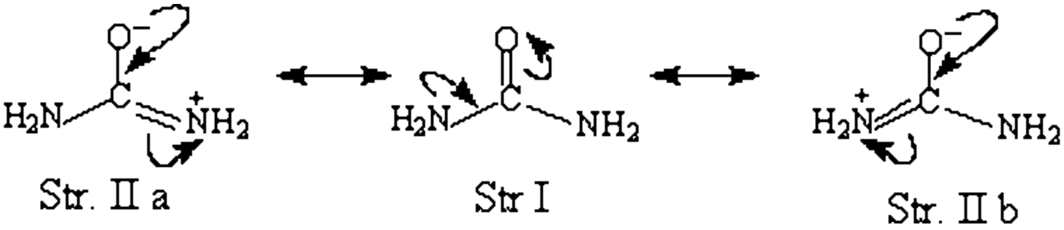
Total: 8a, + 3a, + 5b, + 8b, = 24
Rotational a2 + b, + b, = 3
Translational a, + b, + b, = 3
Vibrational 7a1 + 2a2 + 3b1 + 6b2 = 18

The stretching frequency of the carbonyl vibration of urea is at 1686 cm^{-1} which does not correspond to a “free carbonyl”. Urea has three coordina- tion sites: the carbonyl oxygen and the two nitrogen atoms. Urea, in spite of its three coordinating sites, usually acts as a monodentate ligand.

Urea forms complexes with metal ions like Fe^{3+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Pt, Pd. Co-ordination can occur through oxygen or nitrogen atom and changes in stretching frequency of the carbonyl group has been found to be less than 1662 $cm^{-1}$with no appreciable changes in the N-H frequency(ν_{N-H} = 3500, 3350; in the complex the vibration is observed around 3300 cm^{-1}). The vibrational frequency of C-N bond increases considerably. These changes can be rationalised through the resonance structures of urea, which are shown below.

Changes in the spectrum in this case are usually: (1) no great effect on the N-H stretching frequencies; (ii) a lowering of the C=O stretching frequency. However, the spectra differ significantly from that of free urea if a nitrogen-metal bond is present.

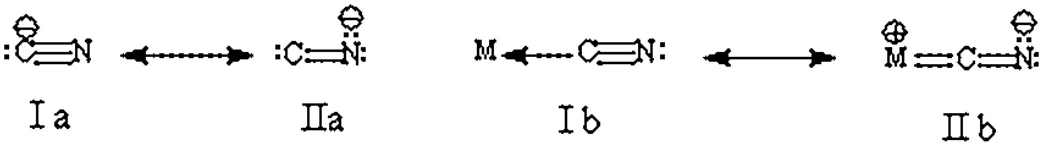
- When coordination occurs through oxygen, there is a decrease in the C-O stretching frequency due to major contribution of structures II a and II b, simultaneously there is an increase in the absorption due to C-N. No appreciable changes in N-H stretching.
- When co-ordination occurs through nitrogen reverse is observed, that is there is an increase in C-O and a decrease in that of C-N stretching frequencies. The increase is attributed to Structure I, which is the only contributor (both nitrogen atoms are involved in complexation).



Compound	Co-ordinating atom	$\nu_{(C-O)}$in cm^{-1}	$\nu_{(C-N)}$in cm^{-1}
Urea	N	1683	1473
$[Pt(urea)_2Cl_2]$	N	1725	1395
$[Cu(urea)_2Cl_2]$	O	1530	1505
$[Cr(urea)_6]Cl_3$	O	1505	1507

2. **CN^-**

Co-ordinate to the metal atom through carbon. The free CN^- ion has a stretching frequency of 2080 cm^{-1}, in complexes it generally has a higher value and a sharp absorption in the range 2000-2200 cm^{-1} is observed.



In the Free State the contribution of II a is greater than I a towards the resonance hybrid. In complexes the contribution of I b or II b depends on the metal atom to which it is coordinated. It has been found that CN stretching frequency in its complexes depends on electro negativity, oxidation state and co-ordination number of the metal atom.

- The stretching frequency of the ligand CN increases with increase in electro negativity of the metal ion.

