FOURIER TRANSFORM INFRA-RED (FTIR) SPECTROSCOPY

PART ONE   THEORY AND OPERATION PRINCIPLE OF FTIR SPECTROMETER

1. INTRODUCTION

The total internal energy of a molecule in a first approximation can be resolved into the sum of rotational, vibrational and electronic energy levels. Infrared spectroscopy is the study of interactions between matter and electromagnetic fields in the IR region. In this spectral region, the EM waves mainly couple with the molecular vibrations. In other words, a molecule can be excited to a higher vibrational state by absorbing IR radiation. The probability of a particular IR frequency being absorbed depends on the actual interaction between this frequency and the molecule. In general, a frequency will be strongly absorbed if its photon energy coincides with the vibrational energy levels of the molecule. IR spectroscopy is therefore a very powerful technique which provides fingerprint information on the chemical composition of the sample. FTIR spectrometer is found in most analytical laboratories.

2. MATHEMATICAL EXPRESSIONS OF FOURIER TRANSFORMS

In spectroscopy, it is essential to know which frequencies are absorbed and which are not. This requires that the radiation source covers a broad spectral range and the individual frequencies of the radiation are analyzed.

In the conventional dispersive-type spectrometer, a grating or a prism is used to disperse light into individual frequencies, and a slit placed in front of the detector to determine which frequency to reach the detector.

However the FTIR spectrometer operates on a different principle called Fourier transform. The mathematical expression of Fourier transform can be expressed as

\[ F(\omega) = \int_{-\infty}^{+\infty} f(x)e^{-i\omega x} dx \]
And the reverse Fourier transform is

\[ f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega) e^{-i\omega x} d\omega \]

where \( \omega \) is angular frequency and \( x \) is the optical path difference in our case. \( F(\omega) \) is the spectrum and \( f(x) \) is called the interferogram.

It is clear that if the interferogram \( f(x) \), is determined experimentally, the spectrum \( F(\omega) \) can be obtained by using Fourier transform. The relationship between the interferogram and the spectrum will be explained more fully in the latter sections. Section 3 explains how to measure the interferogram using Michelson interferometer.

3. THE MICHELSON INTERFEROMETER

The basic Michelson Interferometer consists of (see Fig. 1):

- a broad-band light source which emits light covering the mid-IR range,
- a beamsplitter made of KBr or CsI,
- Two front surface coated mirrors – one moving and one fixed, and
- a detector.

![Schematic diagram of a Michelson Interferometer.](image)
The working principle of Michelson Interferometer

1) Light from the light source is directed to the beamsplitter. Half of the light is reflected and half is transmitted.

2) The reflected light goes to the fixed mirror where it is reflected back to the beamsplitter. The transmitted light is sent to the moving mirror and is also reflected back towards the mirror.

3) At the beamsplitter, each of the two beams (from the fixed and moving mirrors) are split into two: one goes back to the source (and “lost” since it does not reach the detector) and the other goes towards the detector. Hence the detector sees two beams: one from the moving mirror and the other from the fixed mirror.

4) The two beams reaching the detector come from the same source and have an optical path difference determined by the positions of the two mirrors, i.e. they have a fixed phase difference. Therefore the two beams interfere.

5) The two beams may be made to interfere constructively or destructively for a particular frequency by positioning the moving mirror. If the moving mirror is scanned over a range (corresponding to \( x \) in Section 2), a sinusoidal signal will be detected for that frequency (see Fig. 2), with its maximum corresponding to constructive interference and the minimum corresponding to destructive interference. This sinusoidal signal is called interferogram – detector signal (intensity) against optical path difference.

6) Assume a light source which emits only two frequencies, each frequency will produce its own sinusoidal interferogram. Both interferograms will have maximum at optical path difference \( \delta \) equals to zero (corresponding to the point that the two mirrors are equidistance from the beamsplitter). But the other maxima will not coincide, since their positions are determined by the equation

\[ \delta = 2\Delta x = 2n\lambda_1 \quad , \quad \lambda_1 = \lambda_1, \lambda_2 \]

where \( \Delta x \) is the difference in the distances between the beamsplitter and the two mirrors.
7) Because the source emits a range of frequencies, the detector output is the sum of all the interferograms. The resulting interferogram will have a maximum at $\Delta x = 0$ (centreburst) and tails off rapidly away from the centreburst.

