

VIBRATIONAL SPECTROSCOPY

IR AND RAMAN

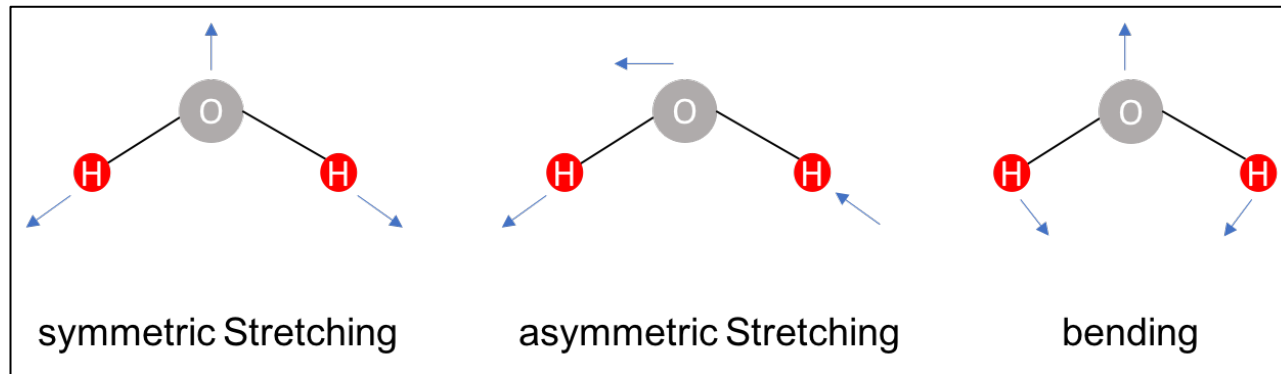
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VIBRATIONAL SPECTROSCOPY

- Infrared (IR) spectroscopy is a class of vibrational spectroscopy, which relies on the transmittance, absorbance, or reflectance of infrared light.
- Raman spectroscopy is an occurrence of inelastic scattering, that probes molecular vibrations to provide a molecular footprint of materials.

Infrared spectroscopy

- In infrared (IR) spectroscopy, when light interacts with a complex, several molecular vibrations occur by absorbing light at specific frequencies.
- The absorbed light frequency depends on the mass of the atoms in the molecule, the bond strength, and the polarity of the bond.
- Some of the molecular vibrations include: stretching, bending, twisting and rocking.
- Figure shows the possible vibration modes of water.



$\nu(s)$: symmetric stretching vibration;
 $\nu(as)$: asymmetric stretching vibration
 δ : symmetric bending vibration.

- In order for a vibration to be IR active, a change in the dipole moment of the molecule must occur.
- The intensity of absorption bands depends on the extent of change in the dipole moment of the molecule upon light interaction.

IR spectroscopy of coordination compounds

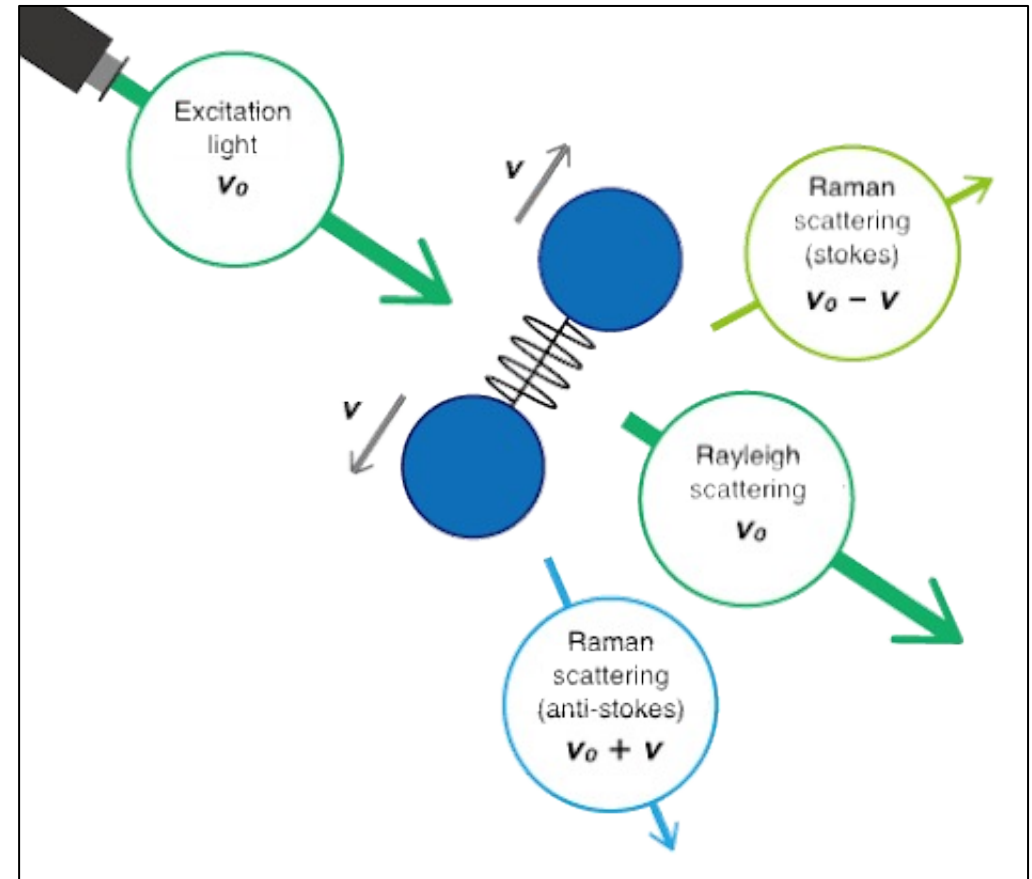
- IR spectroscopy is a great analytical tool for ligand identification in coordination complexes, because data collection is fast, and different ligand binding modes have distinct absorption frequencies.
- FTIR of metal ligand complexes has a list of absorption bands of typical functional groups. When a ligand binds to a metal, the absorption frequency of the ligand changes reflecting the new electronic structure of the complex.
- Coordination complexes with different geometry also absorb light at different frequencies.