  $[Ni(CN)_4]^{2-} < [Pd(CN)_4]^{2-} < [Pt(CN)_4]^{2-}$
  2135 cm^{-1}, 2143 cm^{-1} 2150 cm^{-1}

- The CN stretching frequency increases with increase in the oxidation state of the metal atom. Higher oxidation state of the metal would decrease electron density at the metal center for back bonding with the ligand.

  $[Ni(CN)_4]^{4-} < [Ni(CN)_4]^{2-}$
  1985 cm^{-1}, 2135 cm^{-1}.

- The stretching frequency for CN decreases with increase in coordination number of the metal atom.Increase in Coordination number results in a decrease in positive charge on the metal, which in turn weakens the M-CN sigma bond.

  $[Ag(CN)_4]^{3-} < [Ag(CN)_3]^{2-} < [Ag(CN)_2]$
  2092 cm^{-1} 2105 cm^{-1} 2135 cm^{-1}

3. **Dimethyl sulfoxide**

It is structurally similar to acetone, with a sulfur replacing the carbonyl carbon. The normal absorption of the S=O bond occurs at 1050 cm^{-1}. This is lower than the C=O frequency, since the SO bond has a larger reduced mass than the CO bond resulting in the frequency shift.

Metals can bond to DMSO either through its oxygen or its sulfur. If the bonding is to the sulfur, the metal donates electrons from its π orbitals (the t2g) into an empty π orbital on the DMSO ligand, thereby increasing the S--O bond order. Thus, if the metal is bonded to the DMSO at the sulfur, the frequency of the absorption increases. If the bonding is to the oxygen of the DMSO, the metal forms a bond with one of the lone pairs on the oxygen, and thereby withdraws electron density from the oxygen. This favors the second resonance form, since the oxygen will "seek" to gain electrons to compensate for the electrons donated to the metal. The net effect is that the S=O bond order declines and the S=O absorption appears at lower frequency.

The most characteristic vibrational modes are those dominated by S–O stretching. IR frequencies at 1043 cm^{-1} for solid (213 K) dimethyl sulfoxide, 1058 cm^{-1} for liquid (300 K), and 1101 cm^{-1} for gas (360 K), have been reported for this band.

The SO stretching band has moved down to 950 cm^{-1} in the $[Co(DMSO)_6]^{+2}$ ion and even further, to 915 cm^{-1}, in $SnC1^{4-}2DMSO$.

U,il)vq 97Ovi *5-* I I .;tretch
7141% Asym. C-S &etch 1 **730111**
Sym. C-S stretch (**G85v**

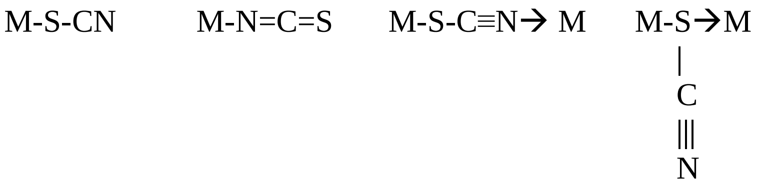
1291rv.sh 1287111
1055rs,hd 1 1 0 2 ~ s 1064~s 1096~s *8-0* str.
1012s 1016m
94tis **829w**
921m 915a
887w 898w 748m 750m
6906 689m . . . . 619 Asym. C-S str.
661m 672m .... ' 611 Sym. C-S str.

4. CNS^- (thiocyanate)

The structure of the SCN ion is a combination of the two resonating structures :

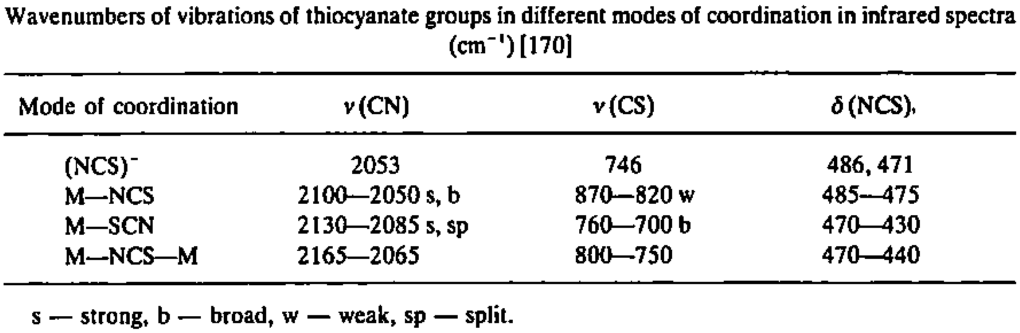
$$S^{-}-C\equiv N \longleftrightarrow S=C=N^{-}$$

