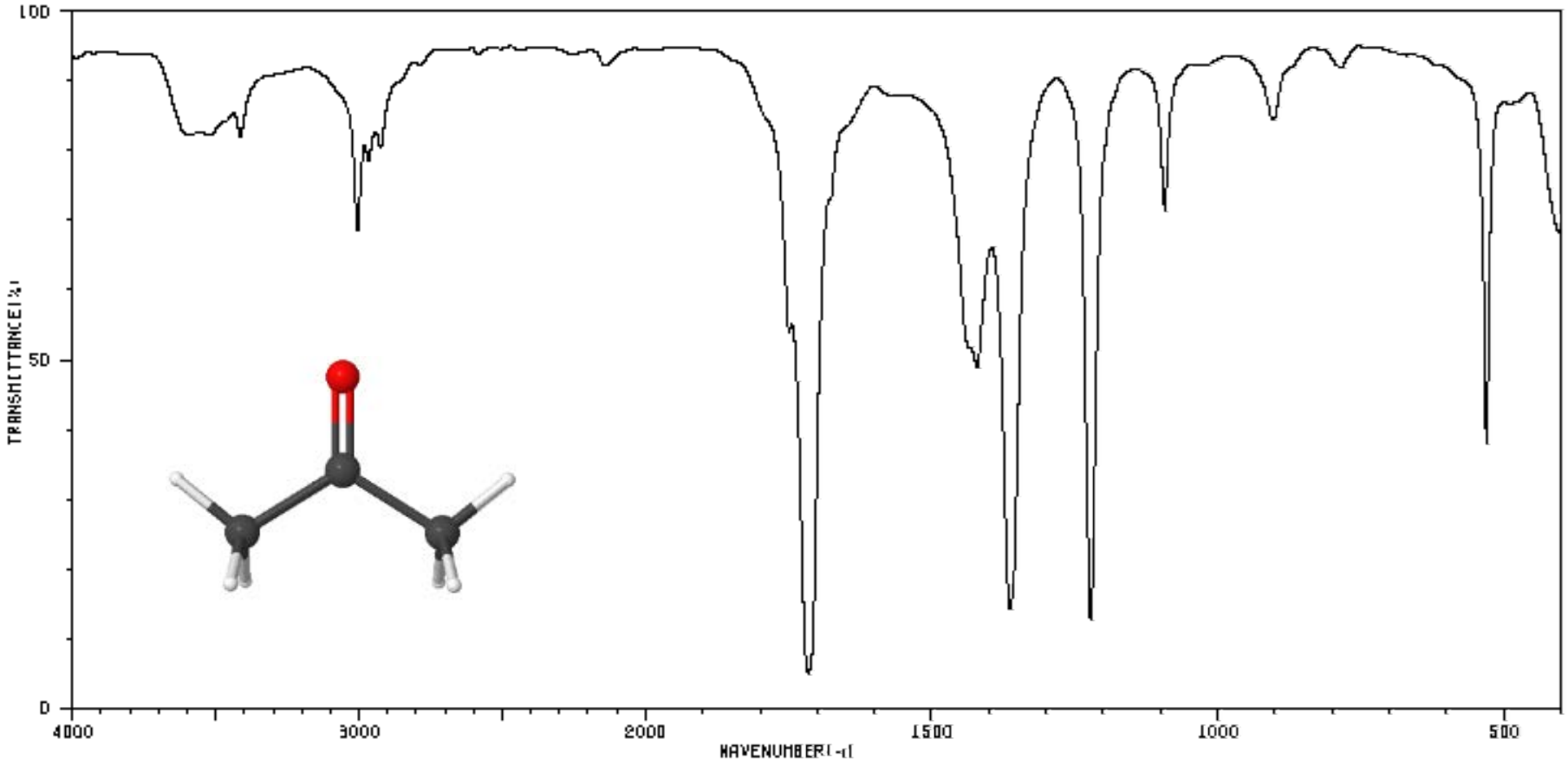
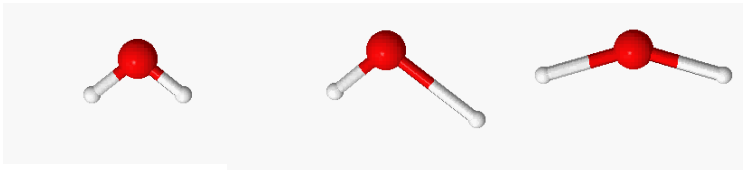
CHEM 344 – IR Spectroscopy



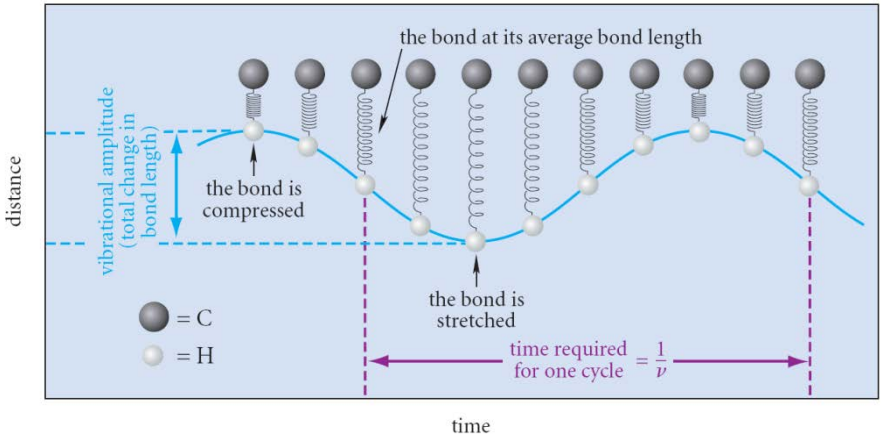
Physical Basis for IR Spectroscopy

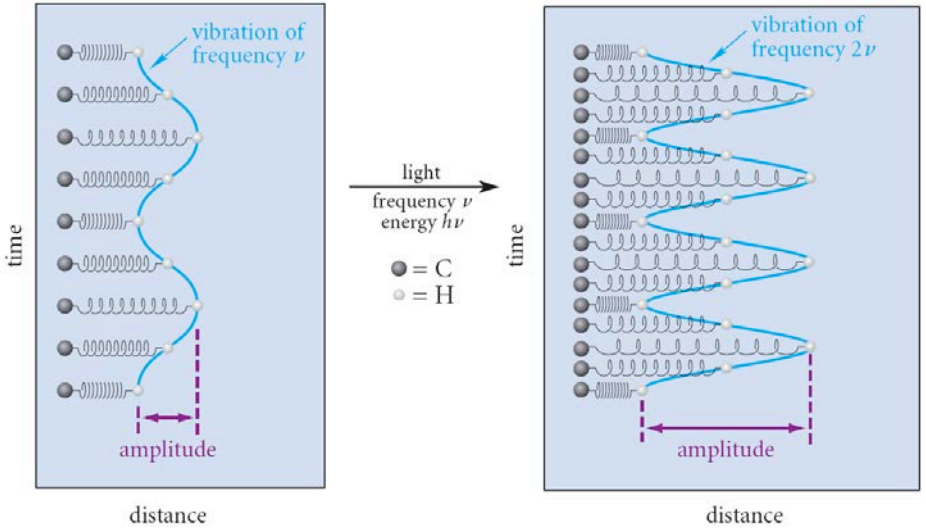
Inf**r**ared (**IR**) spectroscopy can be used to determine functional groups and bond strengths based upon molecular vibrations. Chemical bonds are not rigid, but in continuous states of vibration.