Advantage of IR techniques

- Infrared (IR) spectroscopy is a good analytical tool for geometry identification of coordination compounds.
- It is a fast and relatively simple analytical technique.
- Moreover, metal-ligand chemistry has been studied extensively via IR spectroscopy and tables of different ligand frequencies have been reported in various studies, which makes it easier to determine the ligand and the complex's structure based on those studies.

Raman spectroscopy

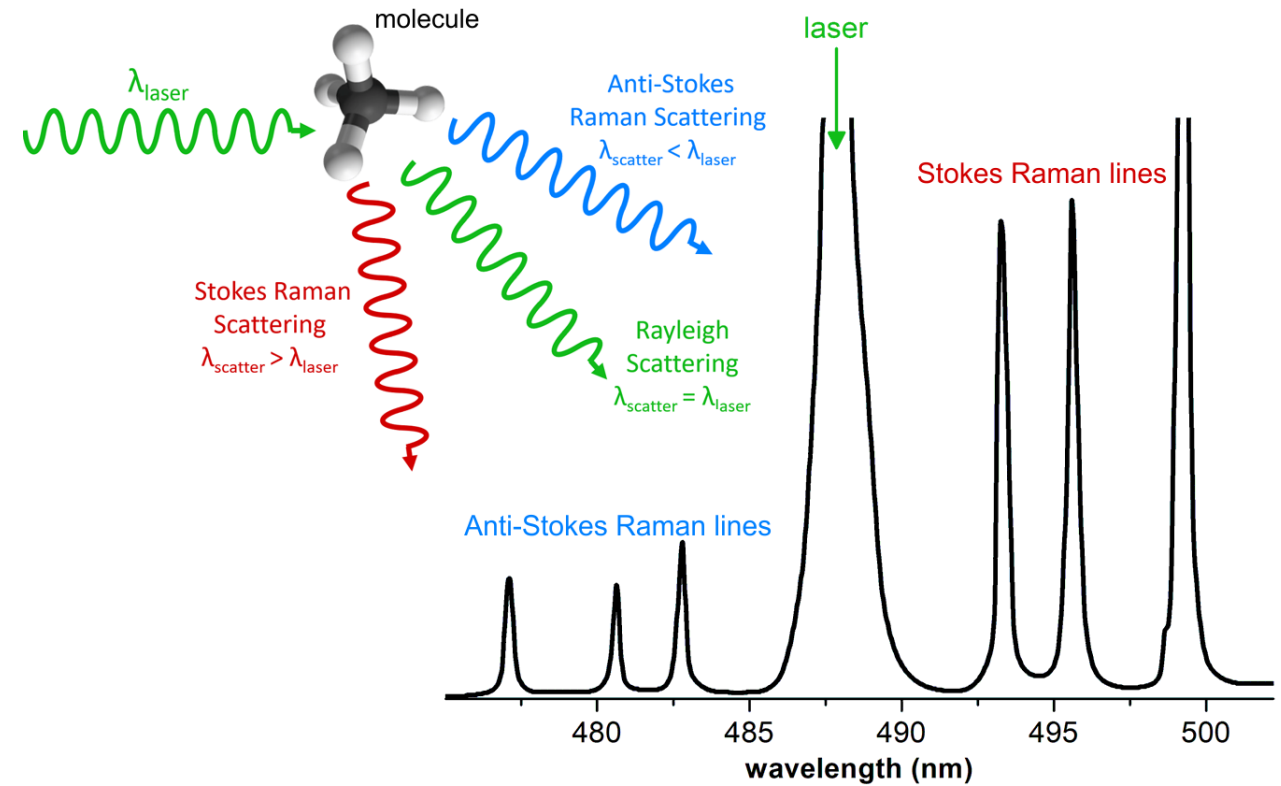
- Raman spectroscopy is a popular technique for the analysis of molecular structure and is considered complementary to infrared spectroscopy.
- Raman spectroscopy is based on the Raman effect, which was first identified by the Indian physicist Chandrasekhara Venkata Raman in 1928.
- The Raman effect is based on scattering of light, which includes both elastic (Rayleigh) scattering at the same wavelength as the incident light, and inelastic (Raman) scattering at different wavelengths, due to molecular vibrations.
- Raman scattering is about a million times less intense than Rayleigh scattering. Therefore, to obtain Raman spectra, it is necessary to prevent Rayleigh scattering from overpowering the weaker Raman scattering.



Molecular vibrations and Raman scattering

Raman spectroscopy

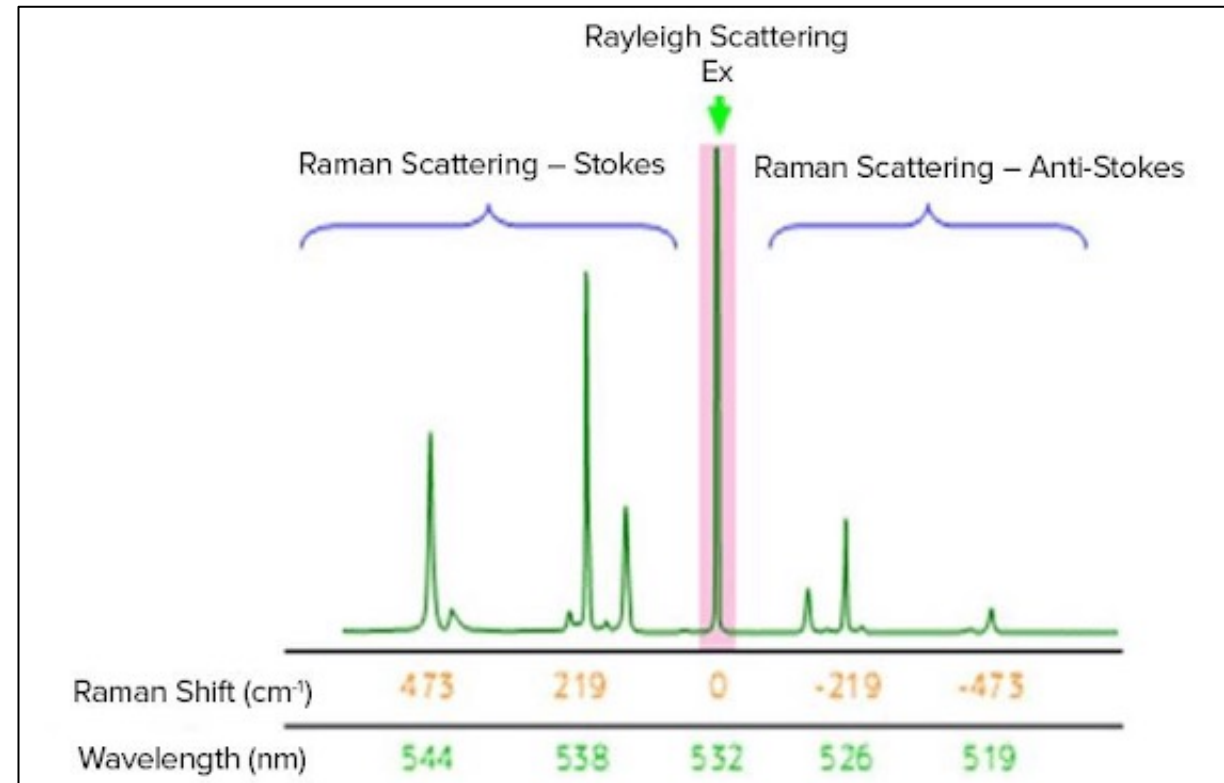
- Raman spectra are measured by exciting a sample using a high-intensity laser beam, with the resulting scattered light being passed through a spectrometer.
- The Raman shift is the energy difference between the incident light and the scattered light.
- In the resulting spectrum, the vertical axis is the intensity of the scattered light and the horizontal axis is the wavenumber of the Raman shift (cm^{-1}).