When the metal-sulphur bond is formed, the structure with the triple C=N and single C—S bond becomes predominates.The thiocyanate ion forms complexes with most transition metals, but it can coordinate in at least four ways :



$$\text{M-S-CN} \qquad \text{M-N=C=S} \qquad \text{M-S-C}\equiv\text{N}\rightarrow\text{M} \qquad \underset{\underset{\text{N}}{\overset{|||}{\text{C}}}}{\overset{}{\text{M-}\underset{|}{\text{S}}\rightarrow\text{M}}}$$

The type of bond depends on the oxidation state of the metal, steric factors, and the other ligands present.



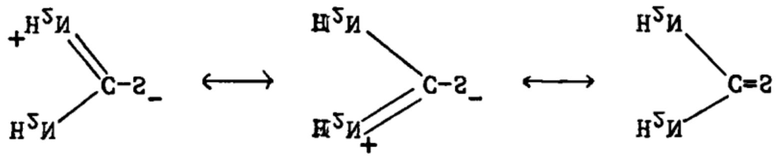
Wavenumbers of vibrations of thiocyanate groups in different modes of coordination in infrared spectra (cm^{-1}) [170]

Mode of coordination	ν(CN)	ν(CS)	δ(NCS),
$(NCS)^-$	2053	746	486, 471
M—NCS	2100—2050 s, b	870—820 w	485—475
M—SCN	2130—2085 s, sp	760—700 b	470—430
M—NCS—M	2165—2065	800—750	470—440

s — strong, b — broad, w — weak, sp — split.

5. **$CS(NH_2)_2$** (Thiourea)

The ligand that fulfils most of the ideal ligand requirements set out in the Introduction is thiourea ($S:C(NH_2)_2$ (tu). It forms complexes with a wide range of both transition and non-transition metals, and can form octahedral, tetrahedral, square-planar, and polymeric complexes. Representative crystal structures are available for each of the stereochemical arrangements, and there are no internal ligand vibrations in the v(M-S) region of the spectrum. Thiourea almost always coordinates through the sulphur atom. The crystal structures of the following thiourea complexes have been reported, and in each case the bonding is through sulphur $NiCl_2\,tu_4$, $ZnCl_2\,tu_2$, $[Pdtu_4]Cl_2$, $CdCl_2\,tu_2$ etc.,



Thiourea possesses C_{2v} symmetry, and on this basis the following distribution of normal modes occurs :

$$\Gamma_{vib} = 7A_1 + 2A_2 + 6B_1 + 3B_2$$

All are raman active; except A_2 allare IR active. The $\nu_{C=S}$ stretching frequency in the region 72 – 713 cm^{-1} is shifted to lower region upon complexation.

The 3000–3465 cm-^{1} region:

In this region, the asymmetric and symmetric NH stretching vibrational bands of NH2 of the free ligand (TU) observed at 3380, 3279, 3177 and 3090 cm^{-1} were shifted to higher wavenumbers on the formation of the metal–thiourea complexes. The formation of S→M bonds in all the investigated complexes is expected to increase the contribution of the highly polar structure to the thiourea molecule, resulting in the increase of the double bond nature of the C–N bond and a greater single bond character for the carbon-to-sulphur bond The band at 1477 cm^{-1} of the ligand (TU) is assigned to the N–C–N stretching vibration. On coordination, this band was shifted to (1478–1543 cm^{-1}) in the complexes. The wavenumber increase observed for the complexes could be explained due to the greater double bond character of the carbon-to-nitrogen bond on complex formation.

