CHEY2016 Lecture 9 Surface-infra red and Raman techniques
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Synopsis

- Overview of IR spectroscopy
- The surface selection rule.
- Special effects due to surface.
- Reflection Adsorption Infra Red Spectroscopy (RAIRS).
- Polarisation Modulation IR (PMIRRAS)
- Attenuated Total Reflection Infra-Red (ATR-FTIR).
- Surface Raman

Overview

If a molecule (e.g. HCl) is irradiated with a infra-red radiation it will absorb certain specific wavelengths. These wavelengths are specific for the molecule and are come about due to a change in the vibrational motion of the molecule, resulting in a change in the net dipole moment.

The vibration of a simple diatomic molecule can be described in terms of *simple harmonic motion*. This assumes that the chemical bond joining the two atoms acts like a Hooke's law spring, with a force constant, k, which is a measure of the bond strength. The vibration frequency is given (in both classical and quantum mechanical regimes) by:

$$\omega = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

with ω in Hz and k the force constant. The vibrational energy levels are given by

$$E_v = (v + \tfrac{1}{2})h\nu$$

With v = 0,1,2, ….. Again, the 'frequency', ν, is often given in cm^{-1}, with

$$e_v = (v + \tfrac{1}{2})\nu \ (\text{in cm}^{-1})$$

In more complex molecules, different functional groups will adsorb energy at specific energies, allowing IR to be used for functional group analysis.

To remind you, this table lists some stretching frequencies of common functional groups:

Group	Approx. frequency (cm^{-1})
-OH	3600
-NH$_2$	3400
=CH$_2$	3030
-C=O	1750-1600

Surface IR

IR spectroscopy is also possible on a surface, where the IR beam can be either reflected off (in grazing incidence mode) or introduced via a crystal to give multiple reflections on the back of a thin metal substrate (Attenuated total reflection (ATR).

The same principals as IR in bulk, gas or liquids apply on surfaces:

– the functional groups must change their net dipole moment on vibration to be infra-red active i.e. to be seen by IR spectroscopy.

Polarisation of light at a surface
The IR incident beam on the surface can be said to have two limiting polarisation states of its electric vector **E**

1. The vector can be parallel to the plane of reflection – called S polarised
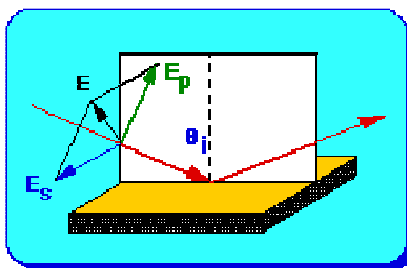2.Perpendicular (P polarised).

Diagram showing that the total electric field of light is the vector sum of the two components E_p and E_s. Clearly for S light $E_s = E$ and $E_p = 0$ and vice versa for P light.

Reflection at a surface
S polarised light reflecting off a surface change its phase by 180º. Looking at the diagram above it is clear that S light will virtually cancel itself out when undergoing a 180º phase change, resulting in a very low electric field density at the surface.

Remember:
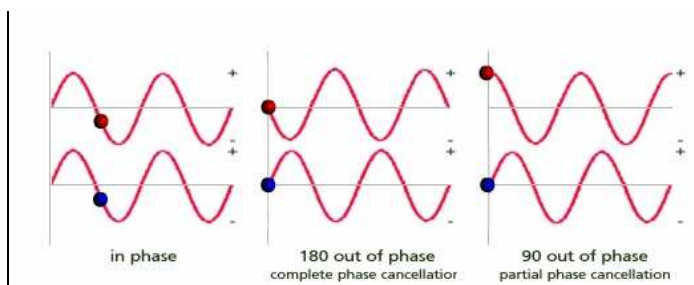
- P polarised light however does not cancel out – but has a phase shift related to the angle of incidence θ_i.

Hence it has a finite electric field at the surface that can interact with surface adsorbed species provided that the dipole change has a finite component perpendicular to the surface.

- This is known as the *Surface Selection Rule*.

Surface Selection Rule
S polarised light is surface inactive – it does not interact with surface adsorbed species (or interacts extremely weakly)
P polarised light interacts with surface adsorbed species that have part of the dipole moment perpendicular to the surface.

