النظرية الأساسية
لطيف الأشعة تحت الحمراء

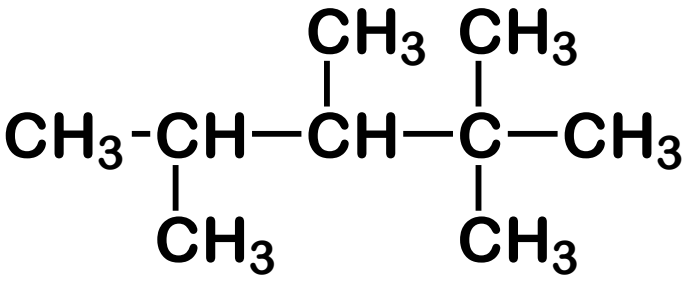
ماذا نتعلم من الصيغة الجزيئية ؟

يمكن تعيين عدد الحلقات او عدد الروابط الثنائية

الهيدروكربونات المشبعة

C_nH_{2n+2} — الصيغة العامة

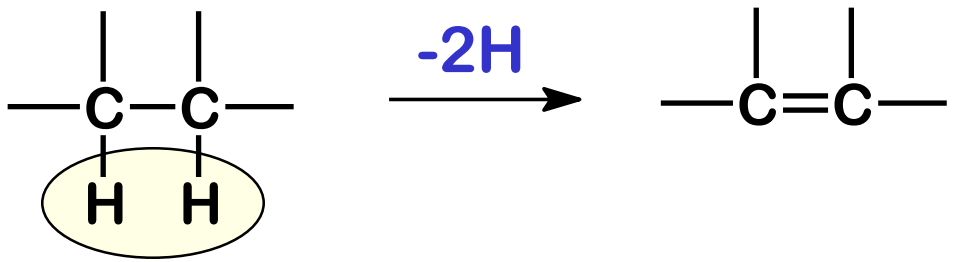
CH_4	CH_4
CH_3CH_3	C_2H_6
$CH_3CH_2CH_3$	C_3H_8
$CH_3CH_2CH_2CH_3$	C_4H_{10}
$CH_3CH_2CH_2CH_2CH_3$	C_5H_{12}

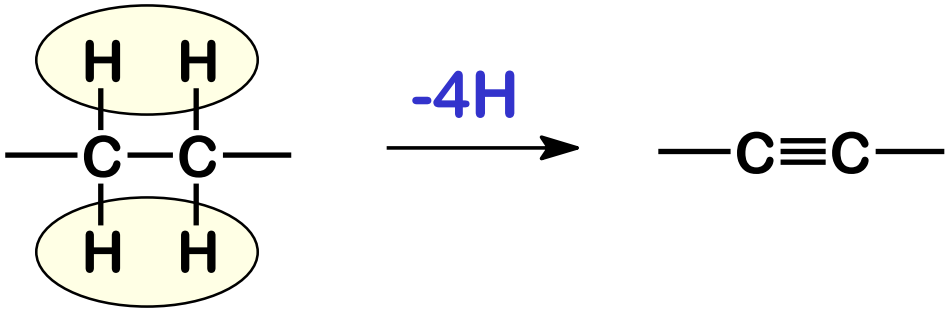


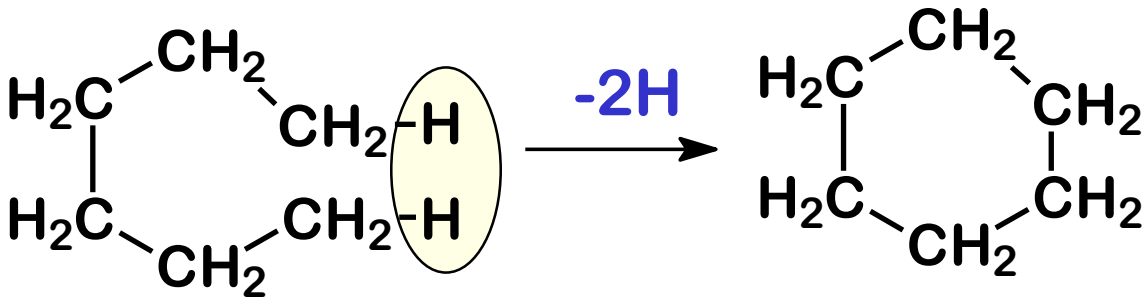
C_9H_{20}

المركبات المحتوية على فروع تتبع الصبغة .