Effect of isotopic substitution on the vibrational spectra of molecules

A molecule can vibrate in many ways, and each way is called a vibrational mode. The wave number of absorbance n can be calculated by

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} \qquad \mu = \frac{m_A \cdot m_B}{m_A + m_B}.$$

in which c is the light velocity, f is the force constant in the atomic scale and the spring constant for the macroscopic model, respectively, and m is the reduced mass. Note that the force constant is a criterion for the strength of

It is generally assumed that the bond length is not altered by isotopic substitution. The chemical bond in the molecule A_B. Therefore, the stronger the chemical bond (electronic effect) and the smaller the reduced mass m (mass effect), the higher the wave number of the absorption band ν.

$$\frac{\omega_2}{\omega_1} = \sqrt{\frac{\mu_1}{\mu_2}}$$

The different isotopes in a particular species may give fine detail in infrared spectroscopy. For example, the O-O stretching frequency of oxyhemocyanin is experimentally determined to be 832 and 788 cm^{-1} for $\nu(^{16}O\text{-}^{16}O)$ and $\nu(^{18}O\text{-}^{18}O)$ respectively.

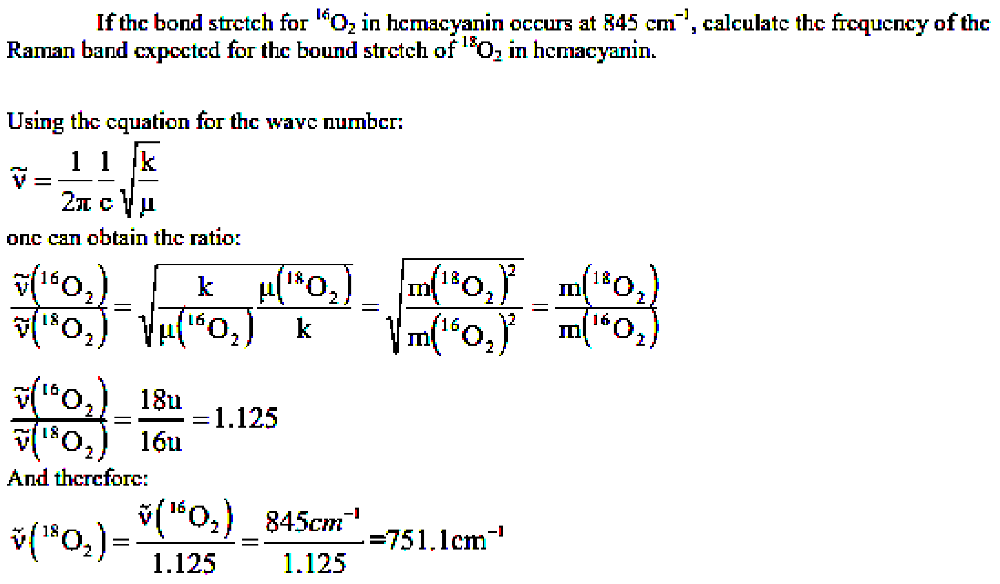
The reduced masses for $^{16}O\text{-}^{16}O$ and $^{18}O\text{-}^{18}O$ can be approximated as 8 and 9 respectively. So,

$$\frac{\nu_{^{16}O}}{\nu_{^{18}O}} = \sqrt{\frac{9}{8}} \approx \frac{832}{788}$$

Isotope Effects:

$H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$ each have unique spectra because the substitution of different isotopes changes the reduced mass of the molecule. H atoms have the largest change in isotopic mass of all atoms, a factor of ~2 in substituting D (i.e. ^{2}H) for H (i.e. 1H). The study of isotope effects, especially upon deuteration is an important tool in mechanistic organic chemistry. The harmonic vibration frequencies of two isotopic variants of a diatomic molecule in the same electronic state are then related by the equation

$$\frac{\omega_2}{\omega_1} = \sqrt{\frac{\mu_1}{\mu_2}}$$



If the bond stretch for $^{16}O_2$ in hemacyanin occurs at 845 cm^{-1}, calculate the frequency of the Raman band expected for the bound stretch of $^{18}O_2$ in hemacyanin.