Scheme of Raman scattering.

What is the Raman shift?

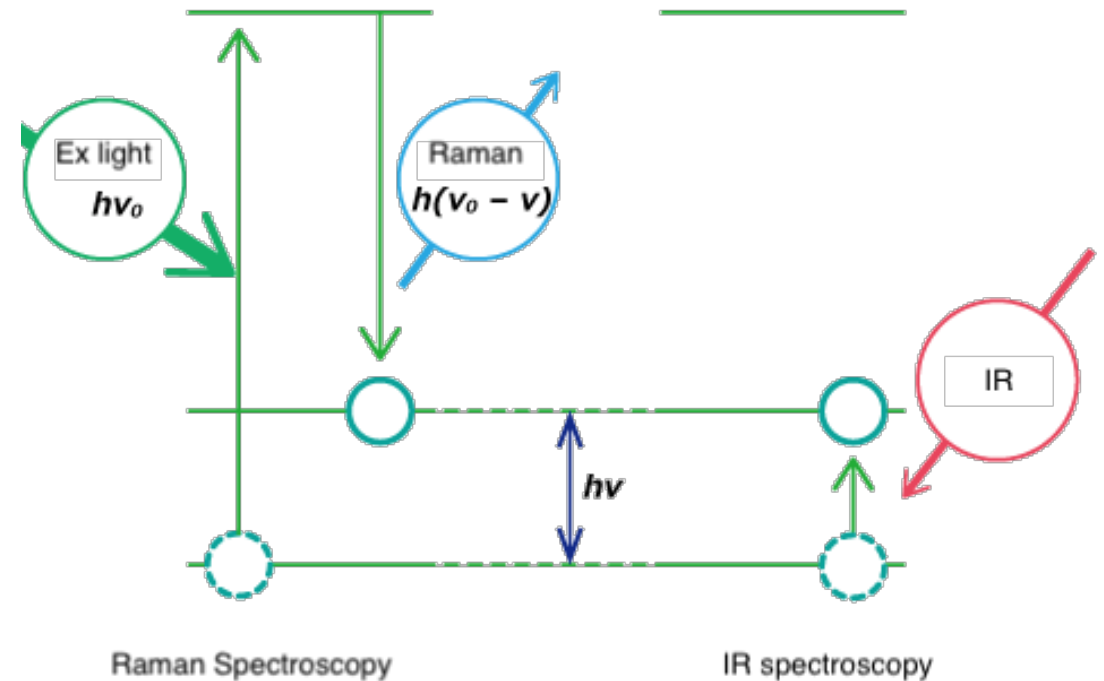
- The Raman shift is associated with two different energy bands. The shift at wavelengths higher than that of the incident light is termed Stokes scattering. The shift at wavelengths lower than that of the incident light is termed anti-Stokes scattering.
- As an example, the Raman spectrum of sulfur measured with an excitation wavelength of 532 nm (green laser) is shown.
- Stokes scattering is observed in the lower wavenumber (longer wavelength) region and anti-Stokes scattering in the higher wavenumber (shorter wavelength) region.
- Typically, higher-intensity Stokes scattering peaks are used for analysis, but anti-Stokes peaks can also be used.



