

# Assignment

## INFRA RED (IR) SPECTROSCOPY



By,

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## Introduction

An important tool of the organic chemist is *Infrared Spectroscopy*, or IR. IR spectra are acquired on a special instrument, called an IR spectrometer. IR is used both to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound. IR spectra are quick and easy to run.

### The Electromagnetic Spectrum:

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Electromagnetic spectrum refers to the seemingly diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in the length and frequency, as illustrated in Figure 1.

Frequency,  $\nu$  (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength,  $\lambda$  (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related:

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu}$$

Where  $c$  is the speed of light,  $3 \times 10^{10}$  cm/sec

Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda}$$

Where

$h$  = Planck's constant,  $6.6 \times 10^{-34}$  joules-sec

Note that energy is directly proportional to frequency and inversely proportional to wavelength.

The IR region is divided into three regions: the near, mid, and far IR (see Figure 2). The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between  $3 \times 10^{-4}$  and  $3 \times 10^{-3}$  cm. Chemists prefer to work with numbers which are easy to write; therefore IR spectra are sometimes reported in  $\mu\text{m}$ , although another unit,  $\bar{\nu}$  (nu bar or *wavenumber*), is currently preferred.

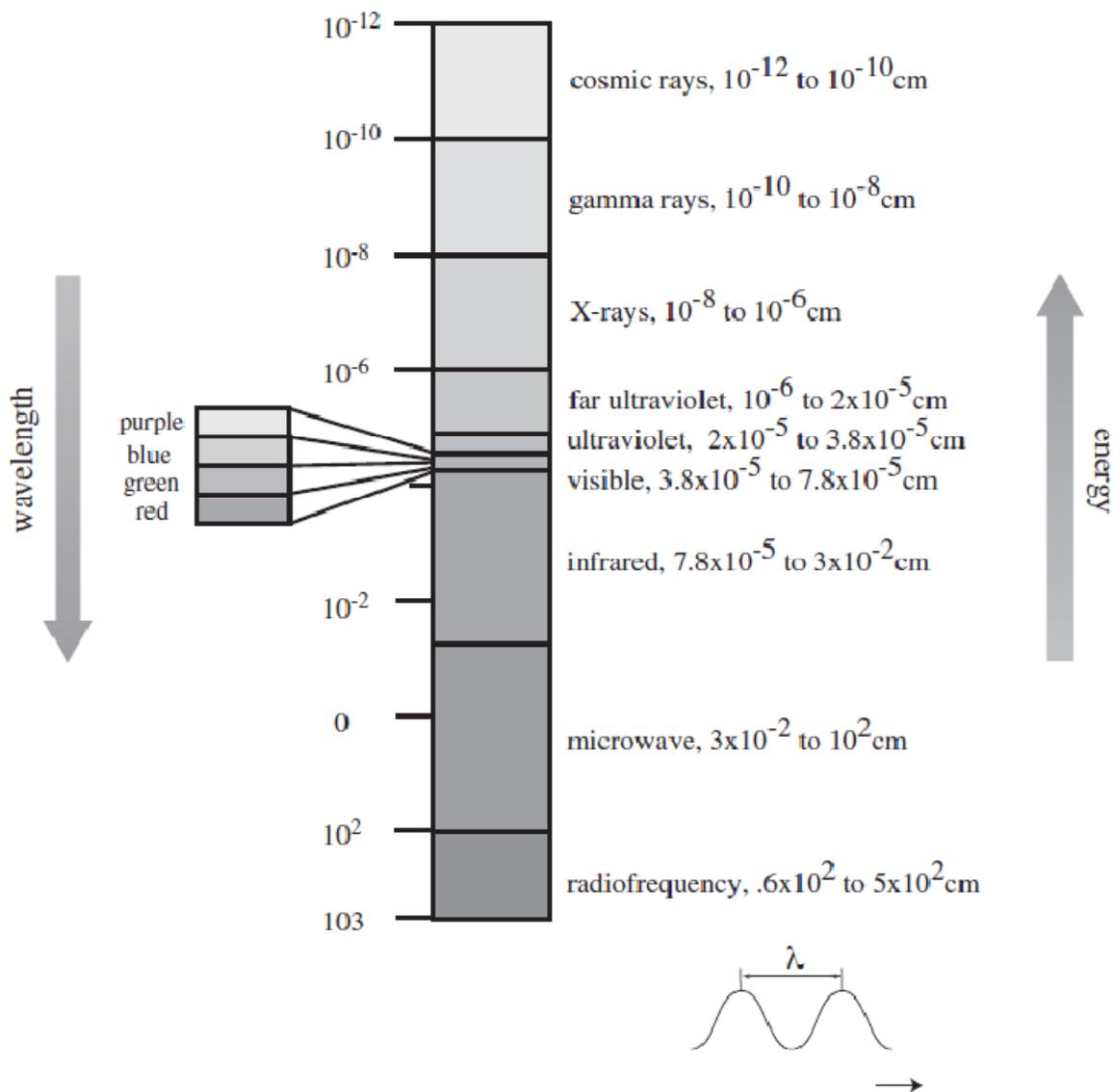


Figure 1 The electromagnetic spectrum

A wavenumber is the inverse of the wavelength in cm:

$$\bar{\nu} = \frac{1}{\lambda}$$

Where  $\nu$  is in units of  $\text{cm}^{-1}$ ,

$\lambda$  is in units of cm

and now:

$$E = hc\bar{\nu}$$

In wavenumbers, the mid IR range is  $4000\text{--}400 \text{ cm}^{-1}$ . An increase in wavenumber corresponds to an increase in energy.

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. A typical IR spectrum is shown below. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. An absorption of radiant energy is therefore represented by a “trough” in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength.

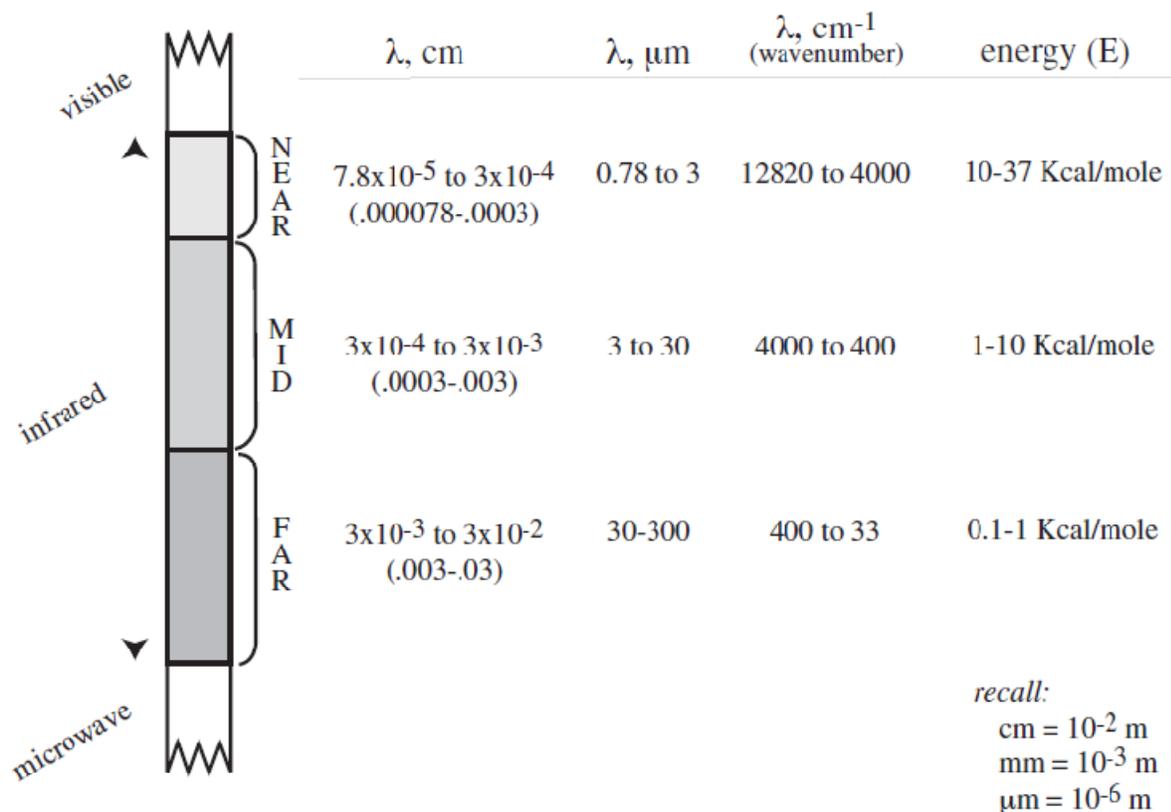


Figure:2 The IR regions of the electromagnetic spectrum

Band intensities can also be expressed as absorbance (A). Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance:

$$A = \log_{10} (1/T)$$

Note how the same spectrum appears when plotted as T and when plotted as A (Figure 3).

