CHEM 344 – IR Spectroscopy
Physical Basis for IR Spectroscopy

Infrared (IR) spectroscopy can be used to determine functional groups and bond strengths based upon molecular vibrations. Chemical bonds are not rigid, but in continuous states of vibration.

3585 cm⁻¹  3506 cm⁻¹  1885 cm⁻¹

Normal modes of vibration of water

If you hit a molecule with a frequency of light that matches the frequency of a vibration, an absorption occurs and that vibrational state is excited.
Factors that Affect Frequency

If chemical bonds are roughly springs, then the vibrational energy is governed by Hooke’s Law.

The frequency is dependent on the force constant (~ bond strength) and the masses of the nuclei.

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Approximate vibrational frequency</th>
<th>Approximate bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>1000 cm(^{-1})</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>C=C</td>
<td>1600 cm(^{-1})</td>
<td>1.33 Å</td>
</tr>
<tr>
<td>C≡C</td>
<td>2200 cm(^{-1})</td>
<td>1.20 Å</td>
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</tbody>
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<tbody>
<tr>
<td>C(sp)–H</td>
<td>3300 cm(^{-1})</td>
</tr>
<tr>
<td>C(sp(^2))–H</td>
<td>3100 cm(^{-1})</td>
</tr>
<tr>
<td>C(sp(^3))–H</td>
<td>2900 cm(^{-1})</td>
</tr>
<tr>
<td>C(sp(^3))–D</td>
<td>2200 cm(^{-1})</td>
</tr>
<tr>
<td>C(sp(^3))–H</td>
<td>2900 cm(^{-1})</td>
</tr>
</tbody>
</table>
IR Spectrum of Butanone

Vertical axis in % Transmittance (most often) for liquid phase IR.

Horizontal axis in wavenumber (cm$^{-1}$) for most IR

Absorptions are observed as sharp or broad reductions in the % of light transmitted through the sample.
IR Spectrum of Butanone

O–H, N–H, C–H stretches
C≡N, C≡C stretches
C=O, C≡N, C≡C stretches
C–O, C–N, C–C stretches and various bends
C–H bends and other low energy vibrations

Great for identifying carbonyl-containing functional groups
IR Spectrum of Heptane

This is a pretty boring IR spectrum due to the lack of functional groups in an alkane.

This region is usually too complicated for interpretation at our level. (You can mostly ignore it.)
IR of 1-Heptene vs. Heptane

1-Heptene

Heptane

C(sp²)-H  C(sp³)-H
Broad and intense signals in this region are diagnostic for H-atoms connected to N or O atoms that are involved in hydrogen bonding.
Three Isomeric Hexynes

IR intensity depends on the change in dipole during the vibration.
Functional Group Identification

Rarely are complete structure determinations made solely with IR spectroscopy. Usually IR provides conformation of the presence of a known molecule or a partial structure determination when used in tandem with other analyses.

### Wavenumber range, cm⁻¹ | Type of absorptions          | Name of region
----------------------------|------------------------------|-------------------
3400–2800                  | O—H, N—H, C—H stretching   | Usually very useful
2250–2100                  | C≡N, C≡C stretching         | Functional group
1850–1600                  | C=O, C=O, C= C stretching   | Usually complicated and less useful
1600–1000                  | C=C, C—O, C≡N stretching; various bending absorptions | Fingerprint
1000–600                   | C—H bending                 | C—H bending

- Single bond region is great for detecting O–H or N–H stretching. Indicates the presence or absence of hydrogen-bonding.

- Triple bond region is usually clear of signals except for R–C≡N, R–C≡C–R’.