تكوين الحلقات والروابط الثنائية





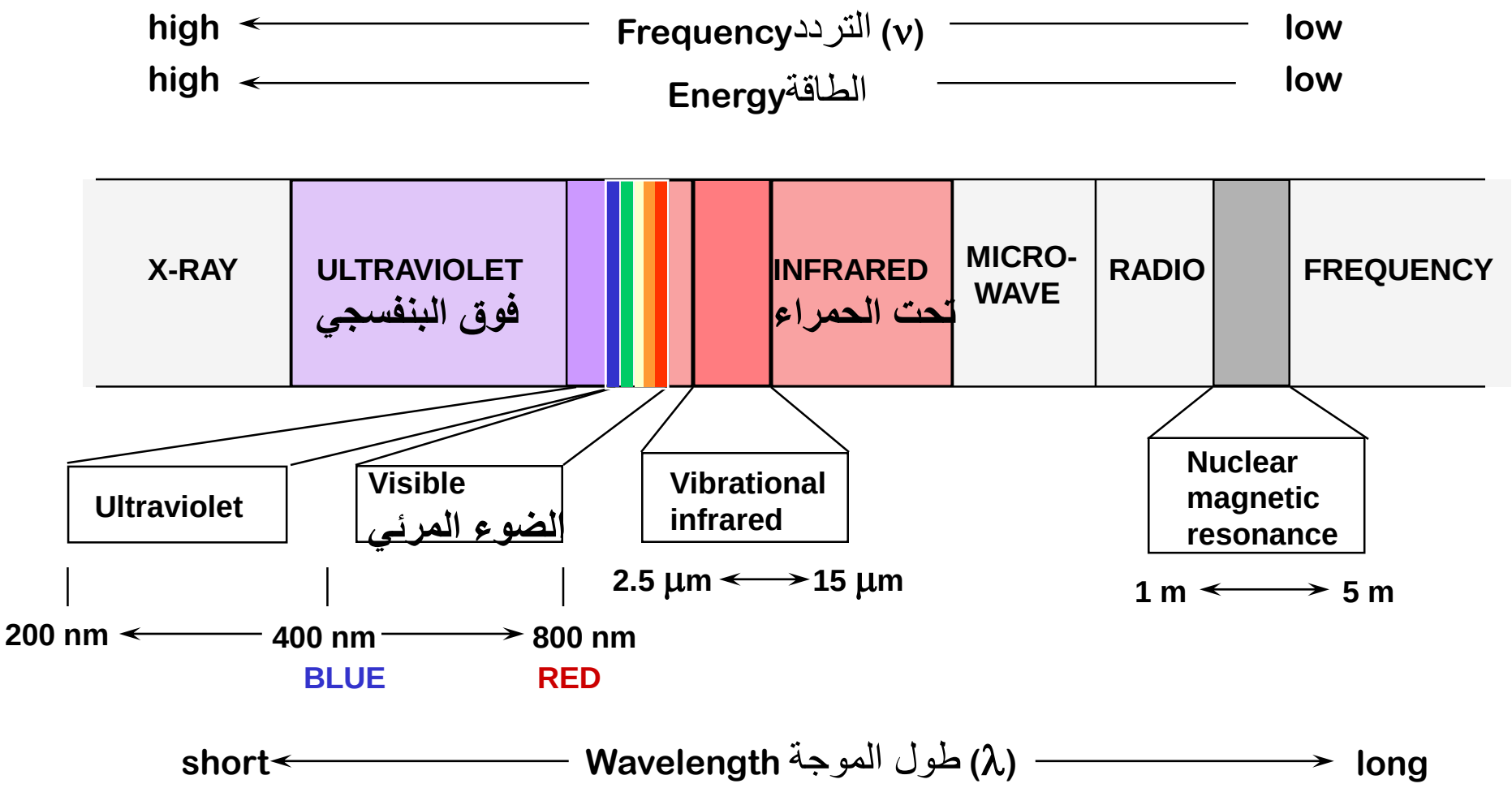


في تكوين الحلقات او الروابط الثنائية فنها تتسبب في خسارة 2هيدروجين.