3585 cm^{-1} 3506 cm^{-1} 1885 cm^{-1}

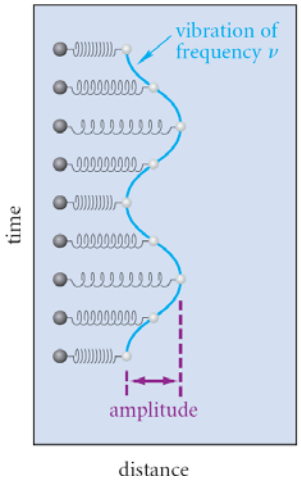
Normal modes of vibration of water





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



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

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.

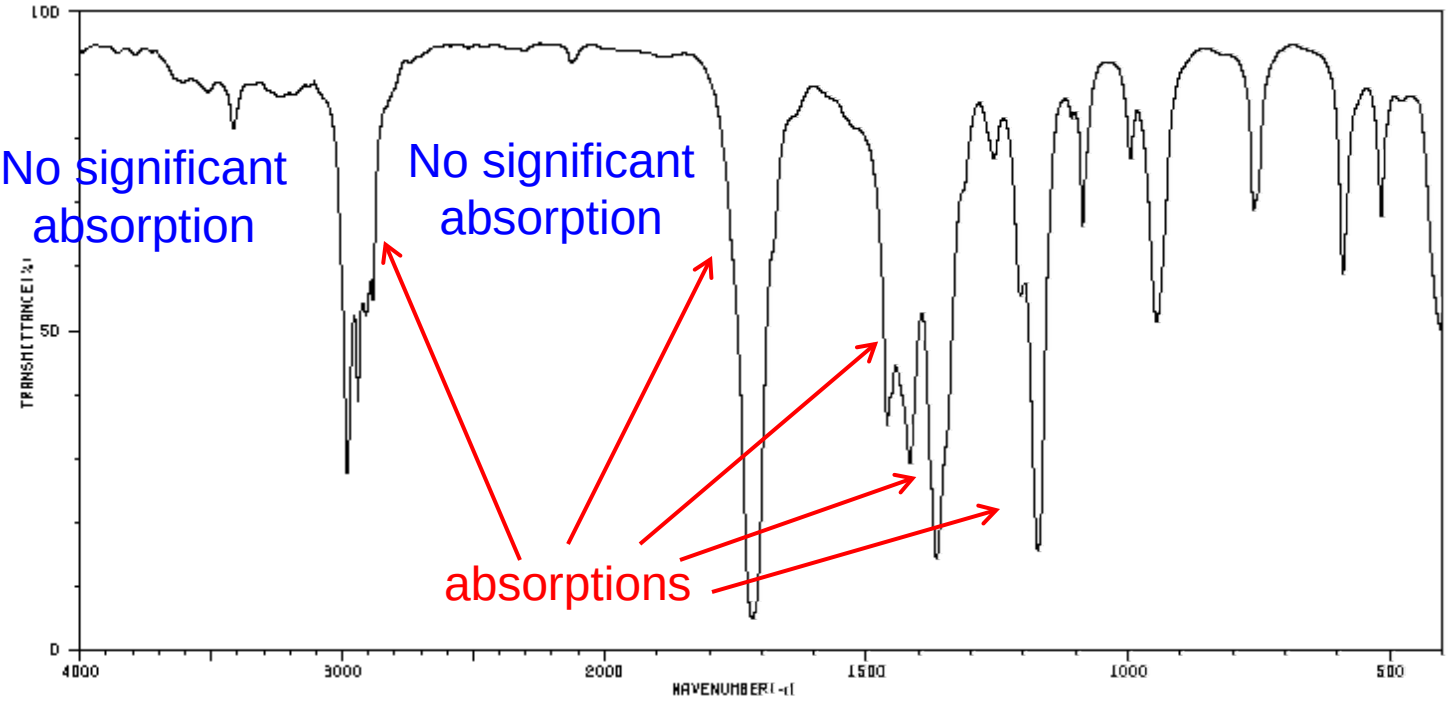
Bond	Approximate vibrational frequency	Approximate bond length
C–C	1000 cm^{-1}	1.54 Å
C=C	1600 cm^{-1}	1.33 Å
C≡C	2200 cm^{-1}	1.20 Å

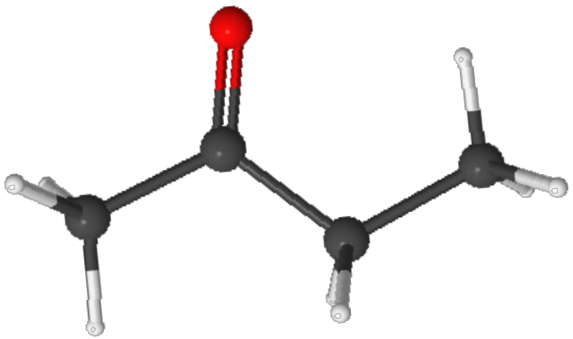
Bond	Approximate vibrational frequency
C(sp)–H	3300 cm^{-1}
$C(sp^2)$–H	3100 cm^{-1}
$C(sp^3)$–H	2900 cm^{-1}

Bond	Approximate vibrational frequency
$C(sp^3)$–D	2200 cm^{-1}
$C(sp^3)$–H	2900 cm^{-1}