This effect is extremely important – as will be seen as when doing IR measurements on surfaces one encounters a number of problems:

Problems of Surface IR:
- **Solvent:** Absorption of light by solvent (or gas) above surface.
- **Surface / Bulk effects –** distinguishing the surface from the bulk sample
- **Sensitivity:** The signal from a monolayer of adsorbed molecule is very small.

The problem of sensitivity can be dealt with principally by working in ATR mode to obtain multiple reflections (see later) .

Reflection Adsorption Infra Red Spectroscopy (RAIRS) - the Study of Adsorbates on Metallic Surfaces by Reflection IR Spectroscopy

It can be shown theoretically that the best sensitivity for IR measurements on metallic surfaces is obtained using a grazing-incidence reflection of the IR light.
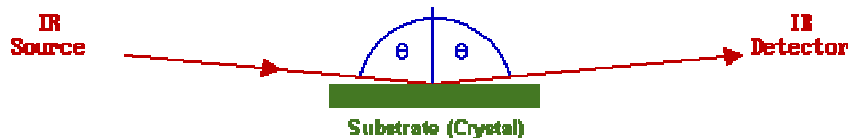
Furthermore, since it is an optical (photon in/photon out) technique it is not necessary for such studies to be carried out in vacuum. The technique is not inherently surface-specific, but

- there is no bulk signal to worry about, due to grazing angle.
- the surface signal is readily distinguishable from gas-phase absorptions using polarization effects (later).

One major problem, is that of sensitivity (i.e. the signal is usually very weak owing to the small number of adsorbing molecules).

Typically, the sampled area is ca. 1 cm^2 with less than 10^{15} adsorbed molecules (i.e. about 1 nanomole). With modern FTIR spectrometers, however, such small signals (0.01% - 2% absorption) can still be recorded at relatively high resolution (ca. 1 cm^{-1}).

Check out: http://www.chem.qmw.ac.uk/surfaces/scc/scat5_4.htm

Using the Surface Selection Rule to remove effects of solvent / gas absorption

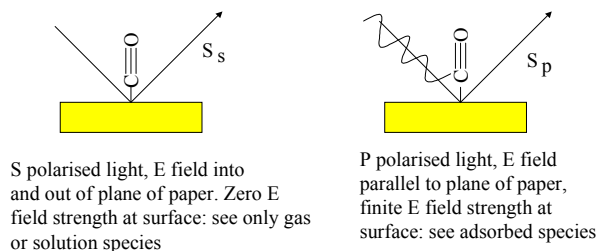**Polarisation Modulation RAIRS (PM RAIRS).**

Principle
P polarised light will detect both surface adsorbed species *and* any molecules in solvent or gas above the surface.
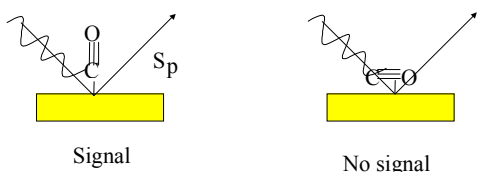
S polarised light will not detect surface adsorbed species, but *will* detect molecules in solvent / gas.

So measure: $\dfrac{S_p - S_s}{S_p + S_s}$ (S = intensity)

- One needs a rather complex piece of electronics to continuously modulate the polarisation called a *photoelectric modulator*.
- Remove solvent effect by subtraction of absorption due to solvent.

S polarised light, E field into and out of plane of paper. Zero E field strength at surface: see only gas or solution species

P polarised light, E field parallel to plane of paper, finite E field strength at surface: see adsorbed species

- Obtain orientation information about surface adsorbed molecules:

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Signal

No signal

Change in orientation of molecule on surface results in changes to IR intensity.

Experimentally, use phase sensitive detector that switches between detecting P and S polarised light.

Photoelectric modulator
switches continually between
P and S detection

Detector coupled to PM
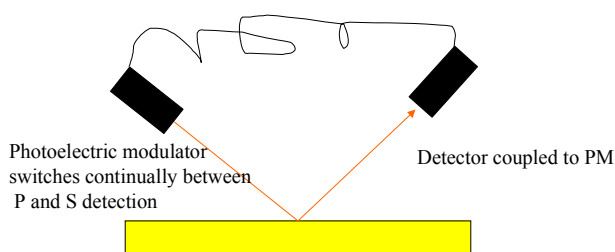
Technique has been used to study CO adsorption on Pt for example.

