ABC’s of Electrochemistry

Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy

Dan Wang
10/06/11
In 1800, Herschel analyzed the spectrum of sunlight. He got a higher temperature just beyond the red light region than that of visible spectrum. He conclude there must be an invisible light beyond visible region. This kind of light became known as infrared light.
1928, Raman discovered the Raman effect (Raman scattering) through his experiments on the scattering of light.

He won the Nobel Prize in Physics in 1930 due to the discovery of Raman scattering.
Raman scattering

The Raman effect comprises a very small fraction of the incident photons (approximately 1 in $10^7$).
Raman spectroscopy and instrument

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light (a laser source), study vibrational modes in a system.

The combination of Raman spectrometer and confocal microscope allows for obtaining the information of both morphological details and molecular structures.
Optical Path of Raman Spectroscopy Measurements

Bruker Senterra
Fourier Transform Infrared Spectroscopy (FTIR)

- Fourier transform infrared spectroscopy (FTIR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum.
- FTIR spectrometer simultaneously collects spectral data in a wide spectral range.
- FTIR spectroscopic analysis is to identify the chemical functional groups in the sample.

Near-IR, approximately 14000–4000 cm⁻¹ (0.8–2.5 μm wavelength)

Mid-IR, approximately 4000–400 cm⁻¹ (2.5–25 μm)

Far-infrared, approximately 400–10 cm⁻¹ (25–1000 μm),

http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy
Sample Preparation for IR spectroscopy

1. Pressing KBr Pellet:
   - solid samples,
   - sample concentration in KBr: 0.2%~1%
   - A translucent pellet: thickness: 0.5~1 mm

2. Thin film between two IR transparent plates:
   - liquid sample and soluble solid powder
   - KBr, NaCl, CaF\(_2\) plates
   - The space between plates: typically < 0.01 mm

3. Preparing a Mull
   - Solid sample can be ground into fine particles but not soluble in solvent
   - Mulling agent: Nujol, paraffin oil
   - Interference from the absorption bands of the mulling agent

4. Others:
   - Liquid cell: volatile liquid
   - Gas cell: gaseous sample
   - No sample preparation: self-supporting thin film,
     Attenuated total reflectance (ATR)-FTIR
Degrees of freedom

• Both IR and Raman spectroscopy characterize the vibrations of chemical bonds.
• The number of vibrations in a molecule related to the degrees of freedom which the structure possesses.

A molecule has n atoms. Totally 3n degrees of freedom (x, y, z axis.)

  Minus 3 degrees of translational freedom
  Minus 3 degrees of rotational freedom

Nonlinear molecules: 3n-6; for example: \( \text{H}_2\text{O} \)  \( 3 \times 3 - 6 = 3 \)
Linear molecules: 3n-5; for example: \( \text{CO}_2 \)  \( 3 \times 3 - 5 = 4 \)
Copyright © 2017 by Elsevier Inc. All rights reserved.

Selection Rules

**IR active**: the vibration results in a change in the dipole moment.

For example
- Unsymmetrical diatomic molecules, e.g. CO
- non-linear molecule like H₂O
- asymmetric stretch of O=C=O

**IR inactive**: for example
- Homonuclear molecules: O₂, N₂, Cl₂, have no net charge in dipole moment occurs during the vibration.
- symmetric stretch of O=C=O (linear molecule)
Raman active: molecule’s polarizability must change during the vibration

For example: symmetric stretch of O=C=O
Raman spectra VS IR spectra

Infrared and Raman spectroscopy are used as complementary techniques.

Skoog, Hollier & Nieman, 5th edn, 1998, Fig. 18-3
IR VS Raman

IR

• Absorption spectroscopy

• Dipole moment change

• Sample preparation is mostly required

• Interference with the measurement environment

Raman

• Scattering spectroscopy

• Polarizability change

• Minimal or no sample preparation

• No interference from atmospheric CO$_2$ or H$_2$O
Related Raman / IR spectroscopies

1. Surface-Enhanced Raman Spectroscopy (SERS): a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough metal surfaces. (Usually silver or gold). The enhancement factor can be up to $10^{11}$.

2. Resonance Raman Spectroscopy: The excitation wavelength is matched to an electronic transition of the molecule or crystal, so that vibrational modes associated with the excited electronic state are greatly enhanced.

3. Attenuated total reflectance (ATR)-FTIR: avoids the problem of strong attenuation of the IR signal in highly absorbing media, such as aqueous solutions.

http://en.wikipedia.org/wiki/Raman_spectroscopy
Spectroelectrochemistry

Raman spectroscopy and FTIR spectroscopy combined with electrochemical methods are powerful techniques for the mechanism and kinetics study, because they can provide fundamental molecular level information and detect intermediate adsorbates on the electrode surface during the reactions.

- An accurate polarization control mode can be applied with the aid of a potentiostat while simultaneously performing Raman spectroscopy.

- The center of the cell top is a piece of cover glass, which allows the Raman excitation laser beam to go through the cell and electrolyte onto the electrode surface.

• OPUS software-----Help----- FTIR tutorial
QUESTIONS?

www.ohio.edu/engineering