طيف الأشعة تحت الحمراء

INFRARED SPECTROSCOPY

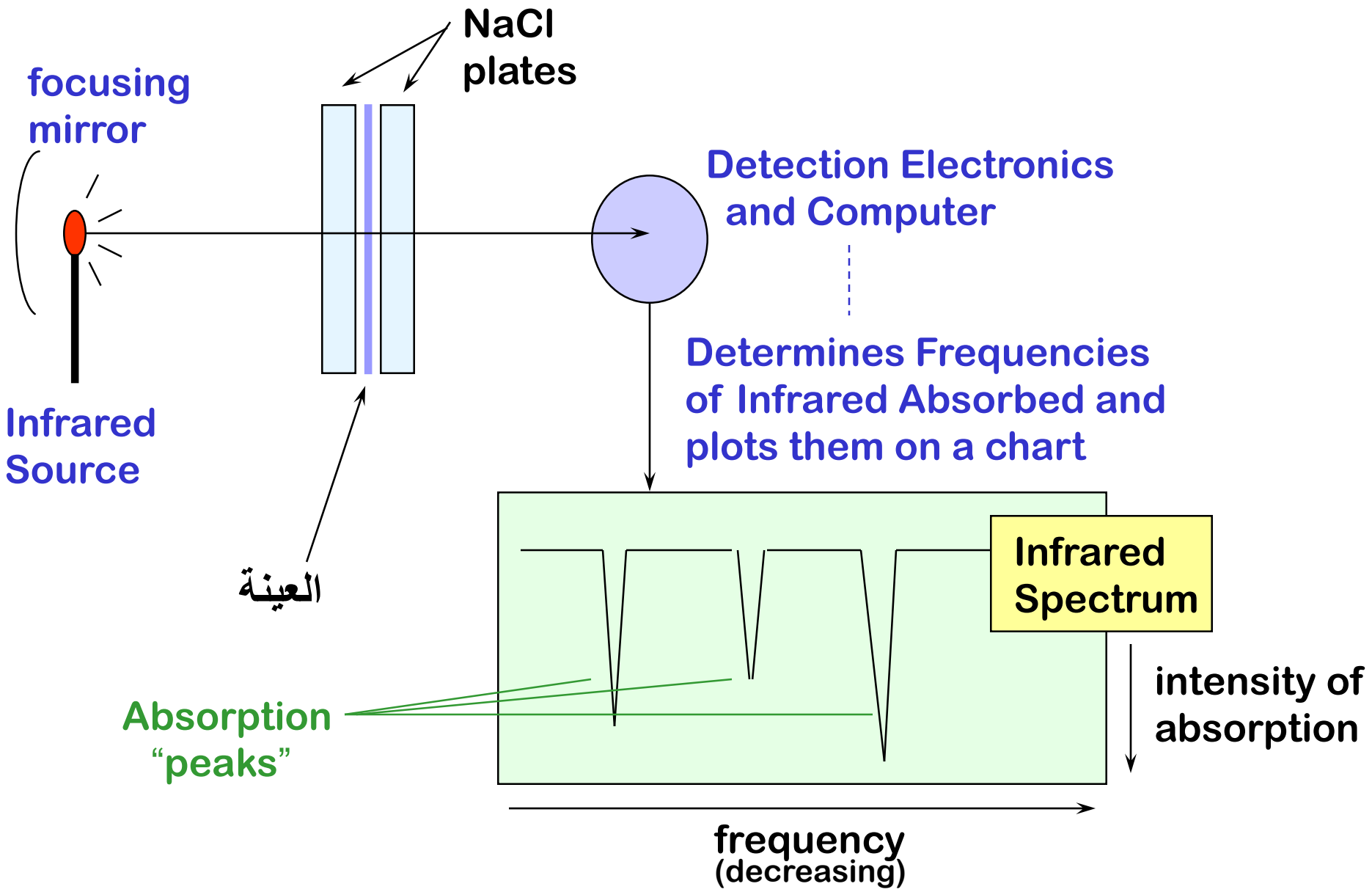
الطيف الكهرومغناطيسي



انواع الطاقة المنتقلة لكل منطقة في الطيف الكهرومغناطيسي

REGION المنطقة	ENERGY TRANSITIONS الطاقة المنتقلة
X-ray أشعة اكس	Bond-breaking كسر للرابطة
UV/Visible فوق البنفسجي-المرئي	Electronic الكترونية
Infrared تحت الحمراء	Vibrational اهتزازات
Microwave ميكروويف	Rotational دوران
Radio Frequency الراديو (NMR)	Nuclear and Electronic Spin دوران الأنوية والإلكترونات

