EXPERIMENT 2.3
FOURIER-TRANSFORM INFRARED SPECTROSCOPY

OBJECTIVE
The objective is to analyze liquid and solid materials qualitatively using an FTIR-ATR spectrometer.

PRELIMINARY QUESTIONS
1) How does IR radiation affect absorbing molecules? Name an example molecule that does not absorb IR and briefly explain why.

2) In an IR spectrum, what information does (i) the peak position and (ii) the peak intensity convey?

3) A peak at a wavenumber of 1656 cm\(^{-1}\) is observed for caffeine. Calculate the wavelength and frequency of this radiation and the energy change due to this absorption.

4) Suppose you are able to figure out, correctly, all of the functional groups for an unknown organic molecule using FTIR. Explain why this might not be sufficient to pin down the exact structure of the molecule. What additional information could be useful?

5) What is the basic operating principle of an ATR based sampling system? What are the advantages of an ATR-based sampling system compared to one based on direct transmittance of IR radiation in terms of sample thickness and preparation techniques?

6) When using an FTIR, which utilizes an interferometer, why do we need a Fourier transform to obtain the actual IR spectrum?

INTRODUCTION
Infrared spectroscopy is a powerful analytical tool to reveal the functional groups in a molecule. More specifically, it provides information about the nature of the bonds in the analyzed sample. Chemical bonds absorb electromagnetic waves at certain energy levels and convert them into rotational and vibrational kinetic energy forms. The bond can be differentiated by that absorbed radiation since different bonds absorb waves at different frequencies (Appendix). In infrared spectroscopy, as the name implies, incident light is sent to the sample at frequencies within the infrared region, between wave numbers of 4000 and 400 cm\(^{-1}\) (figure 1).
Molecular vibrations can be in the form of stretching and bending. As shown in figure 2, stretching is the change in bond length and bending is the change in bond angles. All bonds vibrate to some extent, and upon absorption of radiation, their energy levels are altered at multiples of energy values specific to the bond as predicted by quantum chemistry. Since the energy of light is proportional to the frequency (or wave number) by Planck’s constant, the absorbed light frequency is also specific to the bond of interest.

For FTIR analysis, infrared radiation comprising a range of frequencies is directed at the sample. A detector reads the intensity of the transmitted radiation at all frequencies scanned and the absorbance or transmittance values are calculated and recorded by the software. These values are subtracted from the background, obtained in the absence of
any sample. This is done in order to find the absorbance or transmittance plot specific to the sample only and to eliminate the absorption along the path outside the sample.

**a) Light Source**

A ceramic light source is used. When the near infrared type beam splitter (fluorine calcium=CaF2) is used, Wl(tungsten halogen) lamp is used as the light source.

**b) Interferometer**

An FTIR uses several optical systems; the instruments you will be using rely on a Michelson interferometer, a greatly simplified schematic of which is given in figure 3. Source light enters the beam splitter, which reflects one portion of the beam to the fixed mirror and transmits the other to the moving mirror. Both mirrors reflect their beams back to the splitter. The transmitted light from the fixed mirror and the reflected light from the moving mirror recombine and interfere with each other as they travel towards the collecting mirror. The interference is either constructive or destructive.

![Figure 3. The schematic diagram of a Michelson interferometer.](image)

c) Detector

For FTIR, the DLATGS (deuterated L-alanine triglycine sulfate) detector equipped with a temperature controller is used as the standard. Different materials for the detector and the optical system in general may be selected in regards to their potential interference and interaction within the region of interest (figure 4).
EXPERIMENTAL

Equipment
You will be using either of the two ATR-FTIRs in the analysis lab; the Shimadzu IR-Prestige-21 or the Perkin-Elmer.

Materials
Chemicals for qualitative analysis will be provided.

Procedure
In this experiment you will be given unknown organic compound(s). Obtain their FTIR spectra.

Liquids:
1. Run the background spectrum without any solvent.
2. Pour a few drops of the sample liquid into the trough plate crystal with a plastic pipette, ensuring that the sample completely covers the exposed surface of the crystal.
3. Click [Sample measurement] to analyze the sample.
4. Use a non-abrasive tissue to wick away the sample liquid, then gently clean and dry the surface with a few drops of ethanol and a clean tissue.

Solids:
1. Run the background spectrum without sample.
2. Using tweezers or a spatula, place the sample on the crystal surface. If the samples are granular or powdered, carefully spread them on the crystal until it is covered.
3. Swing the pressure clamp assembly so that the tip is right above the sample.
4. Screw down the clamp until the sample is firmly trapped between the tip and the opposing base. *Do not over-tighten.*
5. Click [Sample measurement] to analyze the sample.
6. Remove the sample. Make sure no powder or granules remain on the crystal, using a cotton bud or non-abrasive wipe if necessary. Run [Monitor scan] to check cleanliness.

Scan settings:
Resolution: 4 or 8 cm⁻¹; accumulation: 45-100 scans, wave number: 4000-650 cm⁻¹

IMPORTANT NOTES
• Clean all tools and the sample crystal with ethanol before preparation.
• Use proper sampling tools, tweezers and a spatula, to avoid contamination.
• Avoid leaving solvent and sample bottles in the vicinity of the instrument (why?).
• Clean all tools and the crystal with an appropriate organic solvent after measurements.
• For liquid samples, simply place a few drops onto the crystal to cover it completely.
• Pastes and other semi-solid samples are spread on the crystal for analysis.
ANALYSIS AND REPORT

Each group will have two unknowns to identify. A multiple choice selection of possible substances will be given and you will pick the most likely match for each sample. For the report, write down the structures of all compounds in the list that will be given to you, and based on these structures and the actual spectrum obtained, discuss in detail for each structure, why it is (or not) the correct identity of the unknown.

Figure 4. Choices for instrument components for different IR regions.

Figure 5. Spectrum map for bond responses
Further reading


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### APPENDIX

## Typical Infrared Correlation Frequencies

<table>
<thead>
<tr>
<th>Group</th>
<th>Symmetry</th>
<th>Frequency (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂</td>
<td>in-plane</td>
<td>1580-1650</td>
<td>weak</td>
</tr>
<tr>
<td>NH₂</td>
<td>out-of-plane</td>
<td>1350-1410</td>
<td>weak</td>
</tr>
<tr>
<td>C=O</td>
<td>in-plane</td>
<td>1650-1660</td>
<td>strong</td>
</tr>
<tr>
<td>C=O</td>
<td>out-of-plane</td>
<td>1530-1590</td>
<td>strong</td>
</tr>
<tr>
<td>C-H</td>
<td>in-plane</td>
<td>2900-3100</td>
<td>medium</td>
</tr>
<tr>
<td>C-H</td>
<td>out-of-plane</td>
<td>2300-2400</td>
<td>strong</td>
</tr>
<tr>
<td>C-C</td>
<td>symmetric</td>
<td>700-800</td>
<td>strong</td>
</tr>
<tr>
<td>C-C</td>
<td>asymmetric</td>
<td>600-700</td>
<td>strong</td>
</tr>
<tr>
<td>C=C</td>
<td>stretching</td>
<td>1100-1700</td>
<td>strong</td>
</tr>
<tr>
<td>C=N</td>
<td>stretching</td>
<td>1550-1600</td>
<td>strong</td>
</tr>
<tr>
<td>C≡N</td>
<td>stretching</td>
<td>2000-2200</td>
<td>strong</td>
</tr>
</tbody>
</table>

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