Raman spectrum of sulfur

Difference between Raman spectroscopy and IR spectroscopy

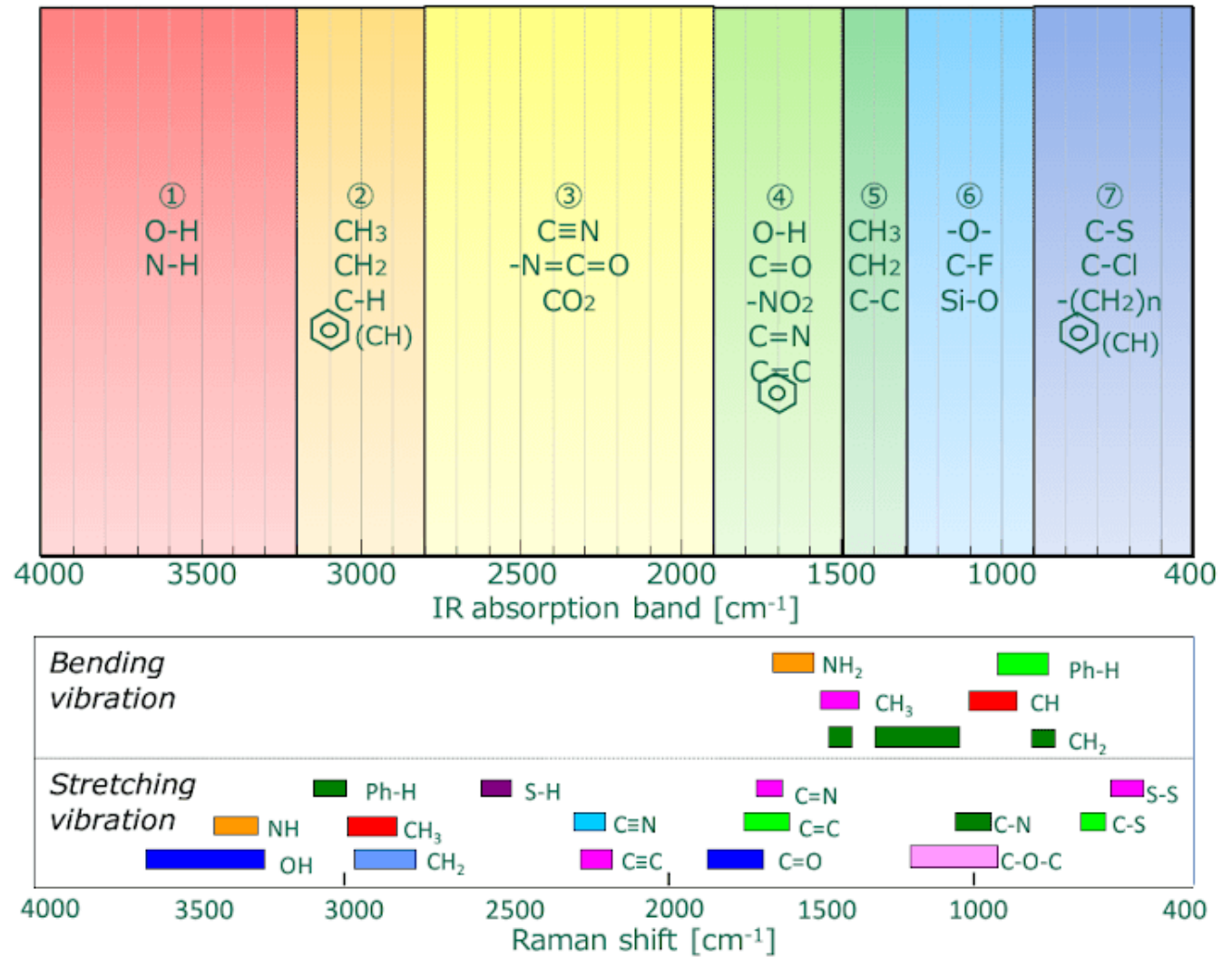
- Both Raman spectroscopy and IR spectroscopy are based on molecular vibrations as illustrated below.
- Infrared spectroscopy is based on absorption of light energy corresponding to the vibrational energy of molecules.
- Raman spectroscopy is based on scattering of incident light at an energy shifted by the vibrational energy ($h\nu$) of the molecule.



Vibration energy level

Difference between Raman spectroscopy and IR spectroscopy

- Vibration modes for the same functional groups are observed at the same wavenumber.



IR absorption bands (upper) vs. Raman shift (lower) for functional groups

Difference between Raman spectroscopy and IR spectroscopy

- Though both are forms of *vibrational spectroscopy*, IR and Raman spectroscopy differ in some fundamental aspects.
- IR spectroscopy is based on the fact that molecular absorption at specific vibrational frequencies causes a change in the dipole moment.
- Raman spectroscopy relies on the change in the polarizability of a molecule at the frequencies (Raman shift) at which the molecule scatters radiation.
- IR spectroscopy is sensitive to hetero-nuclear functional group vibrations and polar bonds, especially OH stretching in water.
- Raman spectroscopy is sensitive to homo-nuclear molecular bonds such as C-C, C=C and C≡C bonds.

VIBRATIONAL SPECTROSCOPY

- The infrared and Raman frequencies of isolated molecules are determined:
 - the arrangement of the atoms in space,
 - the forces between the atoms.

When a ligand coordinates, all of these change!

VIBRATIONAL SPECTROSCOPY APPLICATIONS

□ **Molecular structure can be explored by Vibrational spectroscopy**

■ **Expected both in the vibrational spectral features associated with the free ligand and in those of the system to which it becomes attached:**

■ An example is provided by the thiocyanate anion, SCN^- . In simple ionic thiocyanates, such as KCNS

○ **KCNS**

$\nu(\text{C-N})$ stretch at ca. 2060 cm^{-1} $\nu(\text{C-S})$ stretch at ca. 746 cm^{-1} , $\delta(\text{NCS})$ bend at ca. 480 cm^{-1}

○ **$[\text{Co}(\text{NCS})_4]^{2-}$ where the SCN^- is N-bonded**

$\nu(\text{C-N})$ mode rises to ca. 2070 cm^{-1} , $\nu(\text{C-S})$ increases dramatically to ca. 815 cm^{-1} , $\delta(\text{NCS})$ bend only drops by ca. 5 cm^{-1} (475 cm^{-1})

○ **$[\text{Hg}(\text{SCN})_4]^{2-}$ anion, where the SCN^- anion is S-bonded**

$\nu(\text{C-N})$ mode rises to ca. 2100 cm^{-1} , $\nu(\text{C-S})$ drops to ca. 710 cm^{-1} , the bend drops to ca. 450 cm^{-1} .