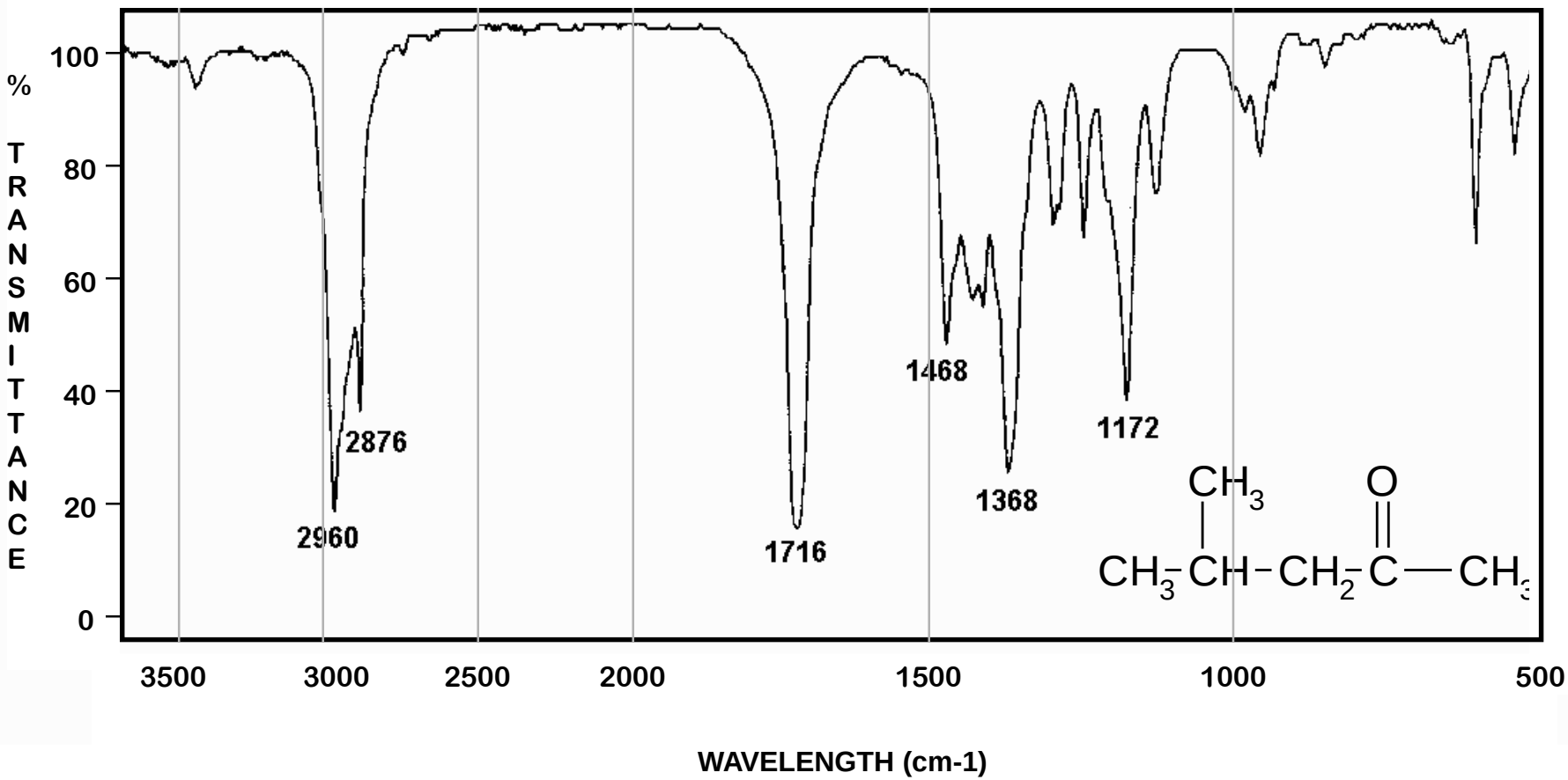
جهاز مبسط للأشعة تحت الحمراء



KETONE

4-Methyl-2-pentanone

C-H < 3000. C=O @ 1715 cm^{-1}



AN INFRARED SPECTRUM

الوحدات المستخدمة في طيف الأشعة تحت الحمراء

WAVENUMBERS العدد الموجي ($\bar{\nu}$)

$\bar{\nu}$ = wavenumbers (cm^{-1})

$$\bar{\nu} = \frac{1}{\lambda(cm)}$$

λ = wavelength طول الموجة (cm)

ν = التردد frequency = $\bar{\nu}c$

c = speed of light

c = 3×10^{10} cm/sec

or

$$\nu \left(= \frac{1}{\lambda}\right) c = \frac{c}{\lambda}$$

$$\frac{cm/sec}{cm} = \frac{1}{sec}$$

يتناسب العدد الموجي طرديا مع التردد