![Diagram](image)

Fig. 2 Relationship between spectrum and interferogram (detector signal). The axis for the detector signal is the optical path difference (see text).

4. **GENERATING THE SPECTRUM**

- As has been explained earlier, interferogram is determined experimentally in FTIR spectroscopy, and the corresponding spectrum – frequency against intensity plot, is computed using Fourier transform. This transformation is carried out automatically and the spectrum is displayed. You may not realize this mathematical transformation taking place.
• The detector sees all the frequencies simultaneously, whereas in a dispersive spectrometer, only one frequency can reach the detector at one time.

• FTIR spectrometer is inherently a single beam instrument. It is imperative to record a relevant background spectrum for each sample examined.

• **Background spectrum**: The empty beam background (no sample in the light path) is recorded first. This spectrum shows the instrument energy profile, which is affected by the characteristics of the source, the beamsplitter, the absorption by the air (mainly due to CO₂ and water vapour) in the beam path, and the sensitivity of the detector at different wavelengths.

• **Sample spectrum**: The sample is placed in the combined beam (just before the detector in Fig. 1). The sample spectrum is the ratio of the spectrum containing sample against that of the background.

• In recording the background spectrum, the light path should be made as close to that of the sample spectrum as possible. For example, in transmission experiment, the background may be recorded with nothing in the light path whereas it should be recorded with KBr powder in the DRIFT experiment.
EXPERIMENT 1  
TRANSMISSION SPECTRUM OF POLYSTYRENE

INTRODUCTION

This experiment is designed for the students to be familiar with the basic theoretical principle and the operation of the FTIR spectrometer. Transmission is the most widely used and most fundamental mode of operation. It is also the easiest to understand and to perform.

When a monochromatic EM wave of intensity $I_0$ passes through a specimen, absorption (and reflection) occurs and the intensity transmitted can be expressed according to the following relationship

$$I = I_0 e^{-\alpha d}$$

where $d$ is the thickness of the specimen and $\alpha$ is called the absorption coefficient. In the IR spectral region $\alpha$ is a strong function of the frequency of the incident light.

The quantity $t = I/I_0$ is called the transmittance and $\alpha d$ is proportional to a quantity called absorbance ($= \alpha d/\ln 10$). Transmittance and absorbance are the two parameters used most often in spectroscopy.

EXPERIMENT

Collect the background spectrum

1) Start the FTIR-8400S software by clicking the IRsolution icon on the desktop.

2) Click Measure tab.

3) Pull down the measurement menu and select Initialize.

4) Wait a few seconds for the lamp and mirror green indicators to appear on the Status Monitor Window on the right.

5) Set the following scan parameters on the Scan Parameters Window on the bottom right:
   
   i) Measurement mode: % Transmittance
   ii) Apodization : Happ-Genzel
   iii) Number of scans : 20
   iv) Resolution : 4
6) Enter an appropriate spectrum name in the comment box.

7) Click BKG to start scanning the background.

8) The background spectrum (energy spectrum) collected includes contributions from the light source, beamsplitter, air (carbon dioxide and water vapour) and window absorption.

9) Pull down the File menu and select Print to obtain a hardcopy of the spectrum.

**Collect the polystyrene spectrum**

1) Mount the polystyrene sample onto the sample holder.

2) Click Measure tab.

3) Enter an appropriate spectrum name in the comment box.

4) Click Sample tab to start the scan.

5) When scanning is completed, perform the following steps for peak detection and labelling:
   
a. Click Calculate tab on the right window
b. Enter suitable values for **Noise**, **Threshold** and **Min Area**
c. Click Calc button followed by OK button to display the results
d. To increase or decrease detected peaks, repeat steps b and c

6) Print the spectrum.