VIBRATIONAL SPECTROSCOPY APPLICATIONS

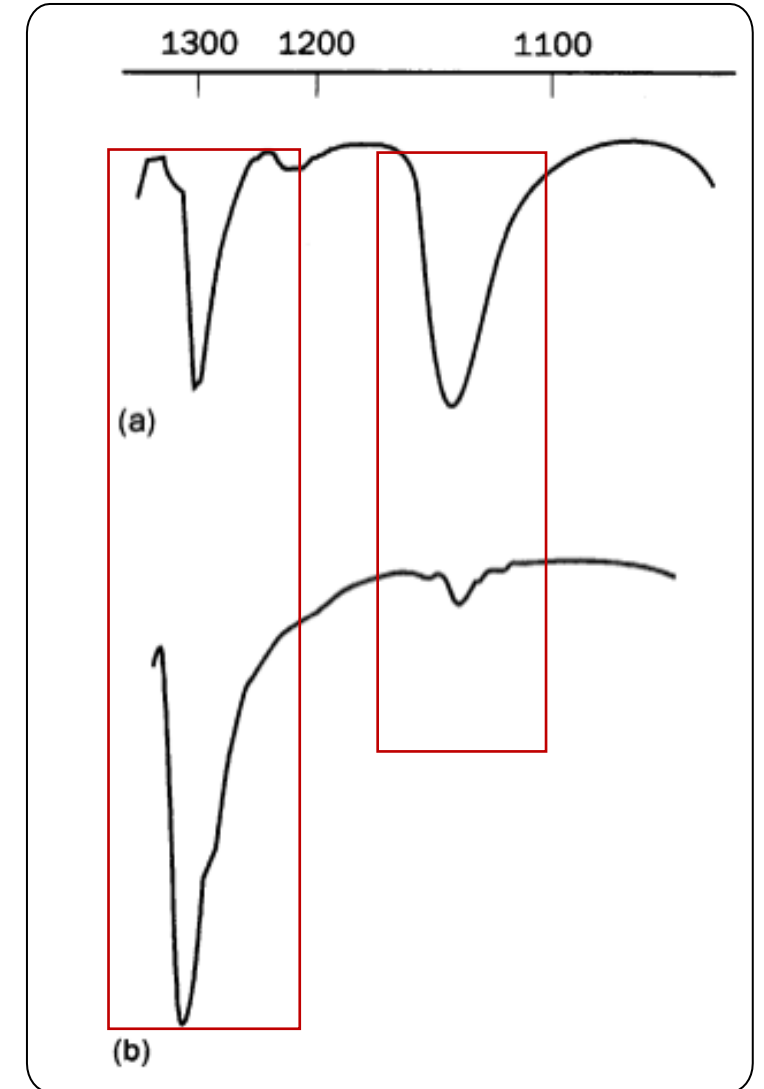
- Thiocyanates (SCN^-), KCNS , $[\text{Co}(\text{NCS})_4]^{2-}$ where the SCN^- is N-bonded and $[\text{Hg}(\text{SCN})_4]^{2-}$ anion, where the SCN^- anion is S-bonded

	KCNS	$[\text{Co}(\text{NCS})]^{2-}$	$[\text{Hg}(\text{SCN})]^{2-}$
ν (C-N)	2060 cm^{-1}	2070 cm^{-1}	2100 cm^{-1}
ν (C-S)	746 cm^{-1}	815 cm^{-1}	710 cm^{-1}
δ (N-C-S)	480 cm^{-1}	475 cm^{-1}	450 cm^{-1}

Note: M-S and M-N could be seen if there is not other ligand.

VIBRATIONAL SPECTROSCOPY APPLICATIONS

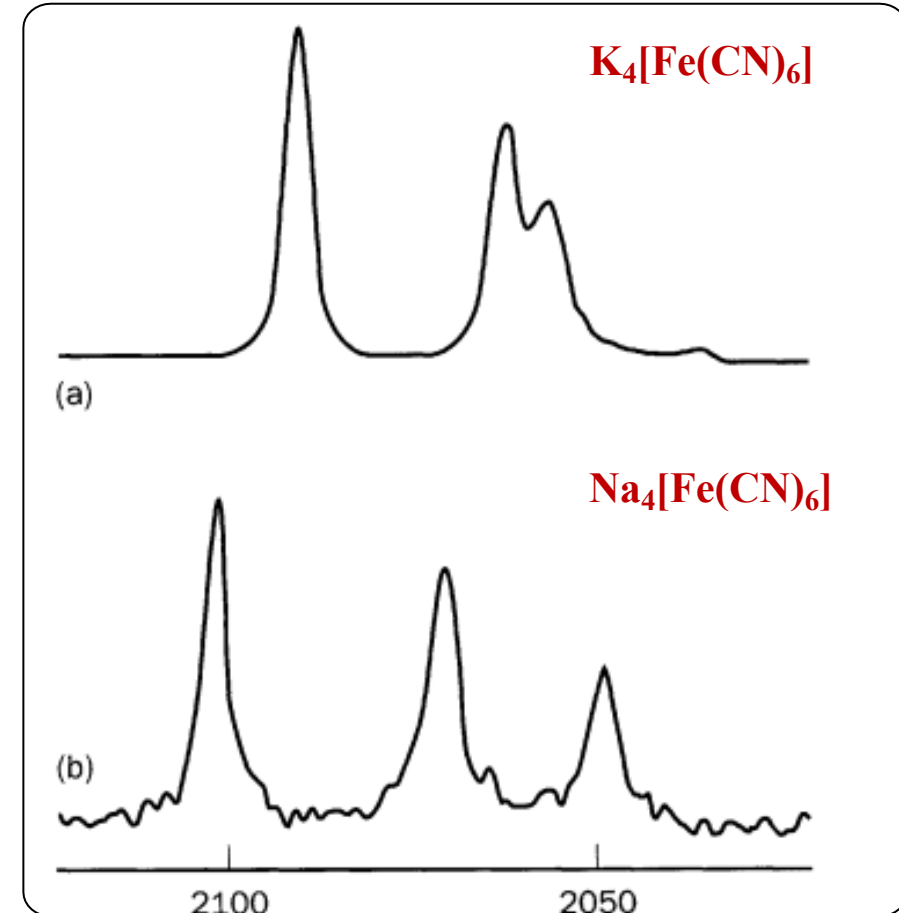
- IR spectra of $[\text{Co}(\text{NH}_3)_5\text{-ONO}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{-NO}_2]^{2+}$ provides a further illustration of the way that vibrational spectra can indicate a mode of coordination.
- So, in complexes of the NO_2^- anion, a $\nu(\text{N-O})$ mode appears at ca. 1300 cm^{-1} when the ligand is N-bonded and at ca. 1150 cm^{-1} when it is O-bonded.
- This is a much-studied and much-exploited pattern which is illustrated for two cobalt(III) complexes.