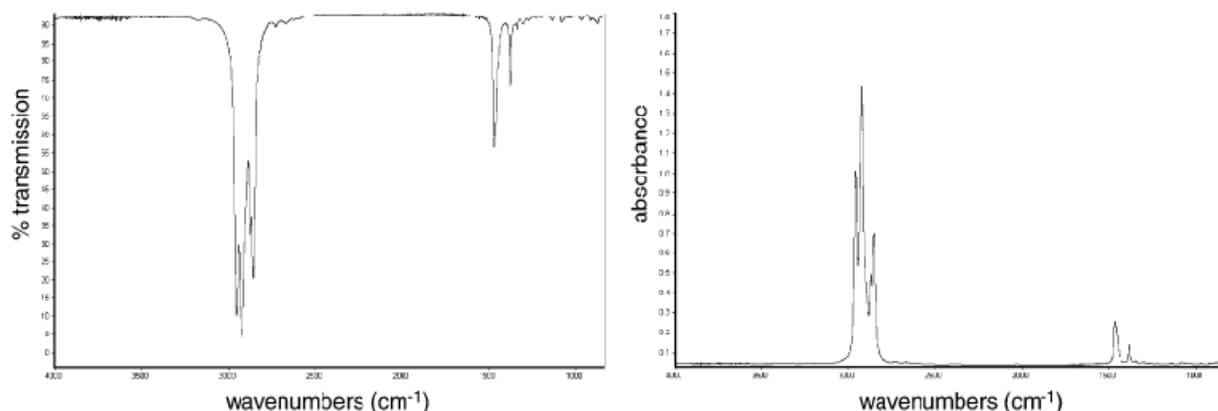


Figure 3 The IR spectrum of octane, plotted as transmission (left) and absorbance (right).

As illustrated in the spectrum of octane, even simple organic molecules give rise to complex IR spectra. Both the complexity and the wave numbers of the peaks in the spectra give the chemist information about the molecule. The complexity is useful to match an experimental spectrum with that of a known compound with a peak-by-peak correlation. To facilitate this analysis, compilations of IR spectra are available, most well-known of which are those by Sadtler and Aldrich.

The wave numbers (sometimes referred to as *frequencies*) at which an organic molecule absorbs radiation give information on functional groups present in the molecule. Certain groups of atoms absorb energy and therefore, give rise to bands at approximately the same frequencies. The chemist analyzes a spectrum with the help of tables which correlate frequencies with functional groups. The theory behind this relationship is discussed in the next section on molecular vibrations.

### **Molecular Vibrations:**

There are two types of molecular vibrations, stretching and bending. As a student of chemistry, you may have come to think of a molecule as having rigid bond lengths and bond angles, as when you work with your molecular model sets. This is not the actual case, since bond lengths and angles represent the *average* positions about which atoms vibrate.

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 correspond 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:

<i>molecule</i>	<i>degrees of freedom</i>
nonlinear	$3n - 6$
linear	$3n - 5$

Calculation reveals that a simple molecule such as propane, C<sub>3</sub>H<sub>8</sub>, has 27 fundamental vibrations, and therefore, you might predict 27 bands in an IR spectrum! (The actual number is sometimes different as discussed in part later.) The fundamental vibrations for water, H<sub>2</sub>O, are given in Figure 4. Water, which is nonlinear, has three fundamental vibrations.

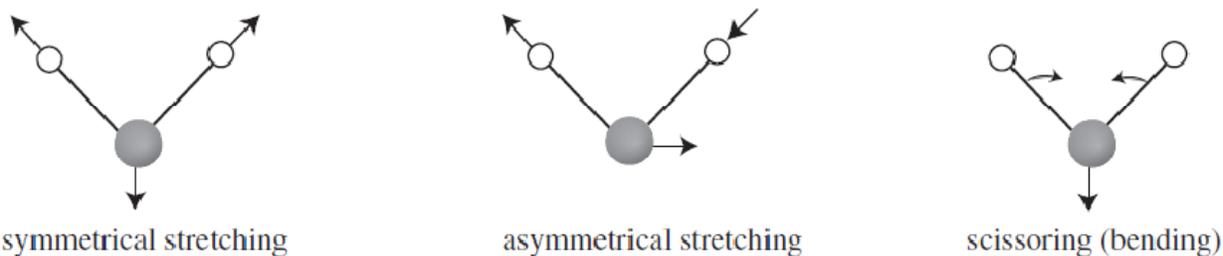


Figure 4 : Stretching and bending vibrational modes for H<sub>2</sub>O.

Carbon dioxide, CO<sub>2</sub>, is linear and hence has four fundamental vibrations (Figure 5). The asymmetrical stretch of CO<sub>2</sub> gives a strong band in the IR at 2350cm<sup>-1</sup>. You may notice this band in samples which you run on the instruments in the teaching labs, since CO<sub>2</sub> is present in the atmosphere. 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<sup>-1</sup>.

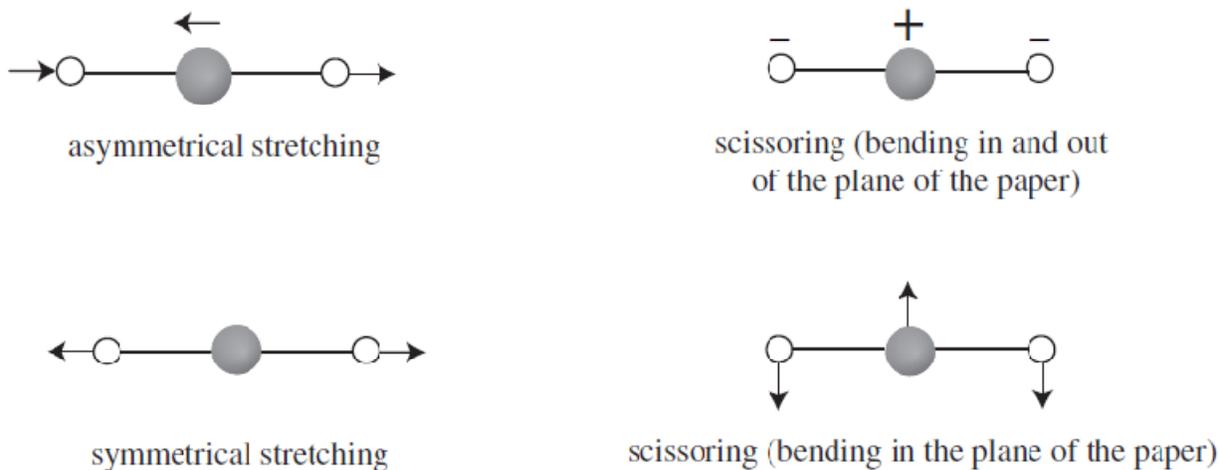
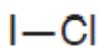


Figure 5 : Stretching and bending vibrational modes for CO<sub>2</sub>.

The symmetrical stretch of CO<sub>2</sub> is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. In order to be IR active, a vibration must cause a change in the dipole moment of the molecule. \*(The reason for this involves the mechanism by which the photon transfers its energy to the molecule, which is beyond the scope of this discussion.) Of the following linear molecules, carbon monoxide and iodine chloride absorb IR radiation, while hydrogen, nitrogen, and chlorine do not. In general, the larger the dipole change, the stronger the intensity of the band in an IR spectrum.