7) Repeat the scan for polystyrene using the following measurement modes:
   
a. Absorbance
b. Interferogram
c. Power

**Note:**

<table>
<thead>
<tr>
<th>Noise</th>
<th>Enter the noise level (0 to 1). Values larger than this level are identified as peaks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold</td>
<td>Peaks with larger absorbance than [Threshold: 0 to 5] are detected when the spectrum is in absorbance mode. Peaks with smaller transmittance than [Threshold: 0 to 100] are detected when the spectrum is in transmittance mode.</td>
</tr>
<tr>
<td>Min Area</td>
<td>Enter the minimum area. The values larger than this area are identified as peaks.</td>
</tr>
</tbody>
</table>
DISCUSSION

1) Discuss the background energy spectrum, e.g. identify the sharp bands and discuss the contributions to the overall profile.

2) From the power spectrum of polystyrene, perform a ratio against the background spectrum. Refer to appendix A for operating details.

3) Make general comments about the interferogram and power spectrum of polystyrene.

EXPERIMENT 2 ATTENUATED TOTAL REFLECTION (ATR)

INTRODUCTION

Under certain conditions, infrared radiation passing through a prism made of a high refractive index infrared transmitting material (ATR crystal) will be totally reflected. When total internal reflection occurs, there exists an evanescent wave extends beyond the surface of the crystal. Hence when a sample is brought in contact with the totally reflecting surface of the ATR crystal, the evanescent wave will interact with sample. It will be attenuated in spectral regions where the sample absorbs energy and hence a spectrum can be obtained. The IR light undergoes several reflections inside the crystal to increase the interaction with the sample (see the wall display for an illustration).

ATR produces a very short pathlength of the IR light in the sample. This makes this technique ideal for highly absorbing materials such as aqueous solutions, rubber and polymers.

The depth of penetration into a sample is given by the equation:

\[ dp = \frac{\lambda}{2n_p \pi (\sin^2 \theta - n_{sp})^{1/2}} \]

where

- \( \lambda \) = wavelength (in air)
- \( n_p \) = refractive index of prism
- \( n_s \) = refractive index of sample
- \( n_{sp} = n_s/n_p \)
- \( \theta \) = angle of incidence
At 45 degrees with KRS-5 crystal this translates into a depth of penetration of 0.1 - 0.2 of wavelength (a few micrometer). Simply stated, \( dp \) is smallest for materials of high refractive index and for high incidence angles. This dependence of band intensities is more prominent in thick samples as complete penetration occurs in thin samples.

**EXPERIMENT - LIQUID ATR**

1) Place the ATR accessory into the sample compartment of the spectrometer.

2) Collect a background spectrum through the empty ATR accessory.

3) Remove the trough from the assembly. Fill it with acetone and replace it back into the assembly.

4) Collect an absorbance spectrum of the acetone.

5) Make a solution of ~50% acetone and ~50% distilled water and collect a spectrum of this mixture.

6) Also collect an absorbance spectrum of distilled water.

7) Perform spectral subtraction, using an appropriate factor, between the acetone/distilled water mixture and distilled water, to obtain the spectrum of acetone.

**DISCUSSION**

1) Explain how the spectrum subtraction is performed.

2) Does the difference spectrum look similar to the pure acetone? Why or why not?
[Manipulation 2]-[Dataset]

Performs addition, subtraction, multiplication, and division between spectra. Calculations are performed between a source spectrum and a reference spectrum multiplied by a factor. The factor value can be increased or decreased while observing the resulting spectrum. You can select a spectrum in the tree view after specifying either Source or Reference.

Spectral Subtraction

The subtraction of a spectrum from another spectrum is known as a "Spectral Subtraction". Normally, spectral subtraction is used to subtract the spectrum of a known component from a spectrum with mixed components, and allow for calculation of the spectrum of the other component. For example, when spectrum S(B) of known component B is subtracted from spectrum S(A+B), which contains components A and B, spectrum S(A) of component A can be obtained by calculation. This is called the subtracted spectrum method. Practically, the reference spectrum must be multiplied by an appropriate factor, taking into account the concentration ratio of the known component of the source spectrum and reference spectrum before obtaining the subtracted spectrum. The concentration ratio can be calculated by comparing the absorbance of the absorption peak that is only seen in the known component in one spectrum with that in the other spectrum. For the above example, spectrum S(A) can be obtained by multiplying spectrum S(B) by the factor that may cancel out the absorbance of the peak particular to component B and then subtracting the multiplied spectrum S(B) from spectrum S(A+B).