- تحول الأطوال الموجية المعبر عنها بالميكرون الى العدد الموجي بالمعادلة التالية :

$$\nu = \frac{10^4}{\lambda}$$

طاقة الإشعة تحت الحمراء (20000-800nm)

- لا تكفي لإحداث اثارة الكترونية في معظم المركبات العضوية الا انها كافية لإحداث اهتزازات امتطاط (stretching) واثناء (bending) في الروابط .
- وتستجيب جميع انواع الروابط في المركبات العضوبة لتحدث فيها اهتزازات من هذا القبيل .
- لذلك تمتص في منطقة الضوء تحت الحمراء بشرط أن يؤدي الإمتصاص الى تغير في العزم القطبي

Molecular vibrations

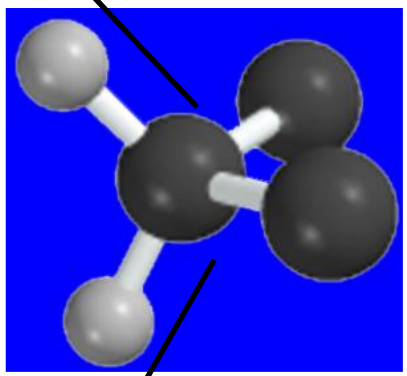
الإهتزازات الجزيئية

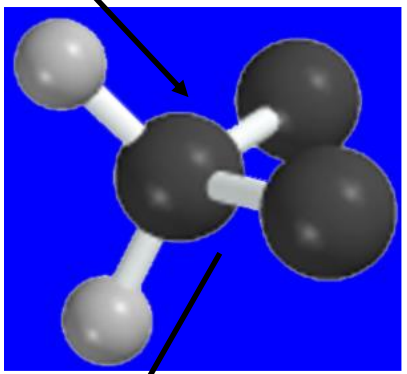
Two major types :