*absorb in IR*

*do not absorb in IR*

Only two IR bands (2350 and 666 cm<sup>-1</sup>) 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<sub>2</sub>, two bands are degenerate, and one vibration does not cause a change in dipole moment. Other reasons why fewer than the theoretical number of IR bands are seen include: an absorption is not in the 4000–400 cm<sup>-1</sup> range; an absorption is too weak to be observed; absorptions are too close to each other to be resolved on the instrument. Additional weak bands which are overtones or combinations of fundamental vibrations are observed.

The stretching and bending vibrations for the important organic group, –CH<sub>2</sub>, are illustrated in Figure 6. (The 3n–6 rule does not apply since the –CH<sub>2</sub> group represents only a portion of a molecule.) Note that bending vibrations occur at lower frequencies than corresponding stretching vibrations.

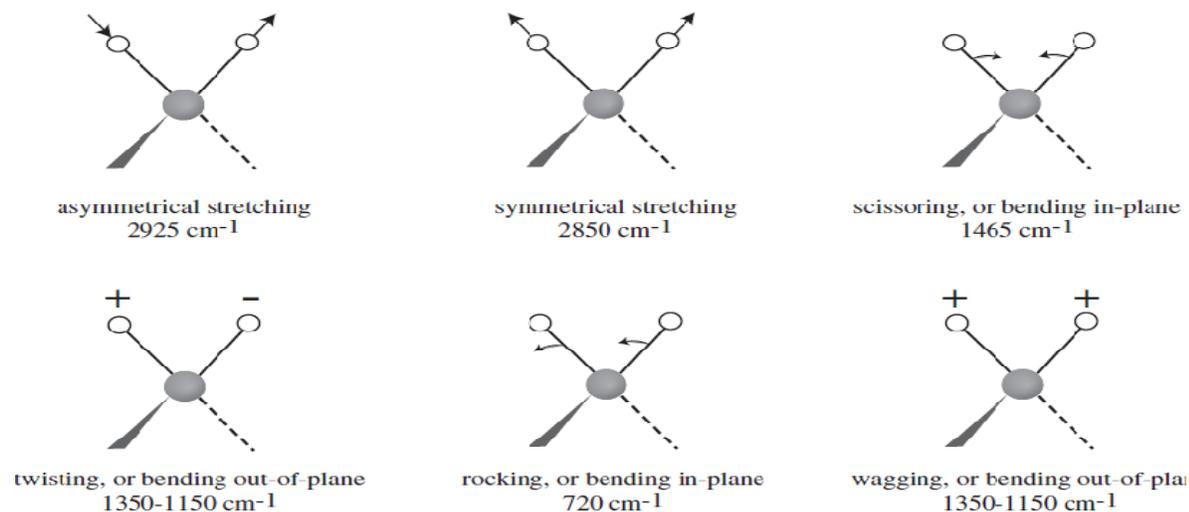
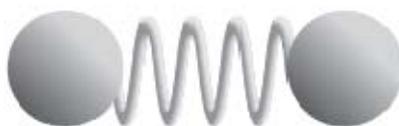


Figure 6 : Stretching and bending vibrational modes for a CH<sub>2</sub> group.

Both the stretching and bending vibrations of a molecule as illustrated in the above figures can be predicted mathematically, at least to a useful approximation, especially using computers. The mathematics of stretching vibrations will be sketched in the following section. An understanding of these vibrations can help even the beginning student correlate high and low frequencies in an IR spectrum.

## Stretching Vibrations:

The stretching frequency of a bond can be approximated by Hooke's Law. In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring:



The energy curve for a simple harmonic oscillator is illustrated in Figure 7. According to Hooke's law, the frequency of the vibration of the spring is related to the mass and the force constant of the spring,  $k$ , by the following formula:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

Where  $k$  is the force constant

$m$  is the mass

$\nu$  is the frequency of the vibration

In the classical harmonic oscillator,  $E = 1/2 kx^2 = h\nu$ , where  $x$  is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.

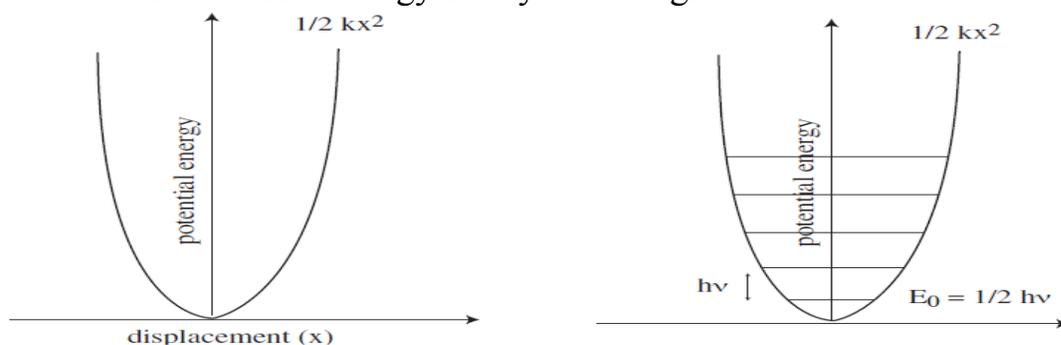


Figure 7 : Energy curve for a vibrating spring (left) and energy constrained to quantum mechanical model (right).

However, vibrational motion is *quantized*: it must follow the rules of quantum mechanics, and the only transitions which are allowed fit the following formula:

$$E = (n + 1/2)h\nu$$

where  $\nu$  is the frequency of the vibration

$n$  is the quantum number (0, 1, 2, 3, . . .)

The lowest energy level is  $E_0 = 1/2 h\nu$ , the next highest is  $E_1 = 3/2 h\nu$ . According to the selection rule, only transitions to the next energy level are allowed; therefore molecules will absorb an amount of energy equal to  $3/2 - 1/2 h\nu$  or  $h\nu$ . This rule is not inflexible, and occasionally transitions of  $2 h\nu$ ,  $3 h\nu$ , or higher are observed. These correspond to bands called overtones in an IR spectrum. They are of lower intensity than the fundamental vibration bands.

A molecule is not just two atoms joined on a spring, of course. A bond can come apart, and it cannot be compressed beyond a certain point. A molecule is actually an *anharmonic* oscillator. As the inter atomic distance increases, the energy reaches a maximum, as seen in Figure 8. Note how the energy levels become more closely spaced with increasing inter atomic distance in the anharmonic oscillator. The allowed transitions,  $h\nu$ , become smaller in energy. Therefore, overtones can be lower in energy than predicted by the harmonic oscillator theory.

The following formula has been derived from Hooke's law. For the case of a diatomic molecule, ( $\nu$  has been substituted for  $\nu$ , recall that  $\nu = c\nu$  from equations:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$

where

$\bar{\nu}$  is the vibrational frequency (cm<sup>-1</sup>)

$m_1$  and  $m_2$  are the mass of atoms 1 and 2, respectively, in g

$c$  is the velocity of light (cm/s)