Relation between IRsolution manipulation function and the Lambert-Beer's Law

- The photometry mode for manipulations on the spectrum is basically absorbance. Because concentration is related with absorbance described as the Lambert-Beer's Law. Perform manipulations for the transmittance spectrum after the absorbance conversion is automatically performed. For the parameter, enter the value based on the converted absorbance spectrum. Care must be taken for the data processing on the transmittance spectrum.
- Put a check mark on the [Disable Lambert Beer] on the [Environment]-[Manipulation Preferences] to manipulate transmittance spectra in the transmittance mode. This check mark is removed after manipulation every time. When you repeat manipulation, please put the check mark every time.
Parameters

Arithmetic

You can select the calculation type from the following options.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add 2 Datasets</td>
<td>Result = Source + Reference x Factor</td>
</tr>
<tr>
<td>Subtract 2 Datasets</td>
<td>Result = Source - Reference x Factor</td>
</tr>
<tr>
<td>Multiply 2 Datasets</td>
<td>Result = Source * Reference x Factor</td>
</tr>
<tr>
<td>Divide 2 Datasets</td>
<td>Result = Source / (Reference x Factor)</td>
</tr>
</tbody>
</table>

Factor

<table>
<thead>
<tr>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>You can specify the constant to be used for the mathematical operations. To</td>
</tr>
<tr>
<td></td>
<td>enter the constant, type with the keyboard or drag the scroll bar. (0&lt; factor &lt;1)</td>
</tr>
</tbody>
</table>

Scrolling

<table>
<thead>
<tr>
<th>Scroll Bar</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scroll Bar</td>
<td>You can change the value by the scroll bar. The Value increases or decreases</td>
</tr>
<tr>
<td></td>
<td>with &quot;Factor&quot; intervals by clicking the small points on either end of the</td>
</tr>
<tr>
<td></td>
<td>scroll bar. The values are also drastically changed by sliding the slider.</td>
</tr>
<tr>
<td>Factor</td>
<td>You can set the scroll increment when the small points on either end of the</td>
</tr>
<tr>
<td></td>
<td>scroll bar is clicked.</td>
</tr>
</tbody>
</table>

Switch S/R

Spectrum is loaded as reference or source spectrum according to the setting.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Loads the source spectrum.</td>
</tr>
<tr>
<td>Reference</td>
<td>Loads the reference spectrum.</td>
</tr>
</tbody>
</table>

AutoCalc

When check mark is on the [AutoCalc] section, the software automatically determines the factor with which the intensity at the wavenumber position corresponds to the clicked position becomes "0" (or "1" when multiplication or division has been selected) in the resulting spectrum, and then starts the specified calculation with clicking the <Calc> button. When you click the [>] button, a vertical cursor appears in the source spectrum area. And then you can adjust the factor after removing the check mark.

Buttons

<table>
<thead>
<tr>
<th>Button</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc</td>
<td>Executes the calculation and displays the result.</td>
</tr>
<tr>
<td>OK</td>
<td>Confirms the calculation result and displays the resulting spectrum in the</td>
</tr>
<tr>
<td></td>
<td>[View] tab.</td>
</tr>
<tr>
<td>Clear</td>
<td>Cancels the calculation and displays the unaltered spectrum in the [View]</td>
</tr>
<tr>
<td></td>
<td>tab.</td>
</tr>
<tr>
<td>Help</td>
<td>Displays the help window.</td>
</tr>
</tbody>
</table>
**Operation**

1. Activate the spectrum tab to be manipulated in the View tab.
2. The active spectrum will be indicated in bold on its spectrum tab.
3. Select the Dataset command from the Manipulation 2 pull down menu.
4. Click the Source radio button and select a source spectrum in the tree view window on the left, if necessary.
5. Click the Reference radio button and select a reference spectrum in the tree view window to overlay both spectra.
6. Select the Arithmetic option.
7. Adjust the factor in "Value" and click the Calc button. Continue the adjustment until an appropriate result is obtained.
8. Click the OK button to confirm the result and display the resulting spectrum.

**Note**

After you have selected [Divide 2 Dataset], if you select a reference spectrum that contains a wavenumber whose intensity will be "0" as a result of the calculation, an error message is displayed, and the calculation is aborted. The same error occurs when you enter "0" as a factor.