STRETCHING

Symmetric

Antisymmetric



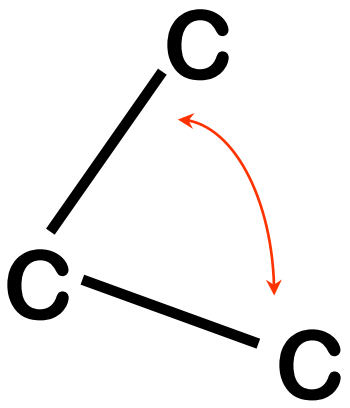


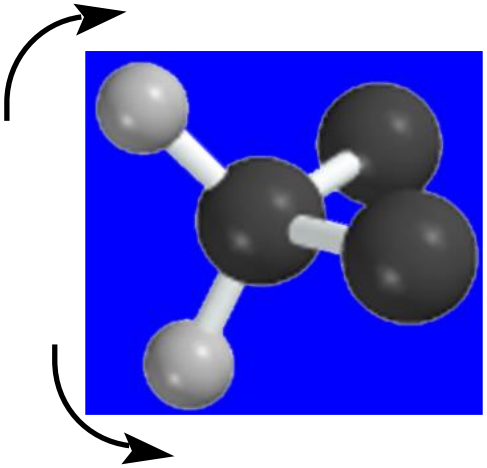
both of these types are “infrared active”
(excited by infrared radiation)

الإهتزازات الجزيئية

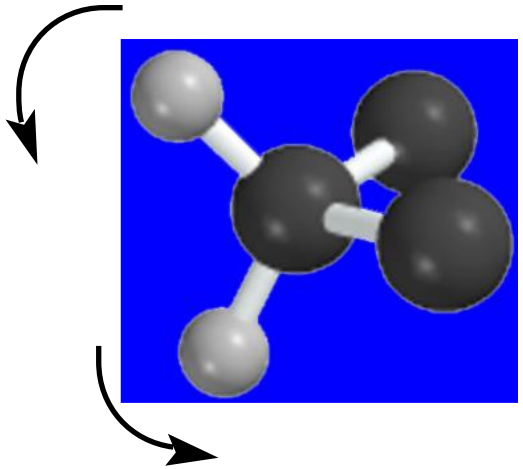
Two major types :

BENDING





In plane



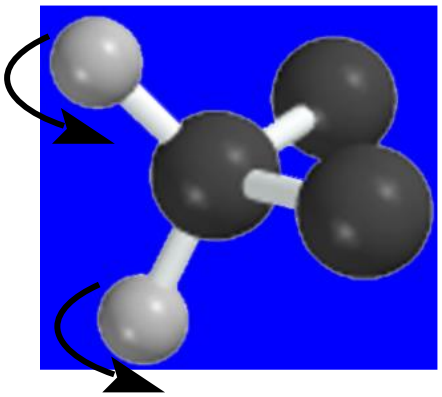
In plane

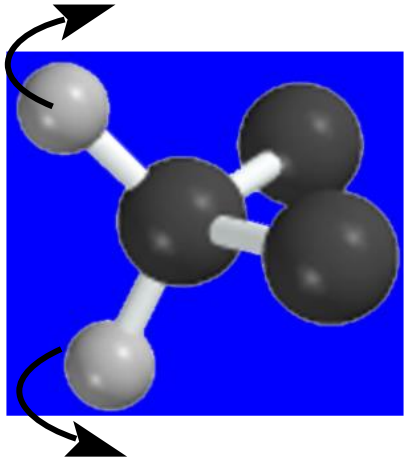
الإهتزازات الجزيئية

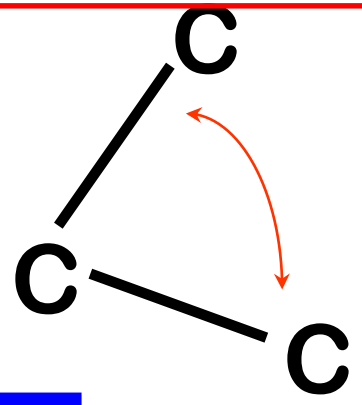
Bending Vibrations of a CH_2 Group

انثناء

BENDING







Out of plane

Out of plane

- ولكثرة ما في الجزيئات من انواع الروابط ولتعدد طرق اهتزازاتها فإن طيف IR يحتوي في العادة على عدد كبير من الإمتصاصات كما يحصل بينها كثير من التداخلات .
- ولذلك فالمختصون يتوصلون الى قدر كبير من المعلومات ولكنهم يكتفون بالتعرف على امتصاصات المجموعات الوظيفية الشهيرة .
- وبعض انماط الإستبدال على الروابط المزدوجة او الحلقات الأروماتية .
- ولذلك اعدت جداول خاصة يستعان بها لهذا الغرض .