The infrared spectra of; (a) $[\text{Co}(\text{NH}_3)_5\text{-ONO}]^{2+}$ and (b) $[\text{Co}(\text{NH}_3)_5\text{-NO}_2]^{2+}$.
The $\nu(\text{N-O})$ peak in the latter at ca. 1300 cm^{-1} overlaps with a peak common to both spectra.

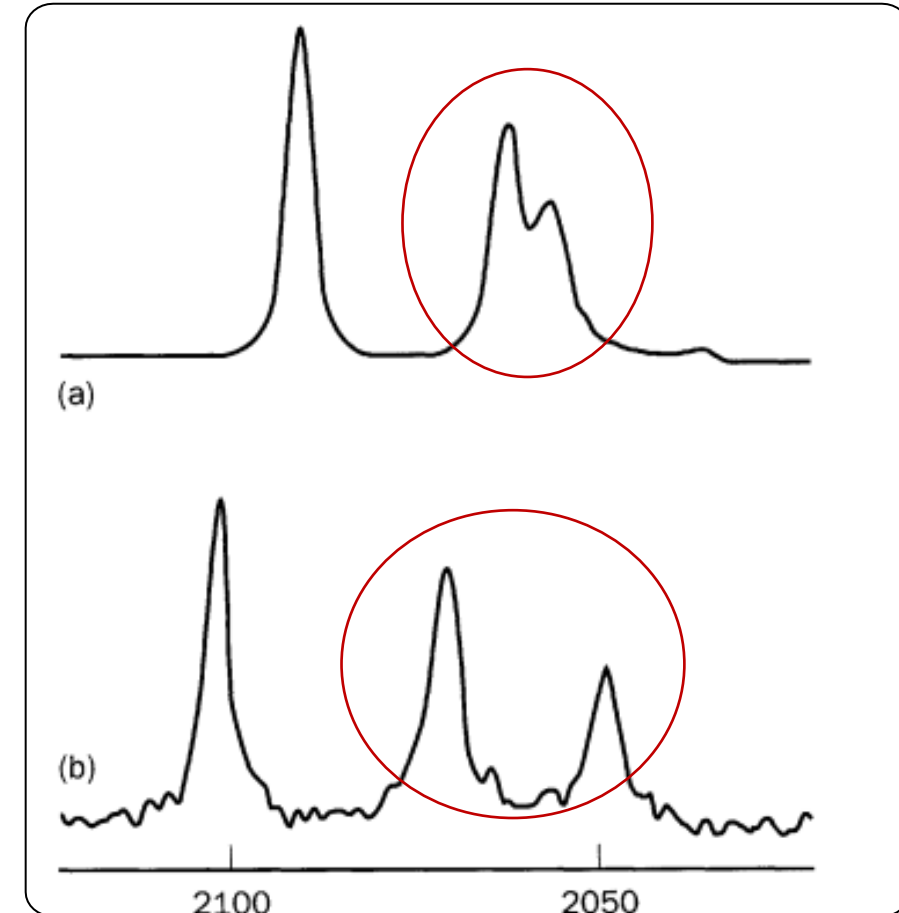
VIBRATIONAL SPECTROSCOPY APPLICATIONS

- Two Raman spectra of the anion $[\text{Fe}(\text{CN})_6]^{4-}$ is shown.
- Although a relationship between them exists, they are surprisingly different.
- The first thing to note is that some of the bands appear above 2080 cm^{-1} , the position of the $\nu(\text{C}\equiv\text{N})$ band in KCN; bands do not invariably drop in frequency when a ligand coordinates, although this is the common pattern.
- The differences between the two spectra show that vibrational interactions can occur between different complex molecules in the solid state.



VIBRATIONAL SPECTROSCOPY APPLICATIONS

- The Raman spectra of crystalline samples of (a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ and (b) $\text{Na}_4[\text{Fe}(\text{CN})_6]$.
- In the $[\text{Fe}(\text{CN})_6]$ anion the $\nu(\text{C}\equiv\text{N})$ vibrations are coupled. The higher frequency bands in both spectra are the A_{1g} (totally symmetric, 'breathing' mode) and the lower E_g the components of which are split apart.
- This latter splitting-and all the frequency differences between the two spectra-show the importance of solid-state effects, in which they originate.



VIBRATIONAL SPECTROSCOPY APPLICATIONS

□ Determination of Coordination Geometry by Vibrational spectra.

- In favorable cases vibrational spectra can be used to determine the ligand geometry around a central metal atom.
- As a typical example of the application of vibrational methods, consider square planar complexes of Pt of the general formula PtL_2X_2 , where X is a halogen and L is a polyatomic ligand.
- If it is *cis* then the molecular geometry is approximately C_{2v} and the $\nu(\text{Pt-X})$ vibrations are of $\text{A}_1 + \text{B}_1$ symmetries so that both modes are both infrared and Raman active.
- The trans isomer has approximate C_{2h} symmetry and the $\nu(\text{Pt-X})$ vibrations have $\text{A}_g + \text{A}_u$ symmetries.

Of these, the former is Raman active and the latter is infrared.

One band is predicted in each spectrum, at a different frequency in each.

A centre of symmetry means that bands active in the infrared are not Raman active and vice versa (not infallible)

VIBRATIONAL SPECTROSCOPY APPLICATIONS

- Square Planar complexes of Pt as (PtL_2X_2)