IR Spectrum of Butanone

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

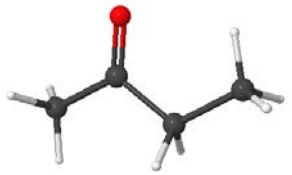


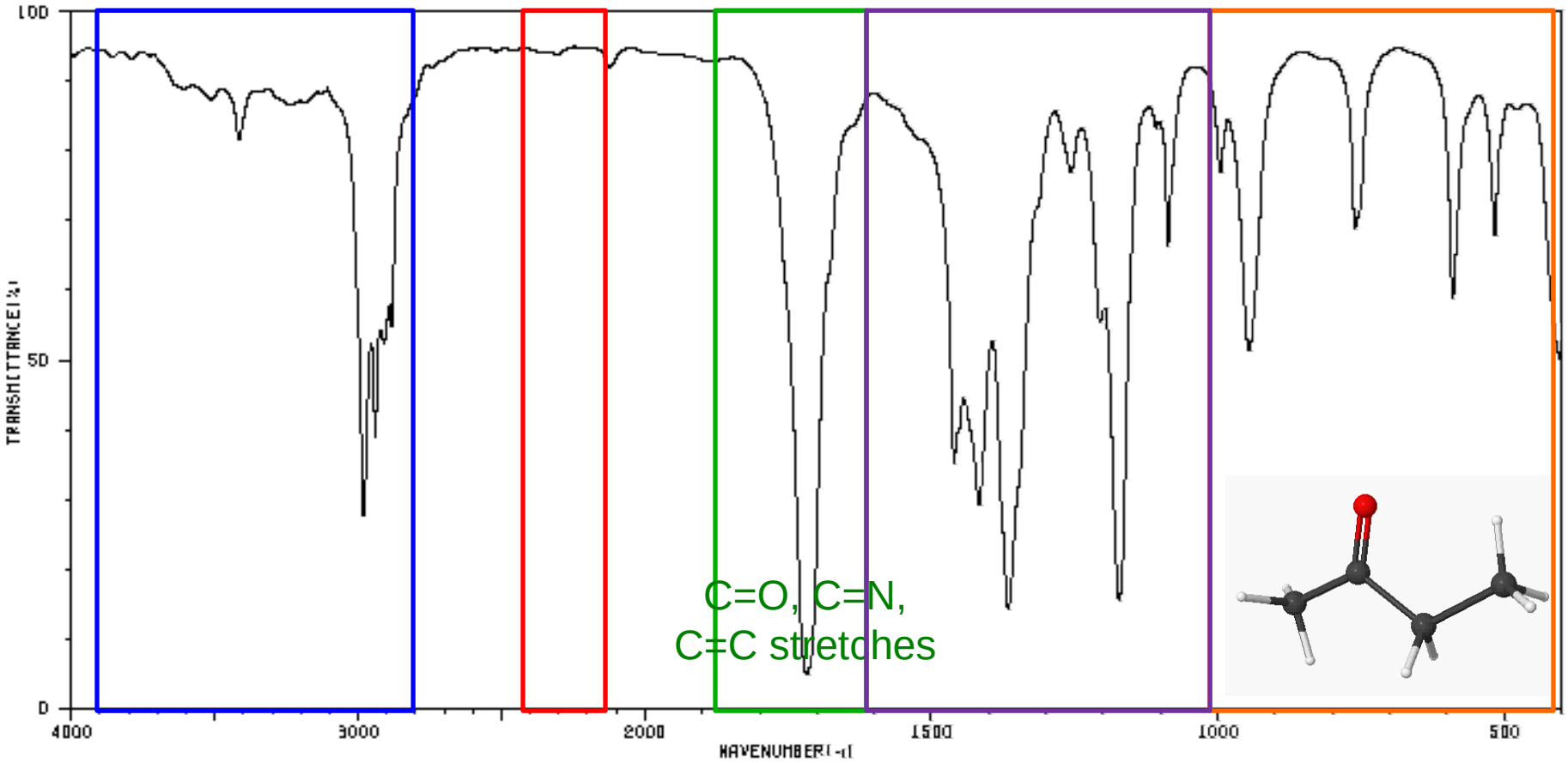


Horizontal axis in wavenumber (cm^{-1}) for most IR

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

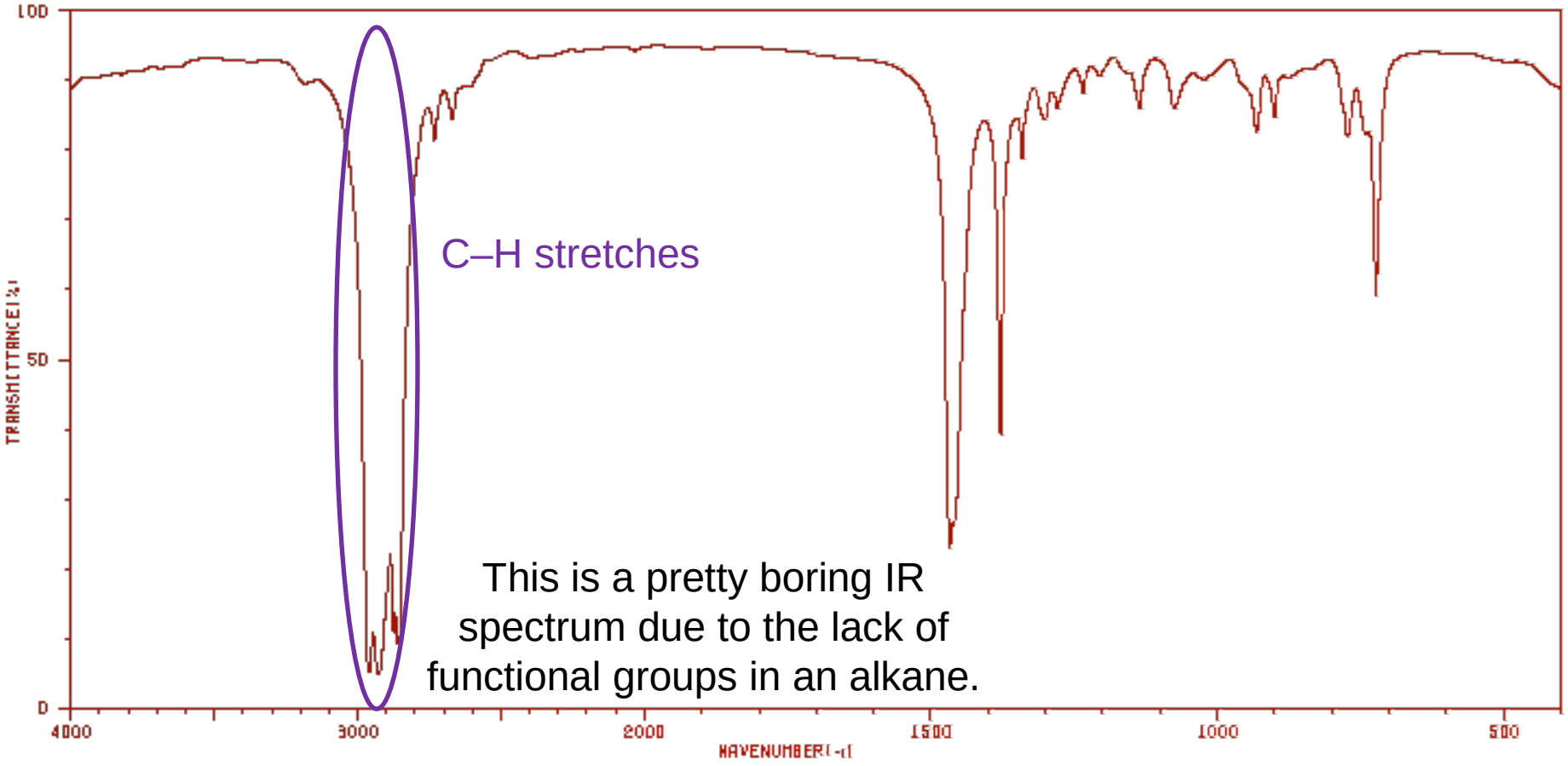
C≡N, C≡C stretches

C–O, C–N, C–C stretches and various bends

C–H bends and other low energy vibrations

Great for identifying carbonyl-containing functional groups

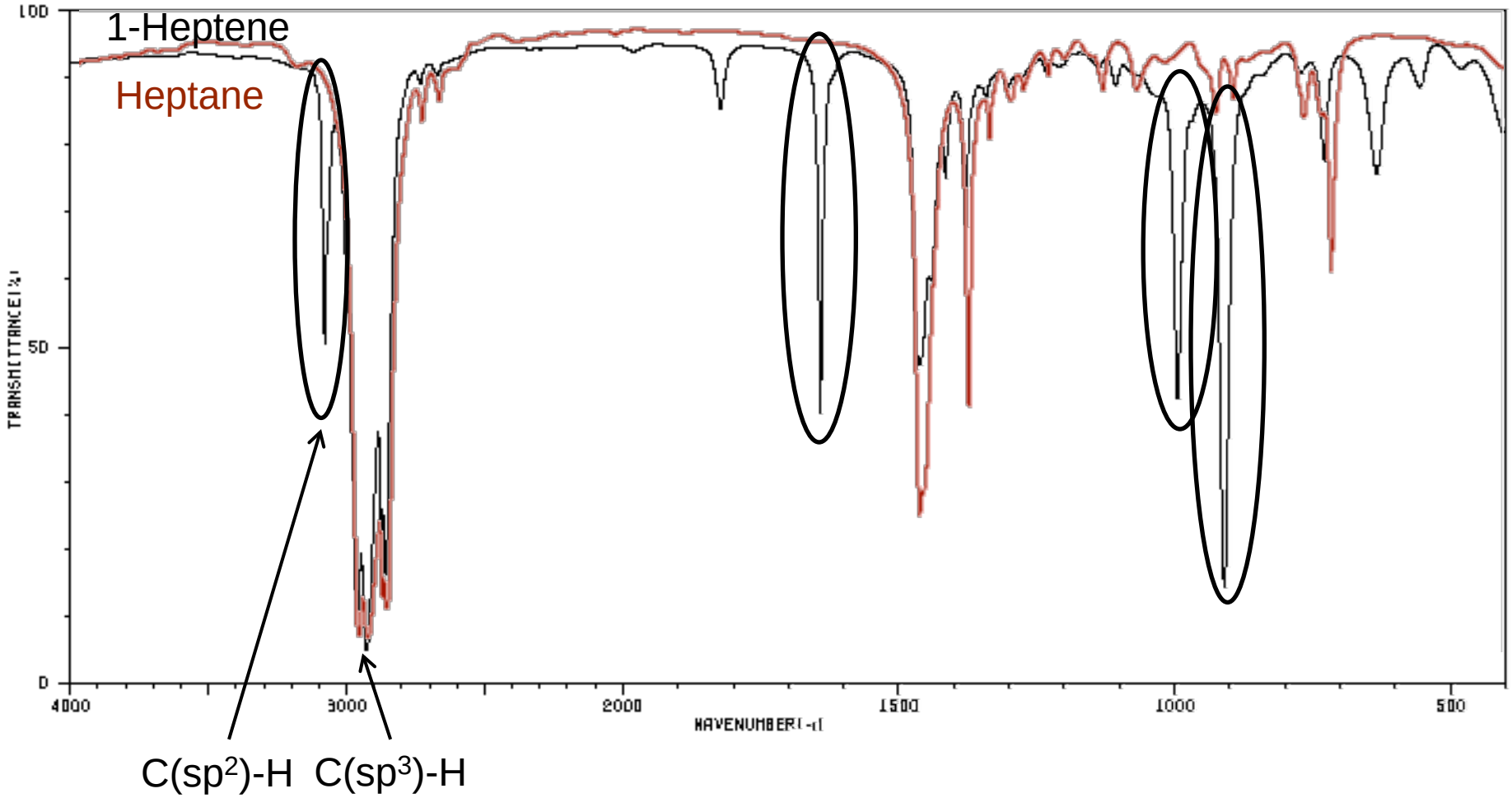