Using the equation for the wave number:

$$\tilde{\nu} = \frac{1}{2\pi}\frac{1}{c}\sqrt{\frac{k}{\mu}}$$

one can obtain the ratio:

$$\frac{\tilde{\nu}(^{16}O_2)}{\tilde{\nu}(^{18}O_2)} = \sqrt{\frac{k}{\mu(^{16}O_2)}\frac{\mu(^{18}O_2)}{k}} = \sqrt{\frac{m(^{18}O_2)^2}{m(^{16}O_2)^2}} = \frac{m(^{18}O_2)}{m(^{16}O_2)}$$

$$\frac{\tilde{\nu}(^{16}O_2)}{\tilde{\nu}(^{18}O_2)} = \frac{18u}{16u} = 1.125$$

And therefore:

$$\tilde{\nu}(^{18}O_2) = \frac{\tilde{\nu}(^{16}O_2)}{1.125} = \frac{845cm^{-1}}{1.125} = 751.1cm^{-1}$$

Vibrational spectra of metal carbonyls with reference to the nature of bonding

CO is an unsaturated ligand, by virtue of C-O multiple bond. Such ligands are capable of accepting metal dπ electron by back bonding, i.e. these ligands are π-acceptor and therefore also called as hard ligands. Being π−acidic in nature, CO is a strong field ligand that achieves greater d−orbital splitting through the metal to ligand π−back donation. A metal−CO bonding interaction thus comprises of a CO to metal σ−donation and a metal to CO π−back donation (Figure 2). Interestingly enough, both the spectroscopic measurements and the theoretical studies suggest that the extent of the metal to CO π−back donation is almost equal to or even greater than the extent of the CO to metal σ−donation in metal carbonyl complexes. This observation is in agreement with the fact that low valent−transition metal centers tend to form metal carbonyl complexes.

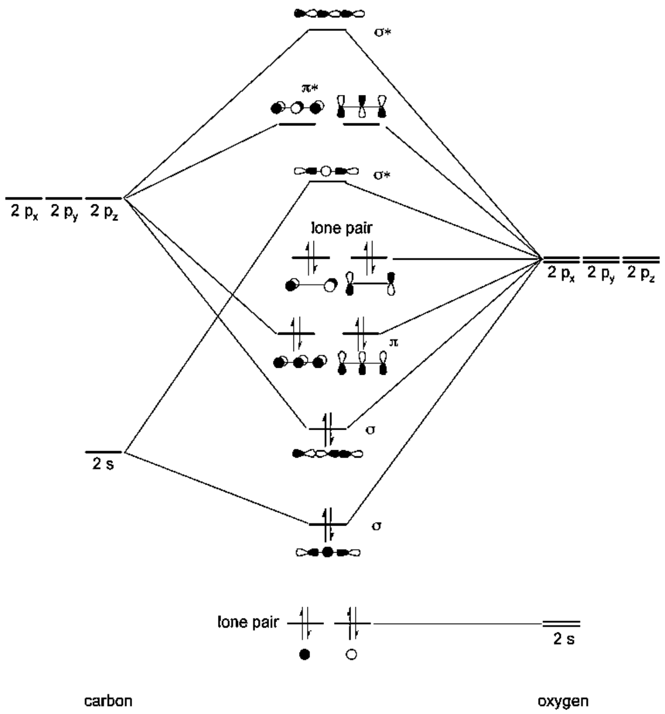
In the metal carbonyl complexes, the direct bearing of the π−back donation is observed on the M−C bond distance that becomes shorter as compared to that of a normal M−C single bond distance. Metal binds to C, not O, because the ligand HOMO is the Carbon, not the Oxygen-lone pair, this is because oxygen is more electronegative & so its orbitals have lower energy. Dipole moment of free CO molecule is close to zero.

The MO diagram of carbon monoxide.

The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as:

(σs b) 2 (σp b) 2 (πy b =πz b) 4 (σs*)2 (πy*=πz*)0 (σp*)0 (σs*) is the highest occupied molecular orbital (HOMO) which can donate the lone pair of electrons for the formation of a OC→M σ bond. (πy*=πz*) are the lowest unoccupied molecular orbitals (LUMO) which can accept the electron density from an appropriately oriented filled metal orbital resulting into formation of a M→CO π bond.

The nature of M-CO bonding in mononuclear carbonyls can be understood by considering the formation of a dative σ-bond and π-bond due to back donation.