X is a halogen and L is a polyatomic ligands



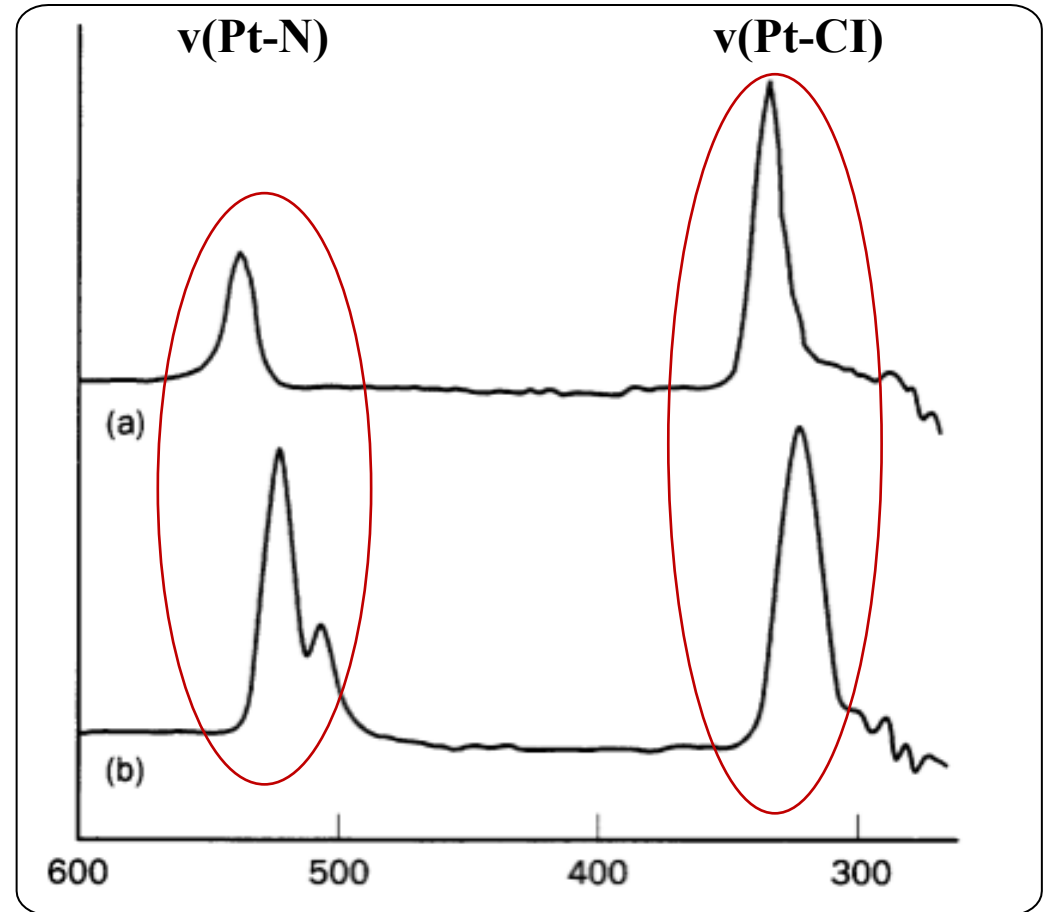
MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

VIBRATIONAL SPECTROSCOPY APPLICATIONS

- The Raman spectra of *cis* and *trans* $[\text{PtCl}_2(\text{NH}_3)_2]$ in the $\nu(\text{Pt-Cl})$ and $\nu(\text{Pt-N})$ stretching regions.
- The presence of two peaks in the $\nu(\text{Pt-N})$ region is sufficient to establish the lower spectrum as that of the *cis* isomer, without aid of the infrared spectrum, even though the $\nu(\text{Pt-Cl})$ only shows one



The Raman spectra of (a) *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ and (b) *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$. The $\nu(\text{Pt-N})$ mode is at ca. 500 cm^{-1} and the $\nu(\text{Pt-Cl})$ at ca. 300 cm^{-1}



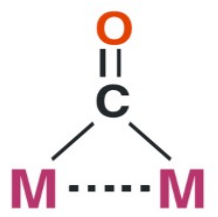
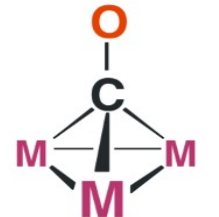
VIBRATIONAL SPECTROSCOPY APPLICATIONS

- In favorable cases vibrational spectra can be used to determine the ligand geometry around a central metal atom. This has been exploited in transition metal carbonyl chemistry.
- Simple metal carbonyl derivatives often have quite high symmetries and, equally important, a variety of possible geometric arrangements.
- The vibrational coupling of $\nu(\text{C-O})$ groups is so great-and the resulting bands so well separated-that simple group theoretical methods may often be used to distinguish between them.
- For instance, an $\text{M}(\text{CO})_3$ unit could have $\text{D}_{3\text{h}}$, $\text{C}_{3\text{v}}$ or C_s symmetries.
- These could be distinguished because they give rise to one, two and three infrared bands in the $\nu(\text{C-O})$ region, respectively.

IR SPECTROSCOPY OF ORGANOMETALLIC COMPOUNDS

■ Carbonyl Infrared (IR) Stretching Frequencies

- **Complexed CO** has a stretching frequency **lower** than that of **free CO**.
- The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the amount of **electron density** on the metal being π -backbonded to the CO.

				
	free CO	terminal mode	μ_2 - bridging	μ_3 - bridging
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500
<i>(for neutral metal complexes)</i>				

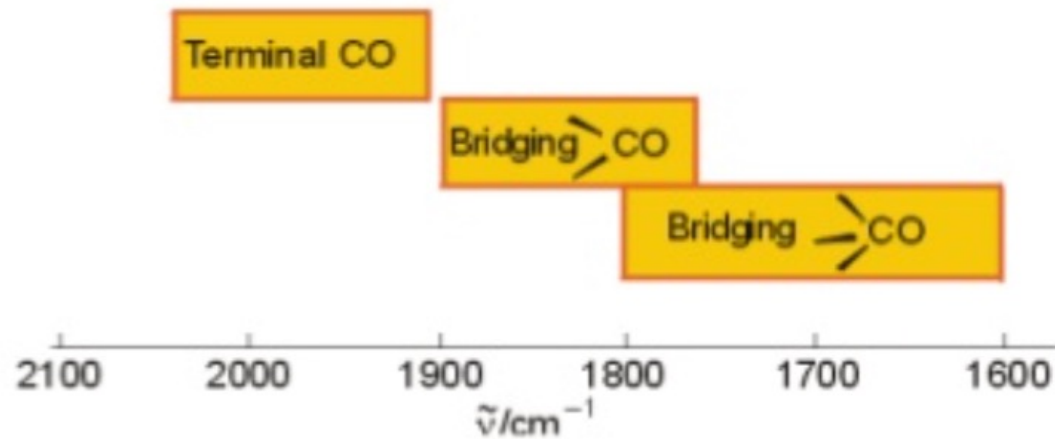
- The number (and intensity) of the carbonyl bands observed depends on:
 - ✓ the **number of CO** ligands present and,
 - ✓ the **symmetry** of the metal complex.