IR Spectrum of Heptane



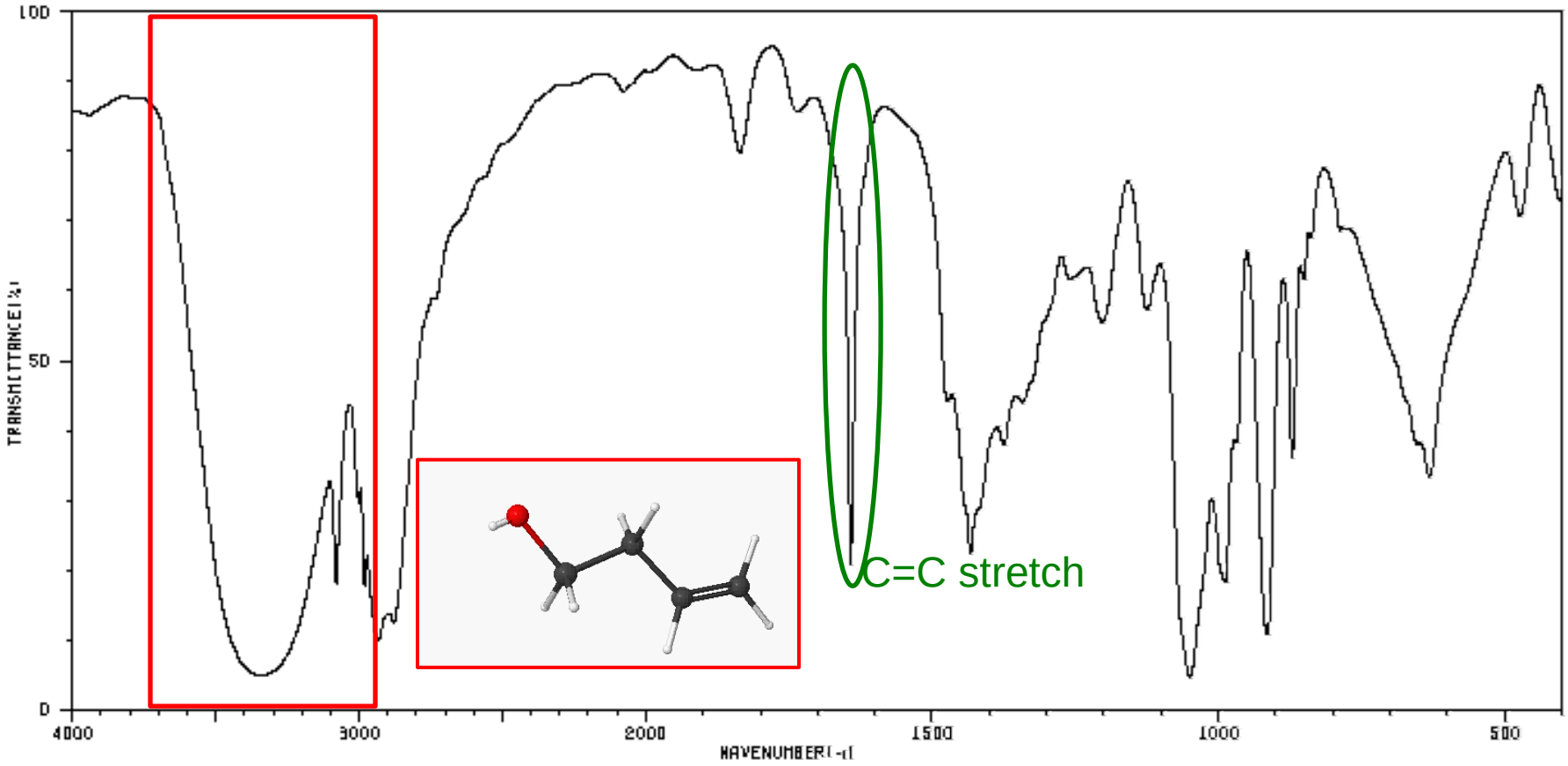
This is a pretty boring IR spectrum due to the lack of functional groups in an alkane.

This region is usually too complicated for interpretation at our level. (You can mostly ignore it.)

IR of 1-Heptene vs. Heptane



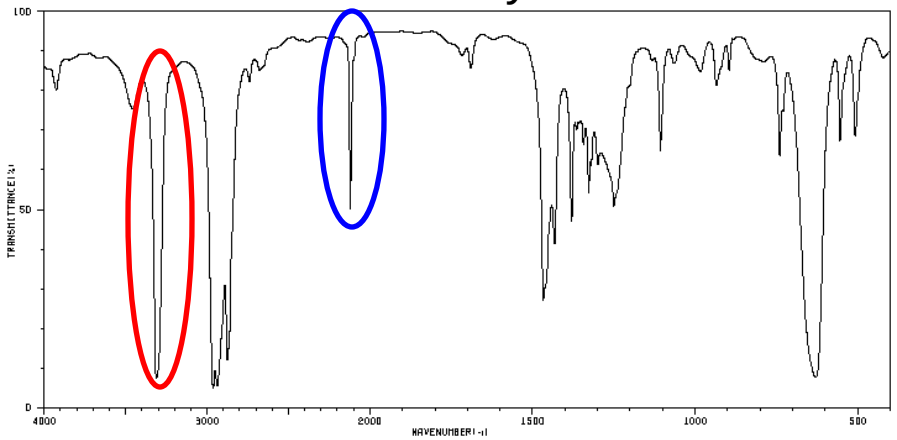
IR Spectrum of 3-buten-1-ol

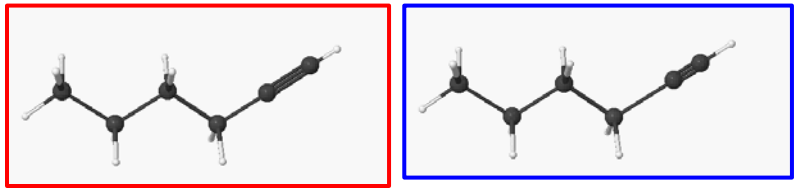


Broad and intense signals in this region are diagnostic for H-atoms connected to N or O atoms that are involved in hydrogen bonding.