Energy-level diagram for CO can be refined by inclusion of s, p mixing. Crucial to the discussions on M-CO bonding properties are the frontier orbitals σ*(HOMO) and π*(LUMO)

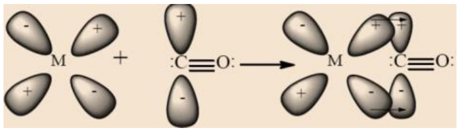
Formation of dative σ-bond:

The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a M←CO σ-bond.

empty d or p-orbital filled sigma-orbital

Formation of π-bond by back donation:

This bond is formed because of overlapping of filled dπ orbitals or hybrid dpπ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule.



filled d-orbital empty pi-orbital

Bridging CO groups:

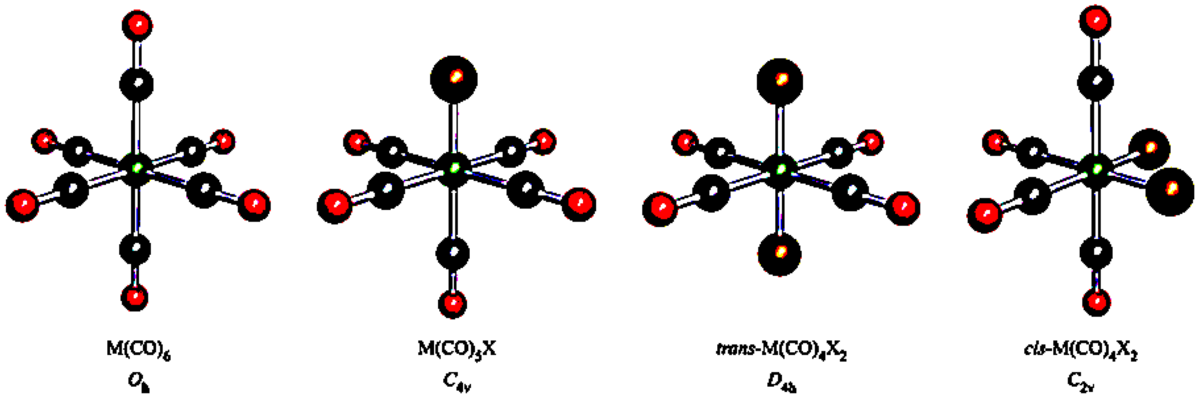
In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μ_n–CO, where n indicates the number of metals bridged. While n=2 is the most common value, it reaches to be 3 or 4 in certain less common carbonyls. In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in μ_2–CO group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

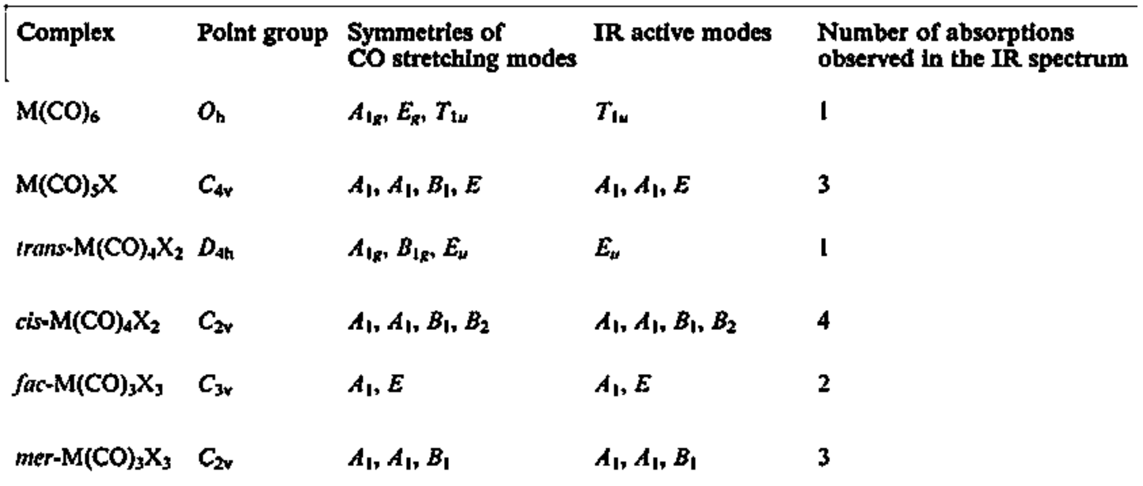
INFRARED SPECTROSCOPY

The carbonyl groups can have two modes of stretching

Typical stretching frequencies:

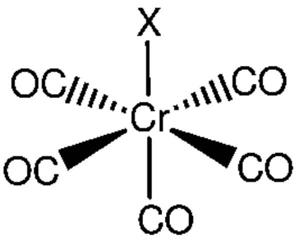
- •Uncoordinated or "free" CO: 2143 cm-1
- •Terminal M-CO: 2125 to 1850 cm-1
- •Doubly bridging (μ-2): 1850 to 1750 cm-1
- •Triply bridging (μ-3): 1675 to 1600 cm-1





Complex	Point group	Symmetries of CO stretching modes	IR active modes	Number of absorptions observed in the IR spectrum
$M(CO)_6$	O_h	A_{1g}, E_g, T_{1u}	T_{1u}	1
$M(CO)_5X$	C_{4v}	A_1, A_1, B_1, E	A_1, A_1, E	3
trans-$M(CO)_4X_2$	D_{4h}	A_{1g}, B_{1g}, E_u	E_u	1
cis-$M(CO)_4X_2$	C_{2v}	A_1, A_1, B_1, B_2	A_1, A_1, B_1, B_2	4
fac-$M(CO)_3X_3$	C_{3v}	A_1, E	A_1, E	2
mer-$M(CO)_3X_3$	C_{2v}	A_1, A_1, B_1	A_1, A_1, B_1	3

The number of ν(CO) can also tell us the shape of the molecule.



X = pyridine or tri-phenylphosphine

- Rule of thumb….
  - **Each unique CO has 1 ν(CO)**
  - **Each set of equivalent CO's have 2 ν(CO)**
    (symmetric and antisymmetric)
- Therefore $(CO)_5CrX$ has 3 ν(CO)
- How many ν(CO) will $Cr(CO)_6$ have?
  - All carbonyl ligands are equivalent.
  - For highly symmetric molecules such as octahedral or tetrahedral, the symmetric stretch does not result in a dipole change and therefore is not IR active.

Geometry and number of C-O stretching vibrations (group theoretical treatment)

The following steps are needed in order to determine the number of IR active vibrational modes in a molecule – metal carbonyls:

1. Determine the point group of the molecule.

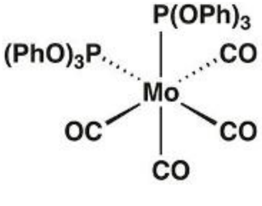
2. Generate a reducible representation of the C-O stretching vibrations within the molecule.

3. Reduce the reducible representation using the reduction formula
4. Identify the number of translational irreducible representations present in the reduced representation from step 3.

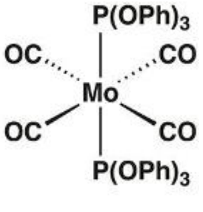
Example:

To demonstrate, we will walk through the application of group theory to the molecule *cis*-$Mo(CO)_4[P(OPh)_3]_2$.

Using the symmetry tree, and assuming that the ligands $P(OPh)_3$ are point ligands (while ignoring the symmetry of those ligands), we find that *cis*-$Mo(CO)_4[P(OPh)_3]_2$ is in the point group C_{2v}.



cis-



trans-

The character table for the point group C_{2v} is shown below.

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

Using the character table for the point group C_{2v}, we generate a reducible representation (Γ_{red}) of the C-O stretching modes in the molecule *cis*-$Mo(CO)_4[P(OPh)_3]_2$

C2v	**E**	**C2**	**σv(xz)**	**σv'(yz)**
Γred	**4**	**0**	**2**	**2**

Reduction of the reducible representation can be achieved using the reduction formula

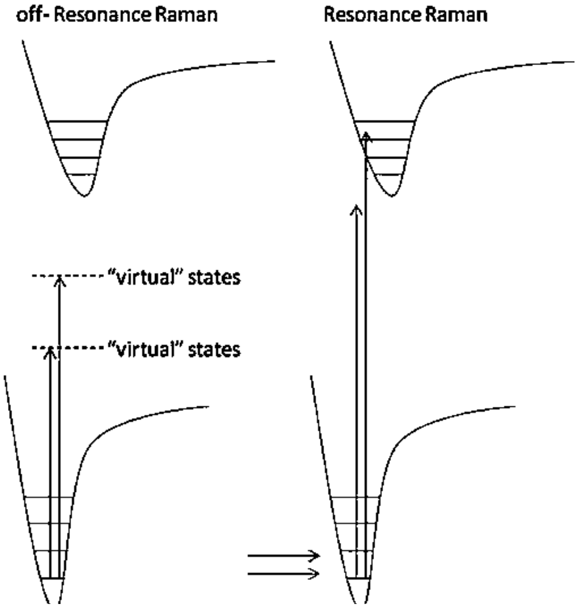
$\Gamma_{red} = 2A_1 + B_1 + B_2$.