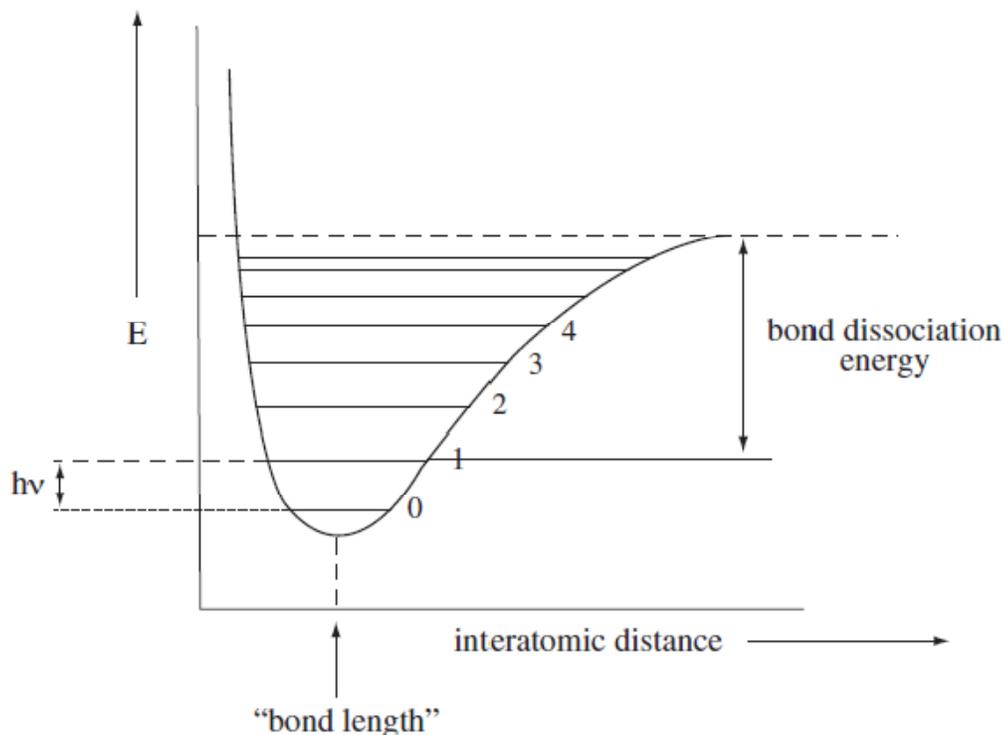


Figure 8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

$f$  is the force constant of the bond (dyne/cm)

Equation shows the relationship of bond strength and atomic mass to the wavenumber at which a molecule will absorb IR radiation. As the force constant increases, the vibrational frequency (wavenumber) also increases. The force constants for bonds are:

single bond  $5 \times 10^5$  dyne/cm  
 double bond  $10 \times 10^5$  dyne/cm  
 triple bond  $15 \times 10^5$  dyne/cm

As the mass of the atoms increases, the vibration frequency decreases. Using the following mass values:

C, carbon  $12/6.02 \times 10^{23}$   
 H, hydrogen  $1/6.02 \times 10^{23}$

$\nu$  for a C–H bond is calculated to be  $3032 \text{ cm}^{-1}$ . (Try this calculation!) The actual range for C–H absorptions is  $2850\text{--}3000 \text{ cm}^{-1}$ . The region of an IR spectrum where bond stretching vibrations are seen depends primarily on whether the bonds are single, double, or triple or bonds to hydrogen. The following table shows where absorption by single, double, and triple bonds are observed in an IR spectrum. You

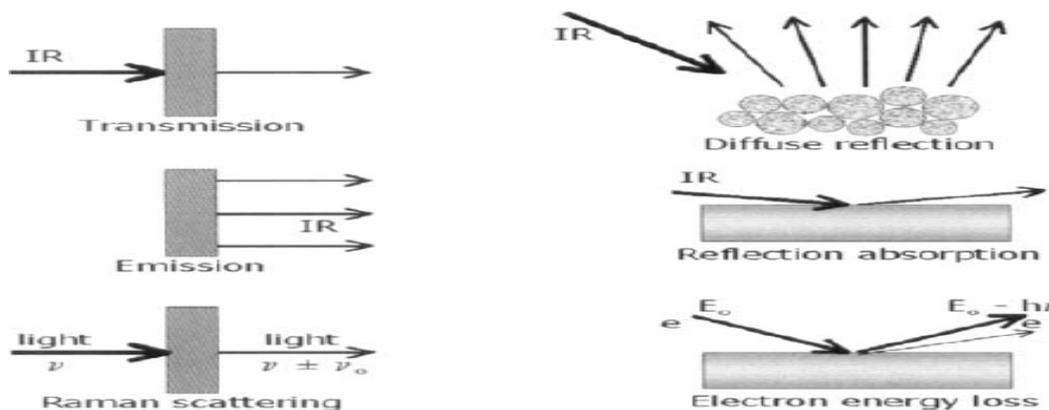
should try calculating a few of these values to convince yourself that the Hooke's law approximation is a useful one.

<i>bond</i>	<i>absorption region, cm<sup>-1</sup></i>
C-C, C-O, C-N	800-1300
C=C, C=O, C=N, N=O	1500-1900
C=C, C=N	2000-2300
C-H, N-H, O-H	2700-3800

Although a useful approximation, the motion of two atoms in a large molecule cannot be isolated from the motion of the rest of the atoms in the molecule. In a molecule, two oscillating bonds can share a common atom. When this happens, the vibrations of the two bonds are coupled. As one bond contracts, the other bond can either contract or expand, as in asymmetrical and symmetrical stretching. In general, when coupling occurs, bands at different frequencies are observed, instead of superimposed (or degenerate) bands as you might expect from two identical atoms in a bond vibrating with an identical force constant. In the case of the -CH<sub>2</sub> group in Figure 6, you note there are two bands in the region for C-H bonds: 2926 cm<sup>-1</sup> and 2853 cm<sup>-1</sup>.

### Infrared Spectroscopy in Catalysis

Several forms of infrared spectroscopy are in use, as illustrated in Fig.9. The most common form of the technique is transmission infrared spectroscopy. In this case the sample consists typically of 1S100 mg of catalyst, pressed into a self-supporting disk of approximately 1 cm<sup>2</sup> and a few tenths of a millimeter in thickness. Transmission IR can be applied if the bulk of the catalyst absorbs weakly. This is usually the



**Fig:9** Six different ways to perform vibrational spectroscopy.

case with typical oxide supports for frequencies above about 1000 cm<sup>-1</sup>, whereas carbon-supported catalysts cannot be measured in transmission mode. Another condition is that the support particles should be smaller than the wavelength of the IR radiation, otherwise scattering losses become important.

A great advantage of infrared spectroscopy is that the technique can be used to study catalysts *in situ*. Several cells for *in situ* investigations have been described in the literature. The critical point is the construction of infrared-transparent windows that withstand high temperatures and pressures. In the diffuse reflectance mode, samples can be measured as loose powders, with the advantages that not only is the tedious preparation of wafers unnecessary but also diffusion limitations associated with tightly pressed samples are avoided. Diffuse reflectance is also the indicated technique for strongly scattering or absorbing particles. The often-used acronyms DRIFT or DRIFTS stand for diffuse reflectance infrared Fourier transform spectroscopy. The diffusely scattered radiation is collected by an ellipsoidal mirror and focussed on the detector. The infrared absorption spectrum is described the Kubelka-Munk function:

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

in which

K is the scattering coefficient

S is the absorption coefficient, a function of the frequency  $\nu$

$R_{\infty}$  is the reflectivity of a sample of infinite thickness, measured as a function of  $\nu$ .

If the scattering coefficient does not depend on the infrared frequency, the Kubelka-Munk function transforms the measured spectrum  $R_{\infty}(\nu)$  into the absorption spectrum  $K(\nu)$ . In *situ* cells for DRIFT studies of catalysts have been described and are commercially available.

Measurements of supported catalysts in diffuse reflection and transmission mode are in practice limited to frequencies above those where the support absorbs (below about 1250 cm<sup>-1</sup>). Infrared Emission Spectroscopy (IRES) offers an alternative in this case. When a material is heated to about 100 °C or higher, it emits a spectrum of infrared radiation in which all the characteristic vibrations appear as clearly recognizable peaks. Although measuring in this mode offers the attractive advantage that low frequencies such as those of metal-oxygen or sulfur-sulfur bonds are easily accessible, the technique has hardly been explored for the purpose

of catalyst characterization. An *in situ* cell for IRES measurements and some experiments on Mo-O-S clusters of interest for hydrodesulfurization catalysts have been described by Weber et al.

For measuring infrared absorption spectra of gases adsorbed on the surfaces of metal single crystals or polycrystalline foils, one uses reflection absorption infrared spectroscopy (RALRS), sometimes also referred to as infrared reflection absorption spectroscopy (IRAS). In RAIRS, the IR beam comes in at grazing angle, i.e. almost parallel to the surface (see Fig. 9). During reflection the p-component of the IR light (the component perpendicular to the surface) excites those vibrations of the chemisorbed molecule for which the component of the dipole moment perpendicular to the surface changes. This rather strict metal surface selection rule is typical for RAIRS. Although absorption bands in RAIRS have intensities that are some two orders of magnitude weaker than in transmission studies on supported catalysts, RAIRS spectra can be measured accurately with standard spectrometers.