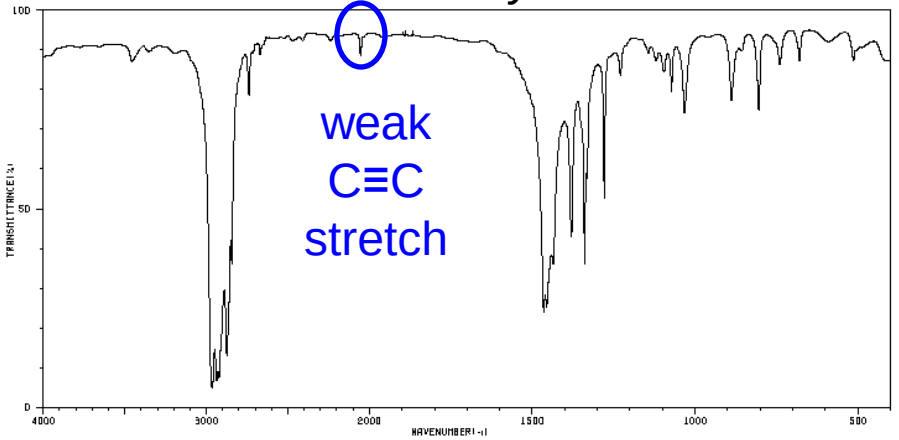
Three Isomeric Hexynes

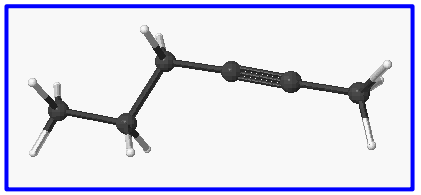
1-Hexyne



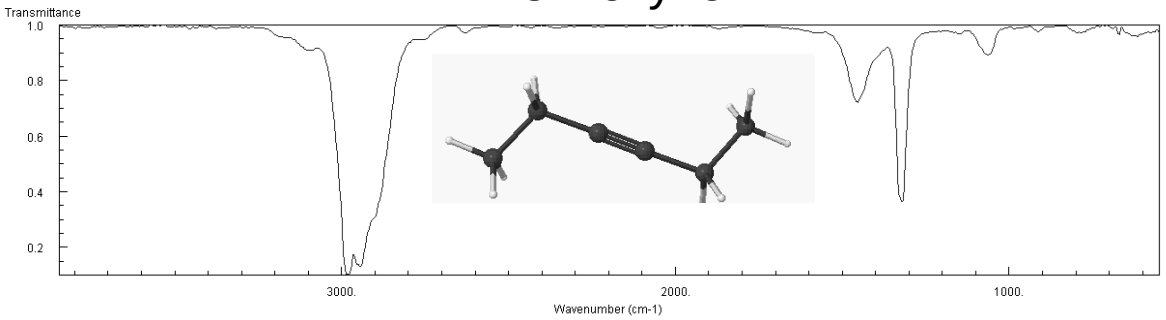


2-Hexyne





3-Hexyne



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.

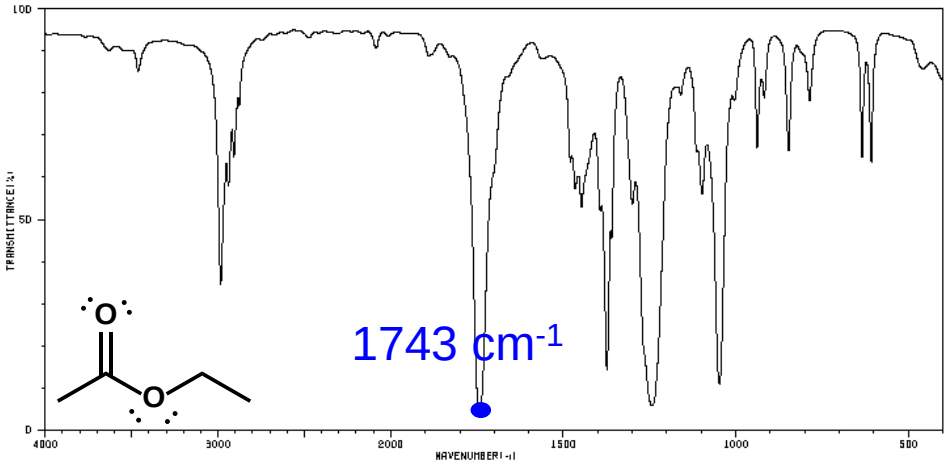
Wavenumber range, cm^{-1}	Type of absorptions	Name of region	
3400–2800	O—H, N—H, C—H stretching	Functional group	Usually very useful
2250–2100	C≡N, C≡C stretching		
1850–1600	C═O, C═N, C═C stretching		
1600–1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint	Usually complicated and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

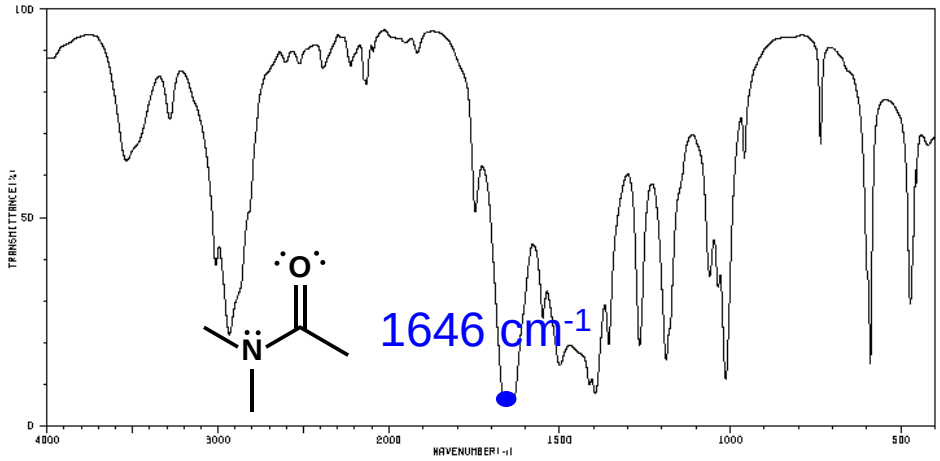
- Single bond region is great for detecting O–H or N–H stretching. Indicates the presence or absence of hydrogen-bonding.
- Triple bond region is usually clear of signals except for R–C≡N, R–C≡C–R'.
- The double bond region is often very diagnostic and can be used to tell the difference between different double bonded molecules and even different carbonyl functional groups.