VIBRATIONAL SPECTROSCOPY APPLICATIONS

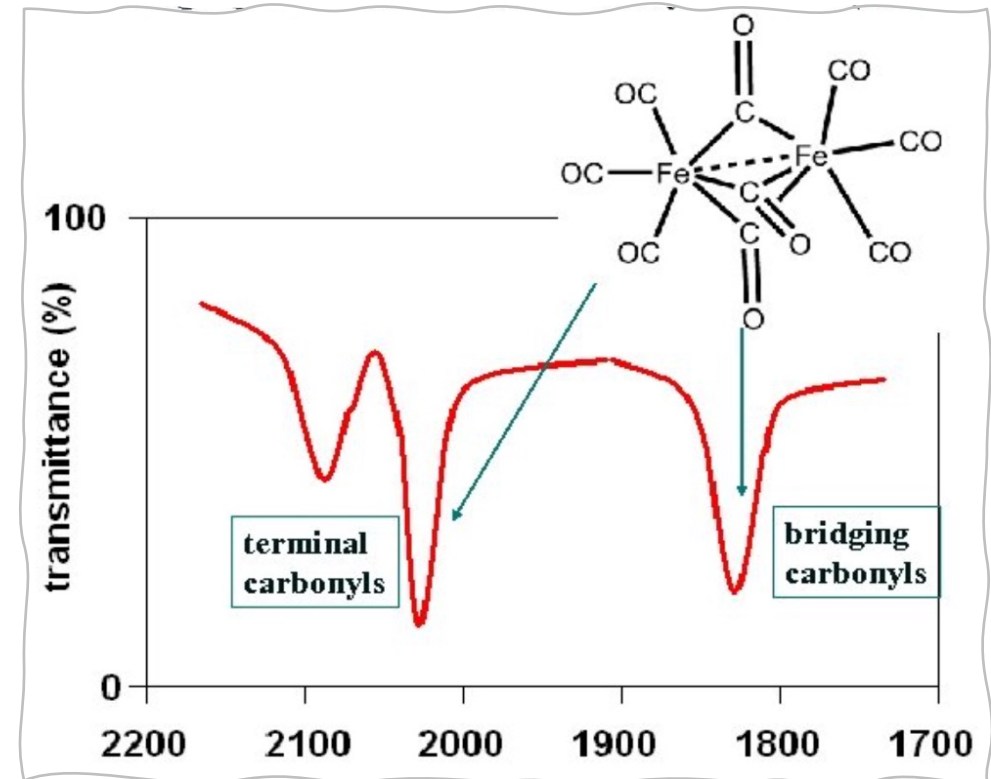
■ Carbonyl Infrared (IR) Stretching Frequencies

I. The effect of **bonding mode** of the CO (terminal, bridging):

- As the CO bridges more metal centers its stretching frequency drops, (More back donation).



- As the CO bridges more metal centers its stretching frequency drops.



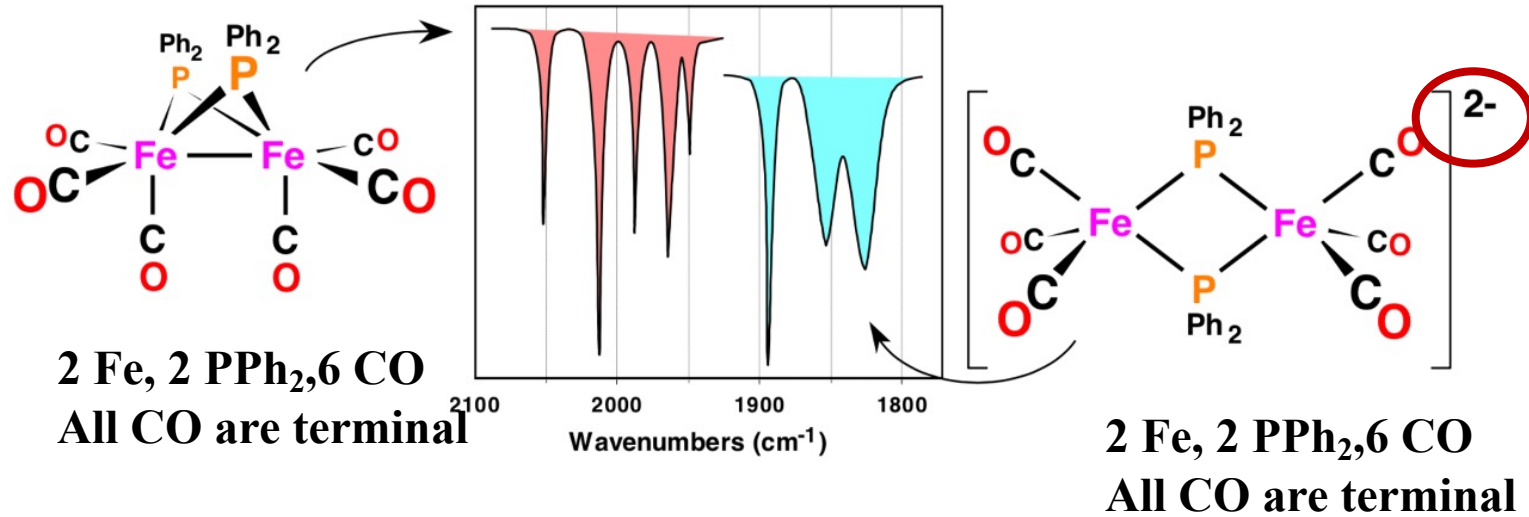
VIBRATIONAL SPECTROSCOPY APPLICATIONS

■ Carbonyl Infrared (IR) Stretching Frequencies

II. Electronic Effects on ν_{CO} :

Charge

As the metal center becomes increasingly electron rich the stretching frequency drops.



■ Trends observed in the IR spectra of carbonyl complexes:

- For simple carbonyl complexes, counting the number of IR and Raman CO stretching frequencies will often permit one to make a **structural assignment**.
- The number of CO stretches expected for possible **geometries/isomers** can be predicted using group theory and the calculated results compared to the experimental data.