## **Equipment:**

The first generation of infrared spectrometers was of the energy-dispersive type. Here, a monochromator (initially a prism; after the mid 1960s a grating) selects the wavelength of interest from the continuum emitted by the infrared source, and the transmission corresponding to that particular frequency by the sample can be measured. Now-a-days, energy-dispersive instruments have largely been abandoned in favor of Fourier-Transform Infrared (FTIR) spectrometers operating on the principle of the Michelson interferometer. These instruments have the great advantage that the entire spectrum is obtained for each scan the interferometer makes, with the result that the total collection time needed to measure a spectrum is much lower. The treatment of the Fourier transform technique is referred to the literature.

Optical components can be made of NaCl, transparent from 650 to 4000  $\text{cm}^{-1}$ , KBr, with a low energy cut-off of 400  $\text{cm}^{-1}$ , or CsI, with an even more favorable cutoff of 200  $\text{cm}^{-1}$ . The source is usually a temperature-stabilized ceramic filament operating around 1500 K. The detector may be a slowly reacting thermocouple in energy-dispersive instruments, but has to be a fast response device in FTIR. The standard for routine applications is the deuterium triglycine sulphate or DTGS detector, while the liquid-nitrogen-cooled mercury cadmium telluride or MCT

detector is used for more demanding applications, as for example in RALRS.

## Applications:

Carbon monoxide on metals forms the best-studied adsorption system in vibrational spectroscopy. The strong dipole associated with the C-O bond makes this molecule a particularly easy one to study. Moreover, the C-O stretch frequency is very informative about the direct environment of the molecule. The metal-carbon bond, however, falling at frequencies between  $300$  and  $500\text{ cm}^{-1}$ , is more difficult to measure with infrared spectroscopy. First, its detection requires special optical parts made of CsI, but even with suitable equipment the peak may be invisible because of absorption by the catalyst support. In reflection experiments on single crystal surfaces the metal-carbon peak is difficult to obtain because of the low sensitivity of RAIRS at low frequencies.

The C-O stretch frequency is often an excellent indicator of the way CO binds to the substrate. Linearly adsorbed CO absorbs at frequencies between  $2000$  and  $2130\text{ cm}^{-1}$ , twofold or bridge-bonded CO between  $1880$  and  $2000\text{ cm}^{-1}$ , threefold CO between  $1800$  and  $1880\text{ cm}^{-1}$  and finally fourfold bonded CO at frequencies below  $1800\text{ cm}^{-1}$ . The precise absorption frequency depends on the substrate metal, its surface structure and, importantly, the CO coverage. The latter dependence is due to mutual interactions between the dipoles of the CO molecule, with the effect that the CO stretch frequency increases with increasing coverage. The presence of dipole coupling effects can be investigated by using mixtures of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ , because there is no resonance between the dipoles of the isotopes. For reviews we refer to Hollins and Pritchard.

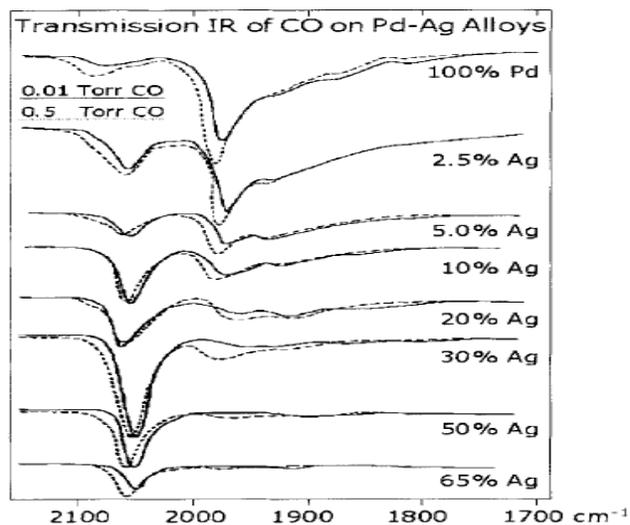
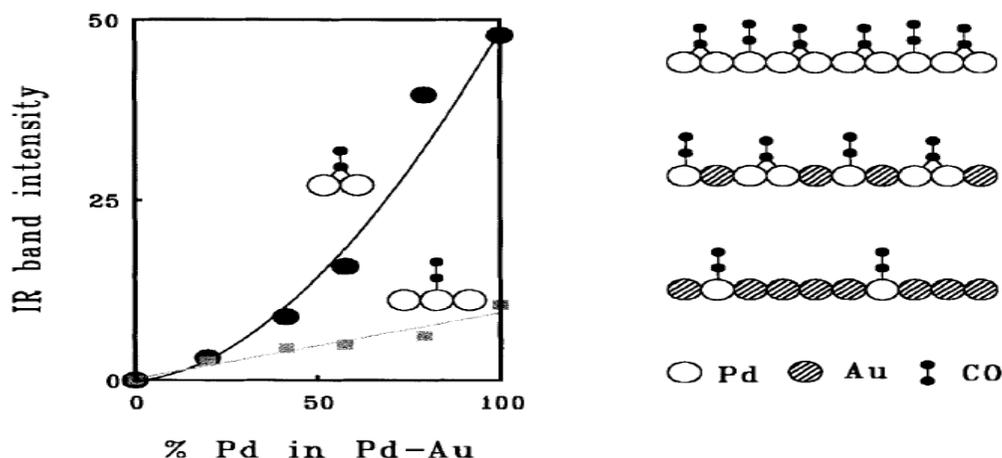


Fig: 10 Transmission infrared spectra of CO adsorbed at room temperature on a series of silica-supported Pd-Ag alloys. CO adsorption on Ag is negligible. The dashed spectra are for higher CO exposures (0.5 Torr), the full spectra for low exposures (0.01 Torr). On pure Pd, CO adsorbs predominantly on multiple sites (frequencies below 2000  $\text{cm}^{-1}$ ). As Pd becomes diluted with Ag, linearly bonded CO becomes dominant, indicating that ensembles of two or more Pd atoms to accommodate multiply bonded CO are no longer present.

Soma-Noto and Sachtler reported an infrared investigation of CO adsorbed on silica-supported Pd-Ag alloys; some of their spectra are shown in Fig. 10. On pure palladium, CO adsorbs mainly in a twofold position, evidenced by the intense peak around 1980  $\text{cm}^{-1}$ , although some CO appears to be present in threefold and linear geometries as well. This is a common feature in adsorption studies on supported catalysts, where particles exhibit a variety of surface planes and defects. Addition of Ag to Pd leads to a pronounced increase in the fraction of linearly adsorbed CO, which is the dominant species in Pd-Ag alloy particles with 30% Ag or more.

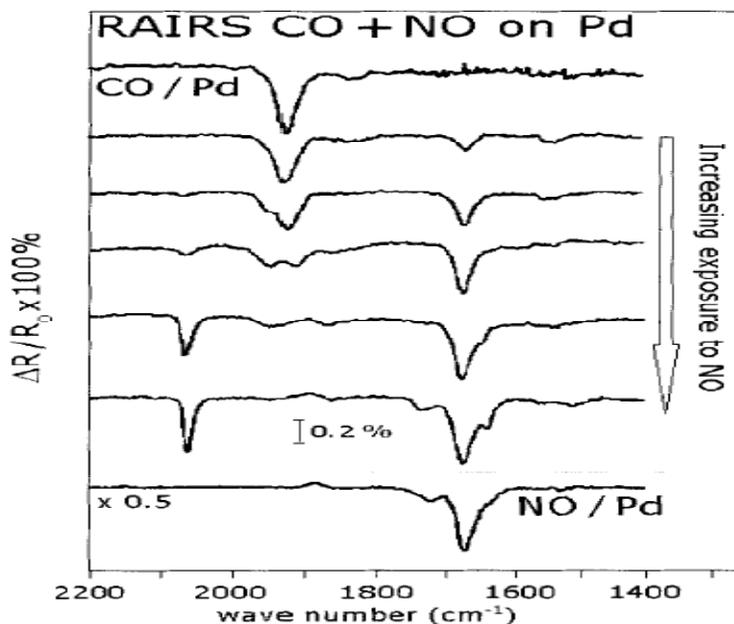
Note that the absorption frequencies themselves do not shift significantly. The results are easily explained by the so-called ensemble effect, without the need to invoke a major electronic effect of Ag on Pd: incorporation of Ag into the Pd lattice rapidly decreases the fraction of Pd ensembles with atoms in the correct geometry for twofold adsorption of CO, leaving linear adsorption on single Pd atoms as the only alternative.