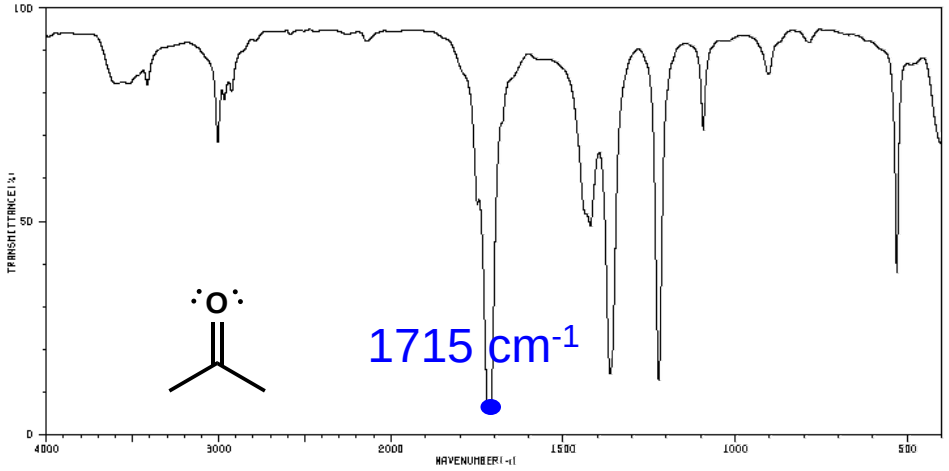
Functional Group Identification

Double Bond Stretching Vibrations

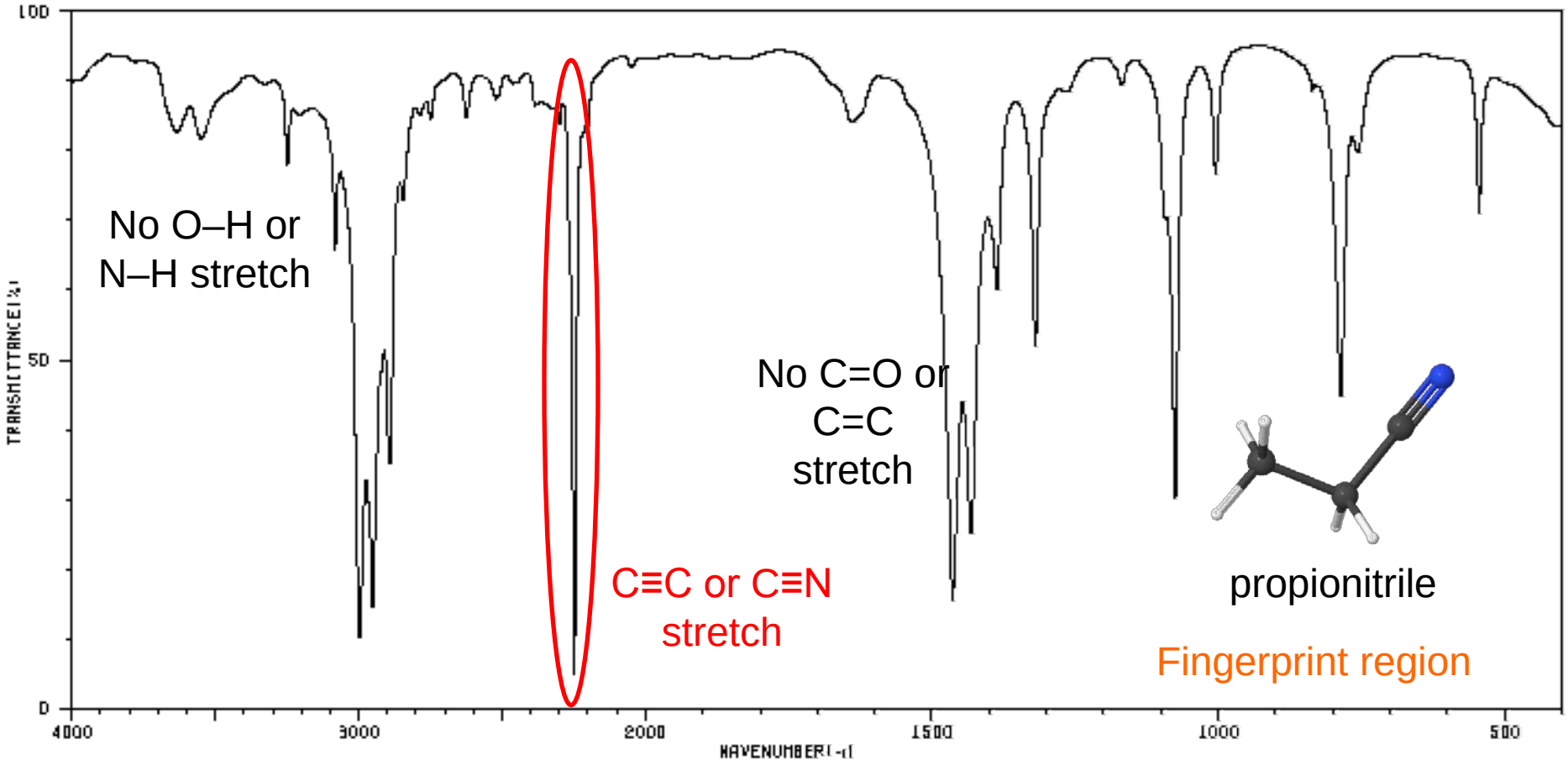
1710 cm^{-1}	Aldehyde or ketone
1680	Conjugated ketone
1745	Cyclopentanone
1780	Cyclobutanone
1730	α-Hydroxy ketone
1740	Ester
1660	Amide
1800	Acid chloride
1810 and 1760	Acid anhydride
1700	Carboxylic acid
1680-1500	C=C stretch
1675-1590	Aromatic C=C stretch