- The double bond region is often very diagnostic and can be used to tell the difference between different double bonded molecules and even different carbonyl functional groups.
Functional Group Identification

Double Bond Stretching Vibrations
- 1710 cm\(^{-1}\): Aldehyde or ketone
- 1680: Conjugated ketone
- 1745: Cyclopentanone
- 1780: Cyclobutanone
- 1730: \(\alpha\)-Hydroxy ketone
- 1740: Ester
- 1660: Amide
- 1800: Acid chloride
- 1810 and 1760: Acid anhydride
- 1700: Carboxylic acid
- 1680-1500: C=C stretch
- 1675-1590: Aromatic C=C stretch

21.4

1743 cm\(^{-1}\)

1646 cm\(^{-1}\)

1715 cm\(^{-1}\)
IR Spectroscopy Practice

12.1 – 12.5

Fingerprint region

No O–H or N–H stretch

No C=O or C=C stretch

C≡C or C≡N stretch

propionitrile

Fingerprint region
Assigned IR spectrum – CON$_6$
IR Spectroscopy in Photochemistry

How to determine which product is formed?

• *Predict (calculate)* the IR spectrum of *each* product.

• Compare experimental IR spectrum to all of the computed IR spectra.
  • A good match between experimental and computed IR spectra establishes the identity of the product.
IR Spectroscopy in Photochemistry

Frequency (cm⁻¹)

λ > 237 nm, 40 min (Ar, 10 K)

Experimental

(B3LYP/6-31G*)

Product

Reactant

(B3LYP/6-31G*)
IR Spectroscopy Practice

- No O–H or N–H stretch
- No C≡C or C≡N stretch
- No C=O stretch
- C=C stretches
- Fingerprint region

anisole
IR Spectroscopy Practice

2,3-dimethyl-2-butene

Fingerprint region

No O–H or N–H stretch

No C≡C or C≡N stretch

No C=O or C=C stretch
IR Spectroscopy – Summary

Infrared (IR) spectroscopy can be used to determine functional groups and bond strengths based upon molecular vibrations.

Frequency of the IR absorptions is dependent upon the bond strengths and the masses of the atoms in the molecule.

IR intensity is related to a change in dipole upon vibration.

IR spectra can be used to easily identify functional groups.
- O–H, N–H, and C–H
- C≡N and C≡C
- C=C, C=N, C=O

Much of the spectra can be ignored at the Chem 344/345 level, but can be assigned with a deeper analysis using computational chemistry.
UWS 14:

- Academic Misconduct - An Overview
- Definition of Academic Misconduct
- Some Special Points About Collaboration & Plagiarism
- If You Are Accused of Cheating
- Disciplinary Penalties
- Dean’s Recommendation of Additional Sanctions
- The Disciplinary Process
- The Right To A Hearing
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Academic Misconduct - An Overview

Part of the value of your degree from the University of Wisconsin-Madison lies in the standards of academic honesty and integrity maintained by the campus. To avoid academic misconduct (cheating), it is important that you understand how it is defined, our expectations of you, and your rights if you are involved in an allegation of academic misconduct.
Get Help! (But, do it smartly and kindly.)

Emailing your TA, Nick Hill, or Brian Esselman is a great idea.
• Don’t wait until 30 min before lab to email us.
• Provide us with sufficient information to assist you. Articulate what you are thinking, what you’ve tried to do to solve your problem and/or what reasoning you’ve done.
• Be respectful.
  • Use the same kind of tone you would in person. Don’t be rude.
  • Check the website, textbook, and lab manual first to see if your answer is easily obtainable (With 800+ students we can’t answer individual questions for everyone, that’s why we made the lab manual and handouts.
• Understand our schedules. Don’t expect responses at 2:00 am.
Advice for success in CHEM 344

Plan ahead
Don’t wait until 10 min before lab begins to read the procedure or write your pre-lab.

Understand what you need to do in lab
Is it a 2-day lab? Do I need to reflux the reaction? Come prepared.

Think about what you are doing in lab while you are doing it!
Why do you need to reflux/cool/add acid/add base/extract/distill?

Know exactly what you need to do for the lab report
Typically NMR and/or GC-MS, post-lab questions (including computational modeling).

Plan ahead (again)
Know when each lab report is due (its printed in the lab manual)
Look at the spectra and questions at least 24 hrs before report is due