Experiments with CO adsorption on Ni-Cu/SiO<sub>2</sub> and Pd-Au/SiO<sub>2</sub> catalysts gave very similar results. In the latter, two CO absorption bands were also seen, one at around 1900  $\text{cm}^{-1}$ , assigned to bridge-bonded CO and another at 2070  $\text{cm}^{-1}$ , characteristic of linear CO on single Pd atoms. Figure.11 shows the intensities of the two bands as a function of Pd content in the Pd-Au alloys. The almost quadratic



**Fig:11** intensities of the CO bands of linear and bridged CO on Pd-Au alloys, as a function of Pd content. The almost parabolic fit to the intensities for CO in twofold positions reflects the probability of finding two adjacent Pd atoms in the Pd-Au surface (data from Kugler and Boudart). Right: schematic illustration of how alloying destroys ensembles of Pd where CO adsorbs in the twofold position.

increase of the twofold CO intensity reflects the probability of finding two adjacent Pd atoms at the surface of the alloy particles. The intensity of linearly adsorbed CO



**Fig: 12 RAIRS** spectra show that lateral interactions force CO to leave the twofold adsorption sites on palladium (IR frequency of about 1920 cm<sup>-1</sup>) when NO is coadsorbed, and push it to the on top site (adsorption frequencies above 2000 cm<sup>-1</sup>). Adsorbed NO gives rise to the absorption peaks below 1800 cm<sup>-1</sup> (from Raval et al.)

is more or less proportional to the Pd concentration, as would be expected for adsorption on single Pd atoms.

Accurate analysis of the band positions revealed another interesting point. Whereas the frequency of linear CO on pure Pd increases substantially from 2070 to 2095 cm<sup>-1</sup> with increasing CO coverage due to dipole-dipole interactions between adjacent molecules, the frequencies of linear CO on the alloys increased much less with coverage. Kugler and Boudart took this as evidence for a small ligand effect of Au on Pd. However, Toolenaar *et al.*, observing similar phenomena in infrared spectra of CO on Pt-Cu alloys, proved that the lower frequencies of linear CO on

the alloy were caused by diminished dipole-dipole coupling between adsorbed CO molecules, which necessarily form less dense overlayers on alloys than on pure **Pt**. Thus the ensemble effect, illustrated schematically in Fig.12, provides an entirely geometric explanation for the variation of both intensities and peak positions in infrared spectra of CO on alloy surfaces.

The surface composition and the availability of certain adsorption sites are not the only factors that determine how CO binds to the surface. Interactions between CO and coadsorbed molecules play an important part as well. A RARS study by Raval *et al.* shows how NO forces CO to leave its favored binding site on palladium (see Fig.12). When only CO is present, it occupies the twofold bridge site, as the IR frequency of about 1930  $\text{cm}^{-1}$  indicates. However, if NO is coadsorbed, CO leaves the twofold site and ends up in a linear mode with a frequency of approximately 2070  $\text{cm}^{-1}$ . Raval and coworkers attribute the move of adsorbed CO to on-top sites to the electrostatic repulsion between negatively charged NO and CO, which decreases the back donation of electrons from the substrate into the  $2\pi^*$  orbitals of CO.

The use of infrared spectroscopy of adsorbed molecules to probe oxide surfaces has been reviewed by Davydov and Rochester. This approach works on sulfide catalysts as well. The infrared signal of NO has been successfully used to identify sites on the surface of a hydrodesulfurization catalyst, as the following example shows.

Sulfided Mo and Co-Mo catalysts, used in hydrotreating reactions, contain Mo as MoS<sub>2</sub>. This compound has a layer structure consisting of sandwiches, each of Mo layer between two S layers. The chemical activity of MoS<sub>2</sub> is associated with the

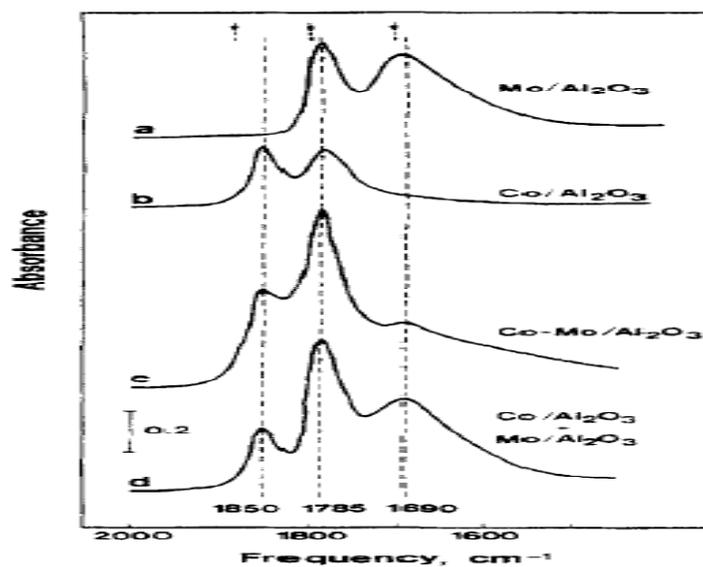


Fig:13 Infrared spectra of NO probe molecules on sulfided Mo, Co, and Co-Mo hydrodesulfurization catalysts. The peak assignments are supported by the **IR** spectra of organometallic model compounds. **These** spectra allow for a quantitative titration of Co and Mo sites in the Co-Mo catalyst (from Topsoe and Topsoe).

edges of the sandwich where Mo can be exposed to the gas phase; the basal plane of the S<sup>2-</sup> anions is largely unreactive. The infrared spectrum of NO on a sulfided Mo/A1203 catalyst (Fig. 13a) shows two peaks at frequencies which agree with those observed in organometallic clusters of Mo and NO groups. NO on sulfided Co/A1203 gives rise to two infrared peaks (Fig. 13b), but at different frequencies from those observed on MoS<sub>2</sub>. These results suggest that NO can be used as a probe to titrate the number of Co and Mo sites in the Co-Mo/A1203 catalyst. Figure 13c confirms that this idea works. Moreover, comparison of the intensities of the NO/Mo infrared signals on Mo/A1203 and Co-Mo/A1203 reveals that the presence of cobalt decreases the number of molybdenum atoms that are accessible to NO. This means that cobalt most probably decorates the edges of the MoS<sub>2</sub> sandwiches, because the edges constitute the adsorption sites for NO.

Transmission infrared spectroscopy is an important tool in catalyst preparation to study the decomposition of infrared-active catalyst precursors as a result of drying, calcination or reduction procedures. In particular, if catalysts are prepared from organometallic precursors, infrared spectroscopy is the indicated technique for investigation.