Attenuated Total Reflection IR Spectroscopy
Technique couples light into sample from underside, via a metal film and prism: removes problems of fluid absorption of light.
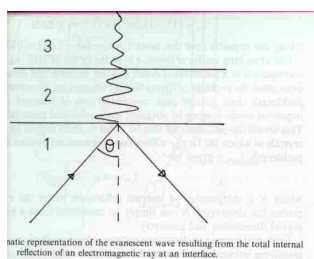
Create an evanescent wave at the surface from reflection on the backside of metal film..

Incident light

Metal film

Multiple internal reflections
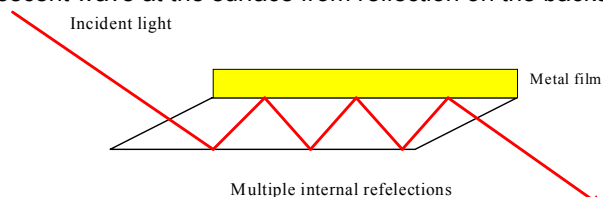
Totally internally reflected laser light couples with electrons in gold and creates a finite electric field on the metal surface which decays exponentially away from surface: evanescent wave.

- Get multiple reflections
- Very sensitive: can measure monolayers
- Get information on molecular functionality and surface orientation.
- Avoid all solvent problems
- Easy to combine with other methods to do simultaneous measurements (e.g. with electrochemistry).

Worked example, check out:
Attenuated total reflection Fourier transform infrared spectroscopic characterization of fluid lipid bilayers tethered to solid supports

Cheng YL, Boden N, Bushby RJ, Clarkson S, Evans SD, Knowles PF, Marsh A, Miles RE
LANGMUIR 14 (4): 839-844 FEB 17 1998

Surface Enhanced Raman Spectroscopy

The Raman Effect and Normal Raman Scattering.

When light is scattered from a molecule most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is the termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect. We will use the term Raman effect to mean vibrational Raman effect only.

The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a Raman spectrum.

The Scattering Process.

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule's electric field. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10^{-14} seconds or less. The virtual state description of scattering is shown in Figure 1.1a.
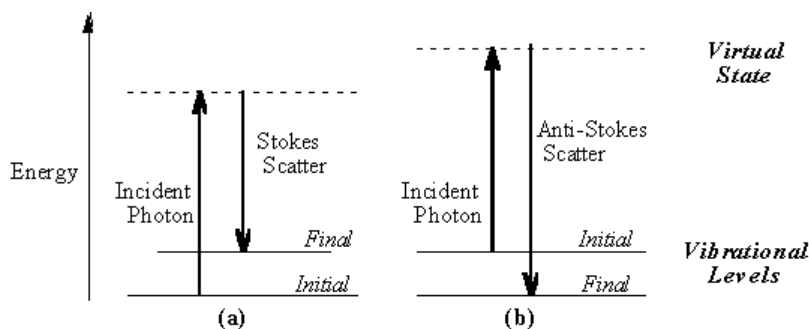
Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

Figure 1.1. Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

Numerically, the energy difference between the initial and final vibrational levels.

1.1.3. Raman Selection Rules and Intensities. A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, **P**, induced in a molecule by an external electric field, **E**, is proportional to the field as shown in equation 2.

$$\mathbf{P} = \alpha \, \mathbf{E} \qquad\qquad (2)$$

If a vibration does not greatly change the polarizability α, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak. An external electric field can not induce a large change in the dipole moment and stretching or bending the bond does not change this.

Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The pi-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the distribution of electron density substantially, and causes a large change in induced dipole moment.

Resonance-Enhanced Raman Scattering.

Raman spectroscopy is conventionally performed with green, red or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as assumed by scattering theory. The situation changes if the wavelength of the exciting laser falls within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases by a factor of 10^2-10^4. This resonance enhancement or resonance Raman effect can be quite useful.

Resonance enhancement does not begin at a sharply defined wavelength. In fact, enhancement of 5X-10X is commonly observed if the exciting laser is even within a few hundred wave numbers below the electronic transition of a molecule. This pre-resonance enhancement can be experimentally useful.

