# CHE-2F4Y Molecular Structure and Energy Levels: Applications of Vibrational Spectroscopy

Vibrational spectroscopy involves a change in vibrational state. Many reasons why we may want to do this:

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- 'Spring' treatment  $\Rightarrow \omega = \frac{1}{2\pi} \sqrt{k/\mu}$  for a diatomic molecule

• Molecule with *N* atoms will contain many bonds ∴ vibrate at many frequencies:

- Also get info on <u>symmetry</u>:
  - 1. The vibrations of a molecule can be broken down into <u>normal modes</u>

2. The symmetry of a normal mode determines whether or not the mode shows up in the IR or Raman (or both or neither!)

• Classic example: C<sub>60</sub>



### **Classical interpretation**

A molecule absorbs/emits radiation at frequency  $\nu$  if it possesses a <u>dipole moment</u> oscillating at that frequency. The situation is similar to transmission and reception of radio signals.

Dipole moment

Defined as:

$$\boldsymbol{\mu} = \sum_{i} e_{i} \mathbf{r}_{i}$$

Examples:

IR spectroscopy

Raman spectroscopy

CHE-2F4Y

# Instrumentation

#### IR

Nowadays, IR almost exclusively carried out using Fourier Transform IR spectrometers (FTIR).





The heart of the machine is the scanning (Michelson) interferometer:

There are two paths that light from the source S can take to the detector, so the beams interfere.

As MM moves, the interference pattern changes. The detected power P(x) forms an interferogram.

A Fourier transform (FT) of this interferogram gives the frequency spectrum:

Interferograms are complex but FT reveals <u>all the same frequency data</u> that a dispersive machine would.

Each scan of x measures the <u>full</u> frequency spectrum.

The position of the mirror and the sampling of P(x) is precisely controlled by the signal from a He-Ne laser.

FTIR machines have many advantages over older dispersive machines:

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### Raman

Most Raman spectrometers are dispersive:



# IR vs. Raman – A comparison

IR	Raman

### Applications: Surface techniques

Vibrational spectroscopy can be carried out on **surfaces** or **molecules adsorbed** onto surfaces. Several reasons for doing this:

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# **General Surface Optics**



#### **Attenuated Total Reflection (ATR)**

IR reflected from a surface. When total internal reflection occurs  $(n_1 > n_2, \theta \ge \theta_c)$  some energy is lost to the second medium in the form of an **evanescent** wave:



In practice, the medium carrying the beam (ATR crystal) is made long and thin so that multiple reflections occur, thus magnifying the effect:



Thus, the detected beam is **attenuated** relative to the input beam.

The amount of energy taken from the beam depends on the interactions between the light and the sample. Therefore, an IR spectrum of the sample can be obtained.

Advantages:

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### **Reflection-Absorption Infrared Spectroscopy (RAIRS)**

In this technique, IR is directed at a surface (usually a metal) at a grazing angle  $(\Box 85^{\circ})$ :



Unlike normal IR the polarisation of the light is important. A strong signal is obtained if p-polarised light is used — a weak one if it is s-polarised:



This gives rise to the surface selection rule:

Only vibrations with dipole changes perpendicular to a metal surface are allowed.

Advantages:

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#### **Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)**

Used on very fine powders.

IR is directed onto a sample held in a small "cup". The light is **diffusely** reflected, collected and its intensity measured.



The technique may be qualitative or quantitative:

- 1. Powdered KBr is used to provide a reference spectrum.
- 2. Powdered sample is used.
- 3. Then the reflectance ratio is calculated:

 $R_{\infty}$  = sample reflectance/KBr reflectance

4. This quantity does not scale linearly with concentration. Correction is applied using the Kubelka-Munk relation:

Example:



Advantages/disadvantages:

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#### Surface Enhanced Raman Spectroscopy (SERS)

Here, the analyte is adsorbed onto a **roughened** (features ~nm) metal surface. e.g.

Found that the Raman signal from the adsorbed molecules is **greatly enhanced** ( $\times 10^{14}$  has been reported).

Enhancement mainly due to an electromagnetic effect:

- Light absorbed by the surface creates very strong localised electromagnetic fields at the sites of roughness.
- Adsorbants : exposed to much stronger fields and this greatly enhances the emitted Raman signal.

In addition, fluorescence is much much smaller, which further improves S/N. This is caused by excited molecules giving their energy to the surface rather than emitting fluorescence (quenching).

Advantages:

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