Hydroxyl groups on the surface of oxidic supports are extremely important in

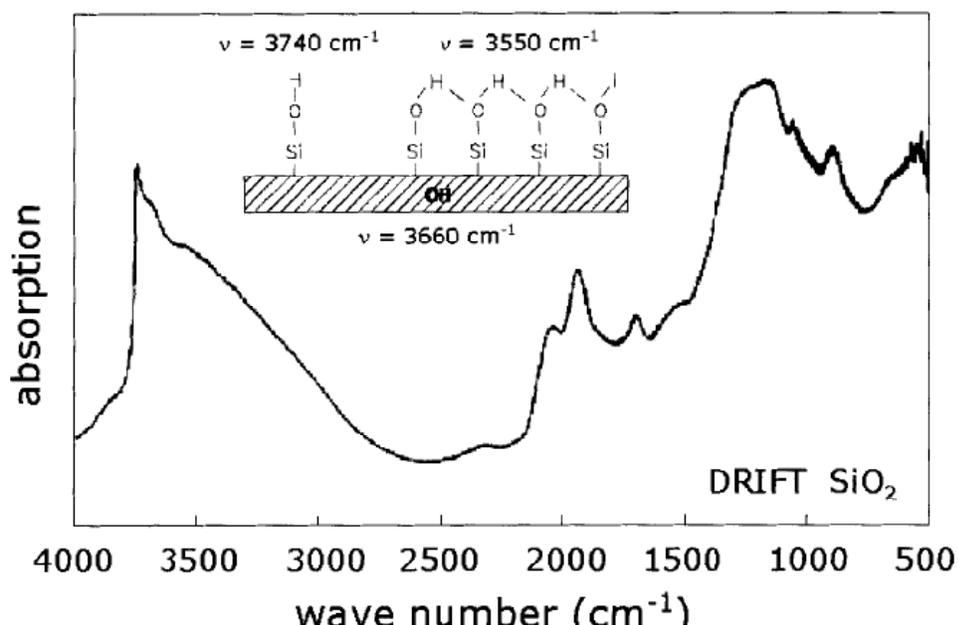


Fig:14 Diffuse reflectance infrared spectrum of a silica support, showing silica vibrations at frequencies below  $1300\text{ cm}^{-1}$ , overtones and combination bands between  $1700$  and  $2050\text{ cm}^{-1}$ , and various hydroxyl groups at frequencies above  $3000\text{ cm}^{-1}$ . The sharp peak at  $3740\text{ cm}^{-1}$  is due to isolated OH groups, the band around  $3550\text{ cm}^{-1}$  to paired, H-bonded OH groups, and the band around  $3660\text{ cm}^{-1}$  to hydroxyls inside the silica (courtesy of R.M. van Hardeveld, Eindhoven).

catalyst preparation, because they provide sites where catalyst precursors may anchor to the support. These OH groups may possess positive, zero or negative charge and are called acidic, neutral or basic, respectively. In solution these groups exchange with metal ion complexes ( $\text{OH}^-$  with a negative ion complex,  $\text{H}^+$  with a cation) or they provide sites where ions of opposite charge adsorb by electrostatic interaction. The different hydroxyls can be distinguished by their infrared spectra. Mestl and Knozinger presented an extensive overview of hydroxyls on various oxide surfaces along with vibrational frequencies.

Figure 14 shows the DRIFT spectrum of hydroxyls on a silica support. The spectrum is dominated by the intense bands of the  $\text{SiO}_2$  at frequencies below  $1300\text{ cm}^{-1}$ , while overtones and combination bands are visible up to  $2050\text{ cm}^{-1}$ . The hydroxyl range between  $3000$  and  $3800\text{ cm}^{-1}$  contains contributions from adsorbed water and several hydroxyl groups on the  $\text{SiO}_2$  surface. The broad absorption band around  $3550\text{ cm}^{-1}$  is due to hydrogen-bonded OH groups. The sharp peak at  $3740\text{ cm}^{-1}$  corresponds to single OH groups that have no interaction with other hydroxyls. The peak around  $3660\text{ cm}^{-1}$  is thought to belong to OH groups inside the silica, because unlike the other OH signals it is not affected by exposing the sample to heavy water,  $\text{D}_2\text{O}$ . Similar correlations exist for the O-H stretch frequencies of OH groups on alumina and titania supports.

In catalyst preparation, one can use this knowledge to determine the relative contributions of various hydroxyl groups before and after application of the active phase onto the support. In this way Sibeijn et al. established that rhenium oxide attached to acidic sites of the alumina support exhibits higher activity for the metathesis of olefins than rhenium oxide on neutral or basic sites. As, however, rhenium species preferentially exchange with basic hydroxyls, one needs to increase the loading above a certain value (6 wt% for an alumina of  $200\text{ m}^2/\text{gram}$ ) before the catalyst exhibits appreciable activity.

Note that in all the examples discussed so far, infrared spectroscopy gives its information on the catalyst in an indirect way, via hydroxyl groups on the support, or via the adsorption of probe molecules such as CO and NO. The reason why it is

often difficult to measure the metal-oxide or metal-sulfide vibrations of the catalytically active phase in transmission infrared spectroscopy is that the frequencies are well below  $1000\text{ cm}^{-1}$ , where measurements are difficult because of absorption by the support.

## Case Studies in Catalyst Characterization

### Disintegration of Rhodium Particles under CO:

The state of a given small particle in a catalyst depends on the composition of the surrounding gas atmosphere, the temperature and the pressure. A rather extreme illustration is provided by the disintegration of rhodium particles in CO.

Infrared spectra of CO chemisorption on rhodium usually give the well-known peaks for the linear and bridged CO stretching modes at about  $2070$  and  $1900\text{ cm}^{-1}$ , respectively. However, when rhodium particles are well dispersed, two additional bands arise at approximately  $2090$  and  $2030\text{ cm}^{-1}$ . These are characteristic of the symmetric and asymmetric stretching modes of the rhodium gem-dicarbonyl (gem comes from Gemini, meaning twins), in which two CO molecules are bound to an Rh ion with a formal oxidation state of  $1+$ . Coordination chemistry provides an analog in the complex  $[\text{Rh}^+(\text{CO})_2\text{C}_1]_2$ , in which the two supported rhodium catalyst during heating in CO, as reported by Knozinger. The spectrum at  $80\text{ K}$  contains the bands of linear CO at  $2078\text{ cm}^{-1}$  and bridged CO at  $1915\text{ cm}^{-1}$ , as well as peaks associated with physically adsorbed and of the rhodium ions are

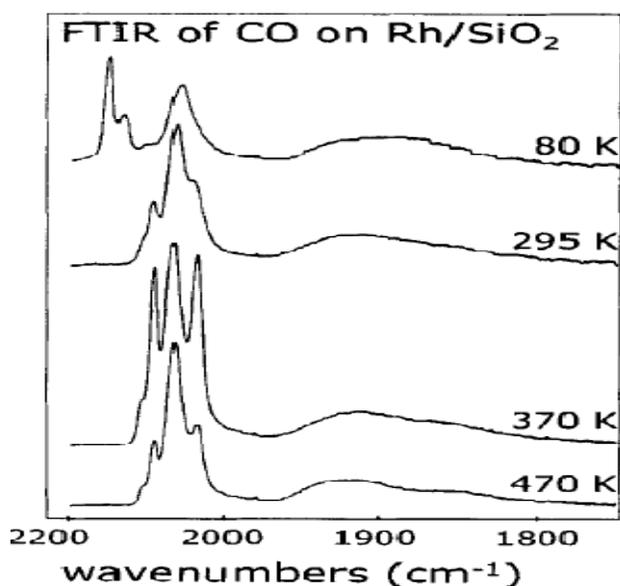


Fig:15 Infrared spectra of CO adsorbed on a well-dispersed Rh/SiO<sub>2</sub> catalyst at 80 K, 295 K, 370 K and 470 K. The spectra show the peaks of linear and bridged CO at 2078 and 1908 cm<sup>-1</sup>, and the bands of the gem-dicarbonyl species at 2098 and 2030 cm<sup>-1</sup>, respectively. The bands above 2100 cm<sup>-1</sup> in the spectrum at 80 K are due to physisorbed and H-bonded CO (from Kniizinger).

connected by two C1 bridges. Figure 15 shows the occurrence gem-dicarbonyl species in a silica-hydrogen-bonded CO at higher frequencies. The latter species disappear and the dicarbonyl bands develop when the catalyst is brought to room temperature under CO, implying that the reactions leading to dicarbonyl formation form an activated process. The important question is in what state is the rhodium in catalysts for which infrared spectroscopy indicates the presence of the dicarbonyl. Van't Blik et al. exposed a highly dispersed 0.57 wt% Rh/A1203 catalyst (H/M=1.7) to CO at room temperature and measured a CO uptake of 1.9 molecules of CO per Rh atom. Binding energies for the Rh 3d5n XPS peak increased from 307.5 eV for the reduced catalyst under H<sub>2</sub> to 308.7 eV for the catalyst under CO. The latter value equals that of the [Rh<sup>+</sup>(CO)<sub>2</sub>Cl]<sub>2</sub> complex, in which rhodium occurs as a Rh<sup>+</sup> ion.