1.3. Surface-Enhanced Raman Scattering.

The Raman scattering from a compound (or ion) adsorbed on or even within a few Angstroms of a structured metal surface can be 10^3-10^6X greater than in solution. This surface-enhanced Raman scattering is strongest on silver, but is observable on gold and copper as well. At practical excitation wavelengths, enhancement on other metals is unimportant. Surface-enhanced Raman scattering (SERS) arises from two mechanisms.

The first is an enhanced electromagnetic field produced at the surface of the metal. When the wavelength of the incident light is close to the plasma wavelength of the metal, conduction electrons in the metal surface are excited into an extended surface electronic excited state called a surface plasmon resonance. Molecules adsorbed or in close proximity to the surface experience an exceptionally large electromagnetic field. Vibrational modes normal to the surface are most strongly enhanced.

The second mode of enhancement is by the formation of a charge-transfer complex between the surface and analyte molecule. The electronic transitions of many charge transfer complexes are in the visible, so that resonance enhancement occurs.

Molecules with lone pair electrons or pi clouds show the strongest SERS. The effect was first discovered with pyridine. Other aromatic nitrogen or oxygen containing compounds, such as aromatic amines or phenols, are strongly SERS active.

Example of SERRS and RR

The RR and SERRS spectra of the of lead(II) complex [Pb(PAN)$_2$] show some striking difference, indicating that the molecules are chemisorbed. A detailed analysis of the SERRS results enabled us to deduce the geometry of the adsorbed species, in which there is interaction with surface Ag atoms through the pyridyl and azo N atoms.
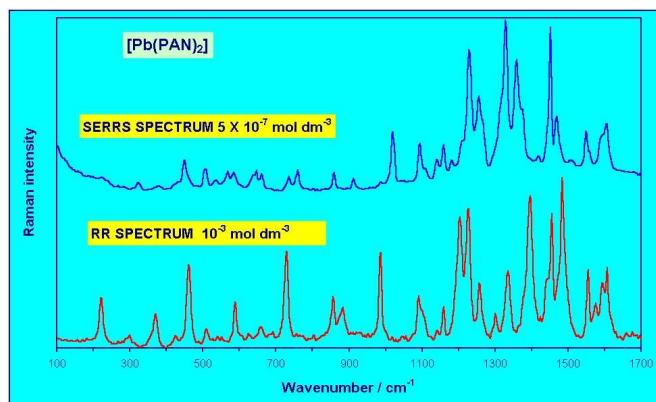
1-(2-pyridylazo)-2-naphtholate (PAN) forms complexes with many divalent metals and is a useful analytical reagent.   The complexes have tetrahedral geometry at the metal ion and exist in two tautomers:
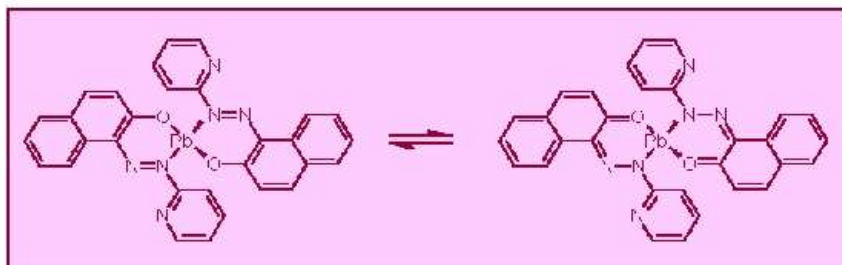
Chemisorption on the colloidal Ag surface stabilises the first tautomer
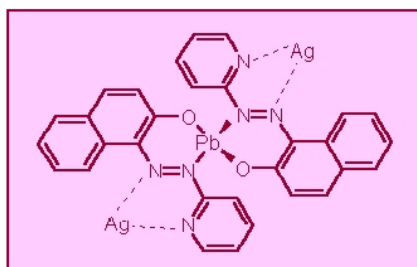
Conclusions

1. Detect a thin (probably monolayer) of the adsorbed molecule.
2. The different spectra gives important information on the structure of the adsorbed layer.

Two enhancement effects:

1. Resonance effect: Molecule is coloured (as are many inorganic complexes).
2. Rough colloidal silver surface gives surface plasmonic enhancement.

Further Reading

http://www.personal.dundee.ac.uk/~tjdines/Raman/research4.htm