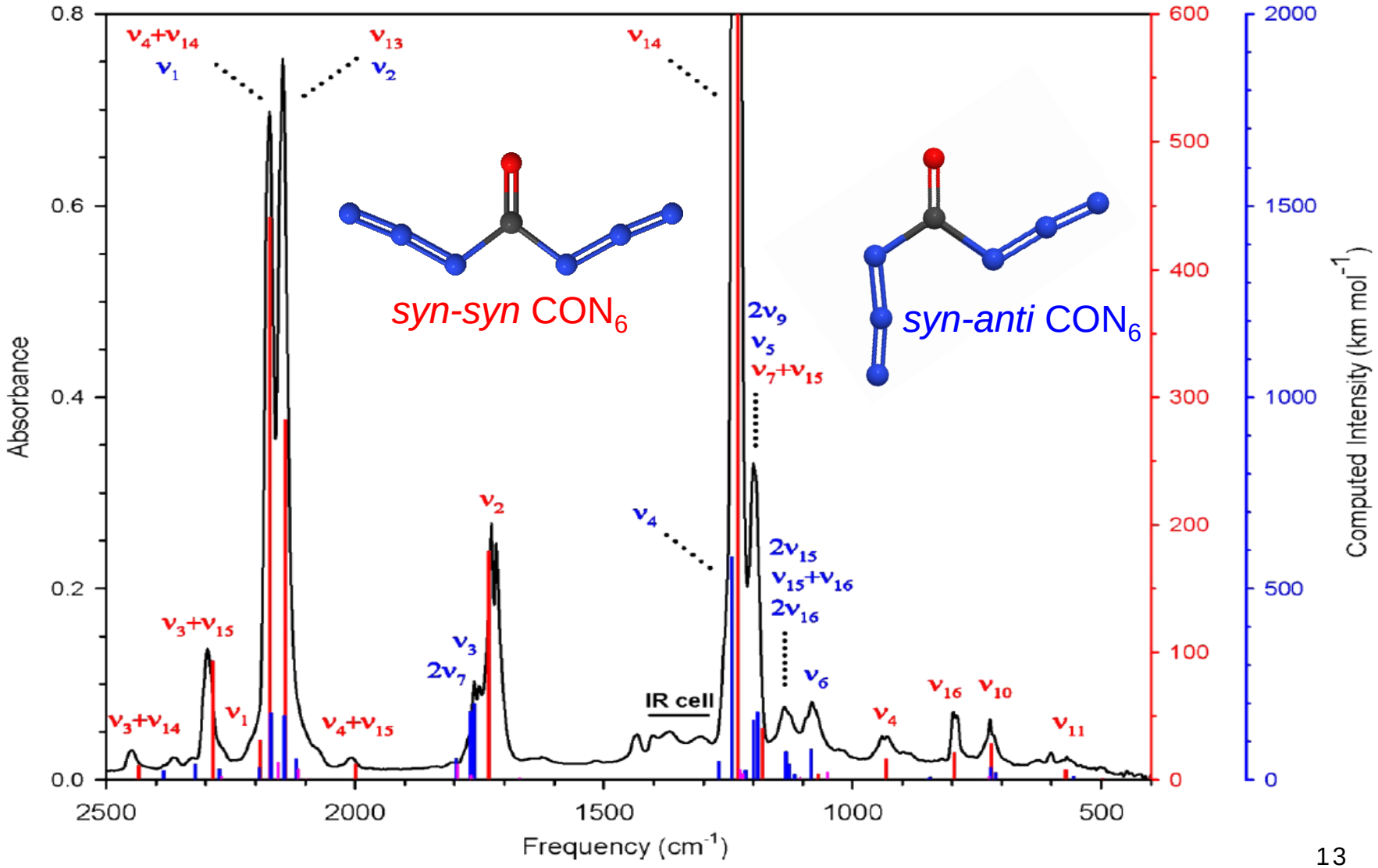




IR Spectroscopy Practice



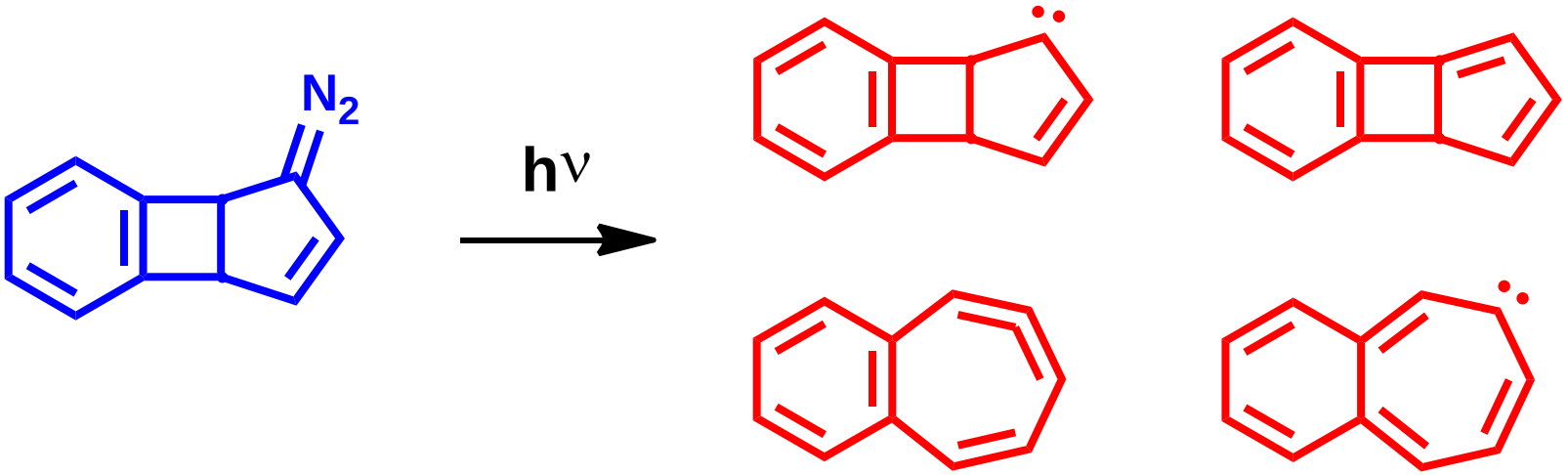
Assigned IR spectrum – CON_6



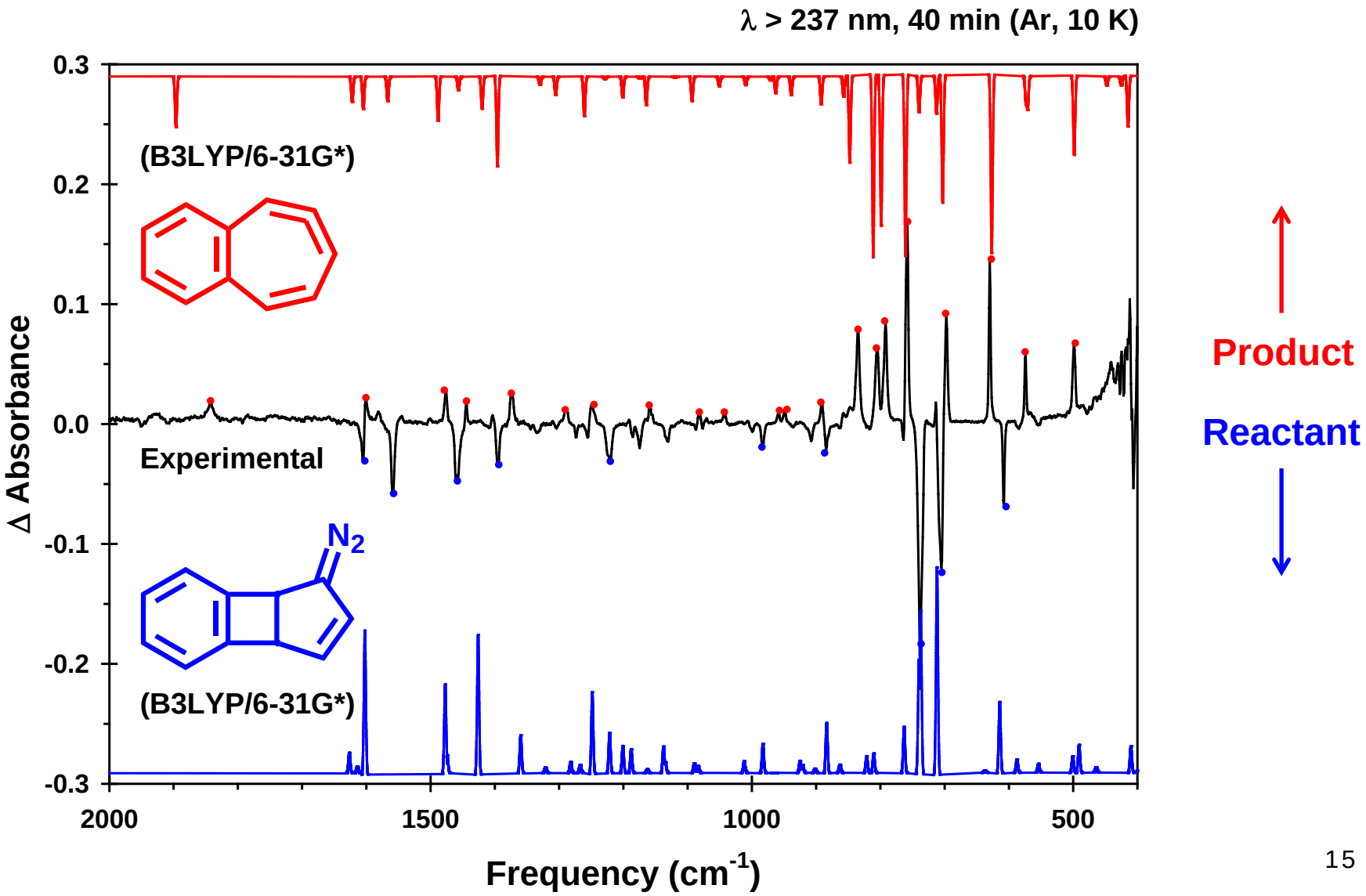
IR Spectroscopy in Photochemistry

How to determine which product is formed?