The infrared spectrum of the Rh/A1203 catalyst under CO showed exclusively the gem-dicarbonyl peaks at 2095 and 2023 cm<sup>-1</sup>. All results point to the presence of rhodium in Rh<sup>+</sup>(CO)<sub>2</sub> entities.

However, how can a rhodium particle accommodate so much CO?

Rhodium K-edge EXAFS spectra (see Fig. 16) indicate that the structure of the rhodium particles changes entirely after CO chemisorption. The rapid decrease of the EXAFS wiggles with increasing wave vectors is typical of coordination by light elements such as oxygen. The Fourier transform of the reduced catalyst shows the contribution of rhodium neighbors, and of oxygen ions in the metal-support interface. The Fourier transform of the catalyst under CO is entirely different. The contribution from rhodium neighbors has disappeared; instead, contributions arise that are consistent with carbon (labeled A in Fig. 16), oxygen from CO (labeled C) and a second oxygen (B) from the support. The latter is at 0.21 nm, a distance characteristic of an ionic Rh-O pair, and has a coordination number equal to three. The conclusion from the EXAFS is that the rhodium particle has disintegrated under CO to mononuclear Rh<sup>+</sup>(CO)<sub>2</sub> complexes that coordinate to three oxygen ions of the support.

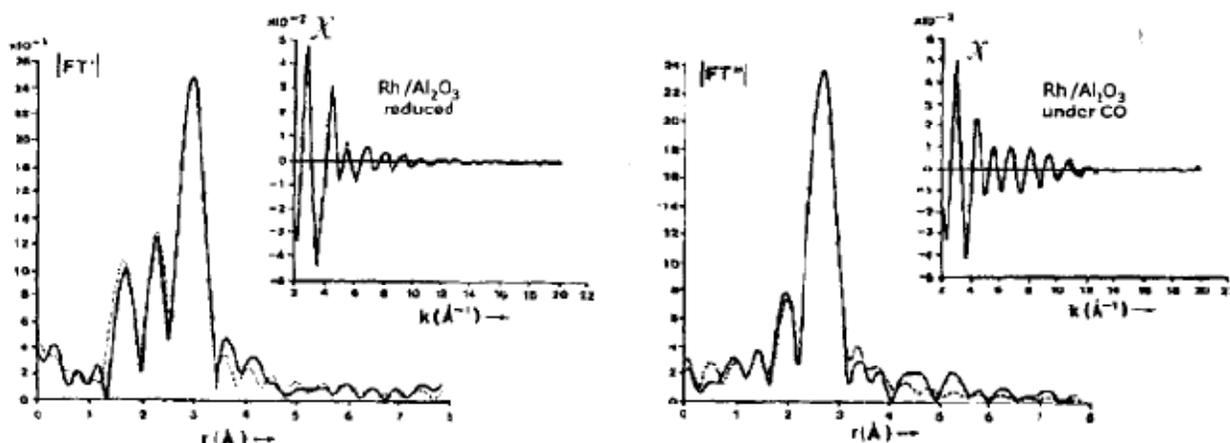
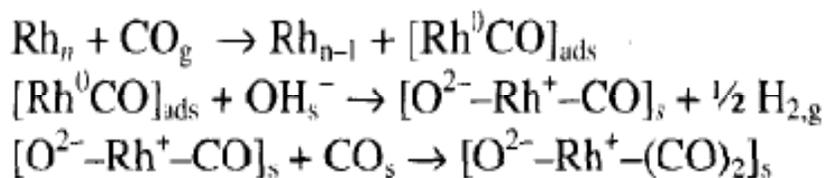


Fig: 16 EXAFS spectra and Fourier transforms of a highly dispersed Rh/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction (left) and after exposure to CO at room temperature (*right*; Courtesy of H.F.J. van't Blik, Eindhoven).

The driving force for the disruption of the particles is the strength of the Rh-CO bond, which with its energy of about 145 kJ/mol is stronger than the 121 kJ/mol of the Rh-Rh bond in metallic rhodium. With respect to the mechanism of the disintegration, Basuet al. presented infrared evidence that surface hydroxyl groups are involved:



Where Rh<sub>n</sub> is a rhodium particle, and the subscripts s, ads, and g stand for support, adsorbed and gas phase, respectively. Thus, the disruption of the Rh<sub>n</sub> particle is caused by the formation of a mononuclear, neutral rhodium carbonyl, which is subsequently oxidized by a hydroxyl group on the support. The first reaction is thought to proceed on coordinatively highly unsaturated rhodium atoms only, which would explain why the disintegration of rhodium has only been observed on highly dispersed particles. CO adsorption on the surface of larger particles is accompanied by adsorption energies that are significantly smaller than the Rh-CO bond energies of carbonyls, implying that the activation energy for particle disintegration becomes high.

## Remarks:

The studies discussed above deal with highly dispersed and therefore well-defined rhodium particles with which fundamental questions on particle shape, chemisorptions and metal-support interactions can be addressed. Practical rhodium catalysts, for example those used in the three-way catalyst for reduction of NO by CO, have significantly larger particle sizes. Such particles have also been extensively characterized with spectroscopic techniques and electron microscopy; These studies deal with the materials science of rhodium catalysts that are closer to the ones used in practice, which is of great interest from an industrial point of view.

## Conclusion

Infrared spectroscopy measures, in principle, force constants of chemical bonds. It is a powerful tool in the identification of adsorbed species and their bonding mode. Infrared spectroscopy is an in situ technique, which is applicable in transmission or diffuse reflection mode on real catalysts, and in reflection absorption mode on single crystal surfaces. Sum frequency generation is a specialty which focusses exclusively on interfaces and offers great opportunities to study adsorbates on catalytic surfaces under high-pressure conditions.

- Integrated approach from catalysis and spectroscopy, in which experts in both fields cooperate closely. This ensures that the spectroscopist investigates catalysts that have obtained the correct treatments, and that the catalytic chemist has at his or her disposal correctly analyzed and interpreted spectra.
- Application of a combination of techniques. Only rarely will one single spectroscopy be able to solve a problem entirely. The case studies demonstrate the advantages of using different techniques on the same catalysts.
- In situ characterization. Catalysts should preferably be investigated under the conditions under which they are active in the reaction.

- Optimized catalysts. Samples should be suitable for investigating the particular aspect of the catalyst one is interested in. For example, meaningful information on the metal-support interface is only obtained if the supported particles are small, and all of the same size.
- Realistic model systems. Some techniques become much more informative if suitable model systems are used. Examples are the thin-film oxides used as conducting model supports, which offer much better opportunities for surface analysis than do technical catalysts. Another example is provided by the nonporous, spherical supports that have successfully been employed in electron
- microscopy. It is important that the model systems exhibit the same chemistry as the catalyst they represent.
- Suitable reference compounds, preferably measured together with the catalysts, to confirm spectral assignments.
- These are the ingredients for successful research in catalysis.

## References:

- R. Prins, V.H.J. de Beer and G.A. Somorjai, Catal. Rev. - Sci. Eng. 31 (1989) I.
- Dr. J. W. Niemantsverdriet hand book of spectroscopy in catalysis.
- R.A. van Santen and J.W. Niemantsverdriet, Chemical Kinetics and Catalysis, Plenum, New York. 1995.
- Valeri P. Tolstoy, Irina V. Chernyshova, Valeri A. Skryshevsky hand book of infrared spectroscopy.
- A.V. Kiselev and V.I. Lygin, in Infrared Spectroscopy of Adsorbed Species, L.H. Little (Ed.), Academic Press, New York, 1966.
- P.R. Griffiths, Chemical Infrared Fourier Transform Spectroscopy, Wiley, Chichester, 1975.