All three of the contributing irreducible representations, A_1, B_1, and B_2, are IR active because they transform as either the x-, y-, or z-axis (see the symmetry of functions in the character table). Therefore, we predict that *cis*-$Mo(CO)_4[P(OPh)_3]_2$ will exhibit 4 C-O stretching modes in its IR spectrum.

Applications of Raman spectroscopy – resonance Raman spectroscopy.

Resonance Raman spectroscopy is a variant of 'normal' Raman spectroscopy. 'Normal' Raman spectroscopy uses laser excitation at any wavelength in order to measure the Raman scattering of this laser light. Notwithstanding the many practical issues caused by the use of different laser wavelengths, the end result will be very similar whatever wavelength is used.

In resonance Raman the excitation wavelength is carefully chosen to overlap with (or be very close to) an electronic transition – this typically means in an area of UV-visible absorption. Such overlap can result in scattering intensities which are increased by factors of 10^2-10^6 – thus, detection limits and measurement times can be significantly decreased. However, since the excitation coincides with UV-visible absorption fluorescence backgrounds can be significant and more problematic than with 'normal' Raman scattering.



APPLICATION Raman Spectra of Inorganic Species

- ♣ The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed.
- ♣ In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm-1, a region of the infrared that is experimentally difficult to study.
- ♣ These vibrations are frequently Raman active, however, and peaks with $\Delta\nu$ values in this range are readily observed.
- ♣ Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.
- ♣ Quantitative applications Raman spectra tend to be less cluttered with peaks than infrared spectra. As a consequence, peak overlap in mixtures is less likely, and quantitative measurements are simpler. In addition, Raman sampling devices are not subject to attack by moisture, and small amounts of water in a sample do not interfere.

Advantages of Raman Spectroscopy

- many organic and inorganic materials are suitable for Raman analysis. These can be solids, liquids, polymers or vapors.
- no sample preparation needed.
- not interfered by water.
- non-destructive.

- highly specific like a chemical fingerprint of a material.
- Raman spectra are acquired quickly within seconds.
- samples can be analyzed through glass or a polymer packaging.
- laser light and Raman scattered light can be transmitted by optical fibers over long distances for remote analysis.
- in Raman spectroscopy, the region from 4000 cm^{-1} to 50 cm^{-1} can be covered by a single recording.
- Raman spectra can be collected from a very small volume (< 1 μm in diameter).
- inorganic materials are easily analysable with Raman spectroscopy.

Disadvatantages of Raman Spectroscopy

- can not be used for metals or alloys.
- the Raman effect is very weak. The detection needs a sensitive and highly optimized instrumentation.
- fluorescence of impurities or of the sample itself can hide the Raman spectrum. Some compounds fluoresce when irradiated by the laser beam.
- sample heating through the intense laser radiation can destroy the sample or cover the Raman spectrum.

S.No.	Raman	IR
1	It is due to the scattering of light by the vibrating molecules.	It is the result of absorption of light by vibrating molecules.
2	The vibration is Raman active if it causes a change in polarizability	Vibration is IR active if there is change in dipole moment.
3	The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment due to that vibration.
4	Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
5	Raman lines are weak in intensity; concentrated solutions preferred	Dilute solutions are preferred
6	Sample preparation is not very elaborate; it can be in any state.	Sample preparation is elaborate Gaseous samples can rarely be used.
7	Gives an indication of covalent character in the molecule.	Gives an indication of ionic character in the molecule.
8	Cost of instrumentation is very high	Comparatively inexpensive.
9	Optical systems are made of glass or quartz	Optical systems are made of NaCl, NaBr, KCl, KBr etc
10	Monochromatic radiations used	Polychromatic in the IR region