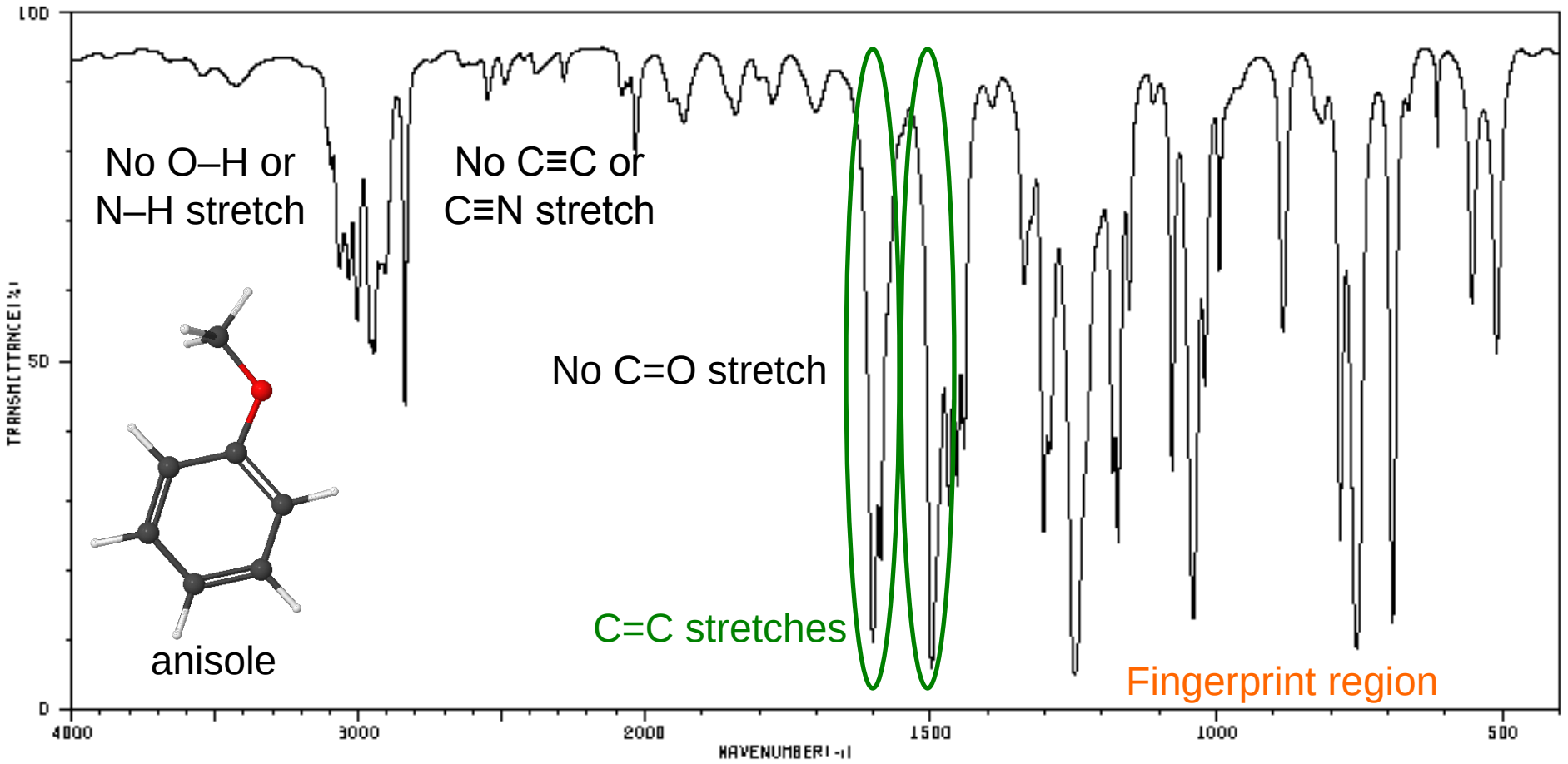
- ***Predict (calculate)*** **the IR spectrum of** ***each*** **product.**
- **Compare experimental IR spectrum to all of the computed IR spectra.**
- **A good match between experimental and computed IR spectra establishes the identity of the product.**



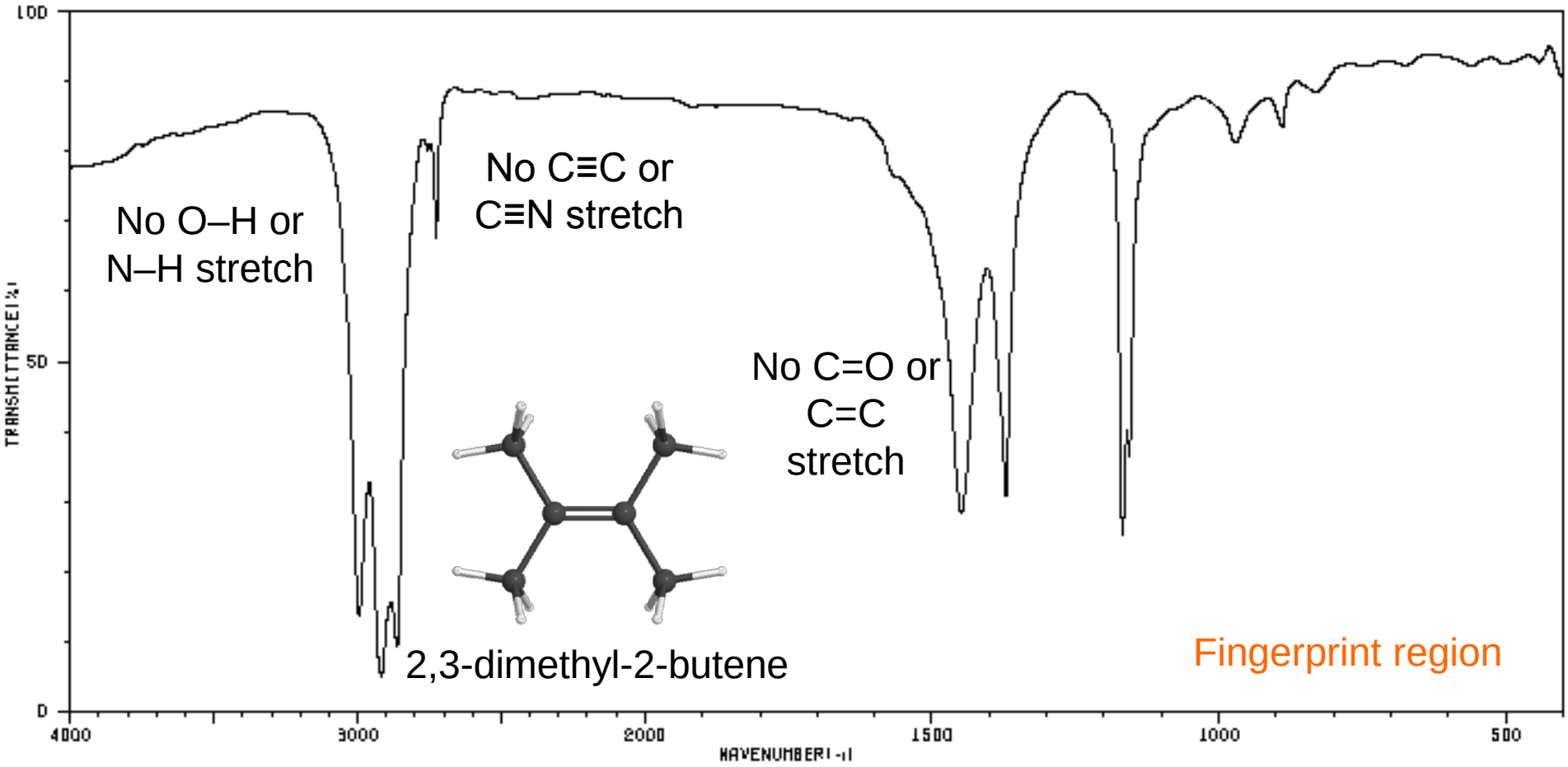
IR Spectroscopy in Photochemistry



IR Spectroscopy Practice



IR Spectroscopy Practice



IR Spectroscopy – Summary

Inf**r**ared (**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.

344 Organic Chemistry Laboratory
Spring 2013

HOW TO SURVIVE THE ORGANIC LAB

STUDENT ADVOCACY & JUDICIAL AFFAIRS
- OFFICES OF THE DEAN OF STUDENTS -

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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
- What To Do If You See Someone Cheating
- Download the complete UWS 14 policy and procedures as a .pdf file

- Information for Attorneys
- Additional Information for Faculty and Staff

Download the UWS 14 policies and procedures.

Looking for non-academic misconduct? Our non-academic misconduct page can be found here.

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.

UW-Madison Resources

UW Police
University Health Services
Counseling and Consultation Services
Office for Equity and Diversity
Visitor and Information Programs
Student Financial Services

Community Resources

Madison Police
Domestic Abuse Intervention Services
Dane County Rape Crisis Center
Tenant Resource Center
Dane County District Attorney
WI Coalition Against Sexual Assault

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