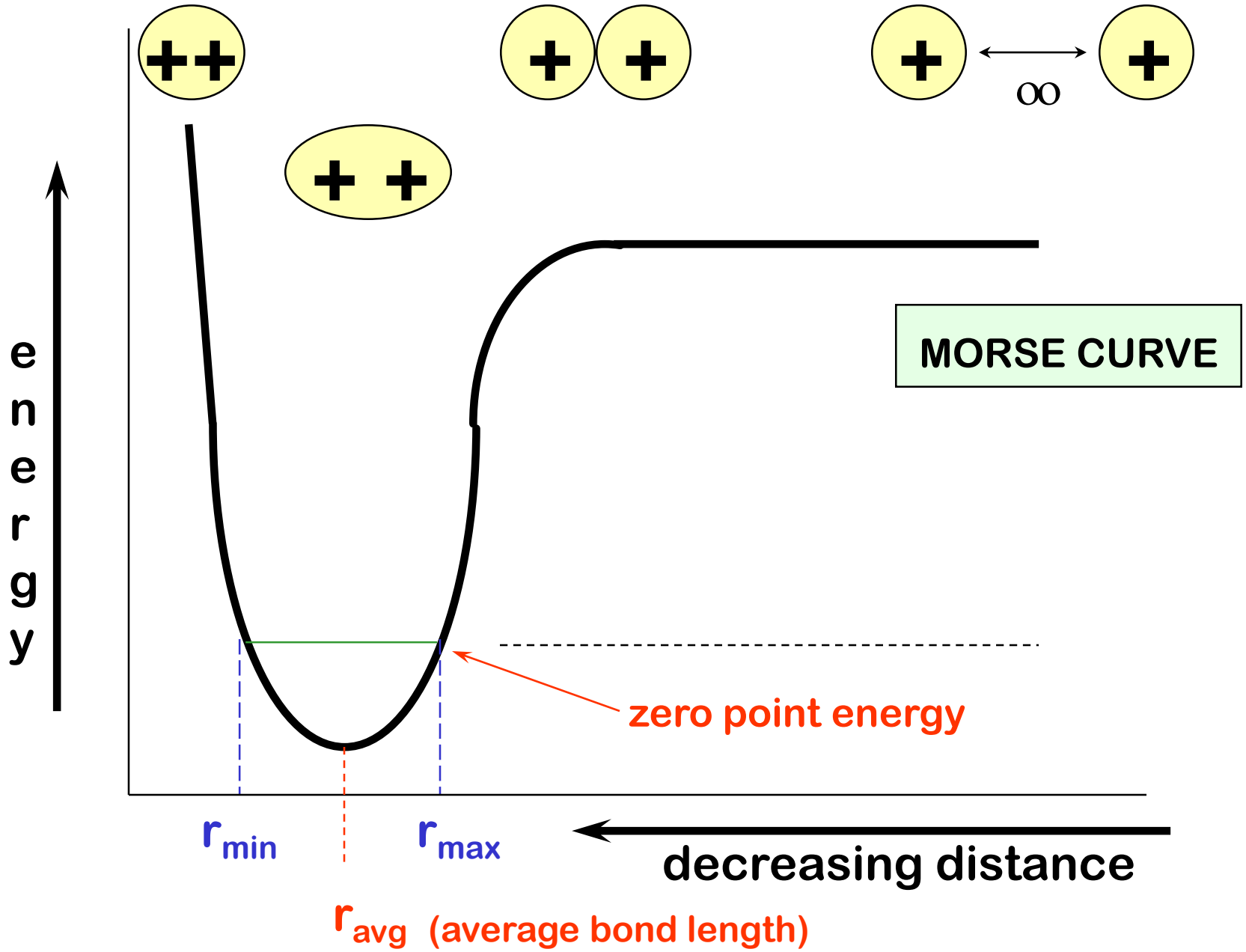
منحنى الرابطة والإهتزازات

منحنى مورس

التمدد

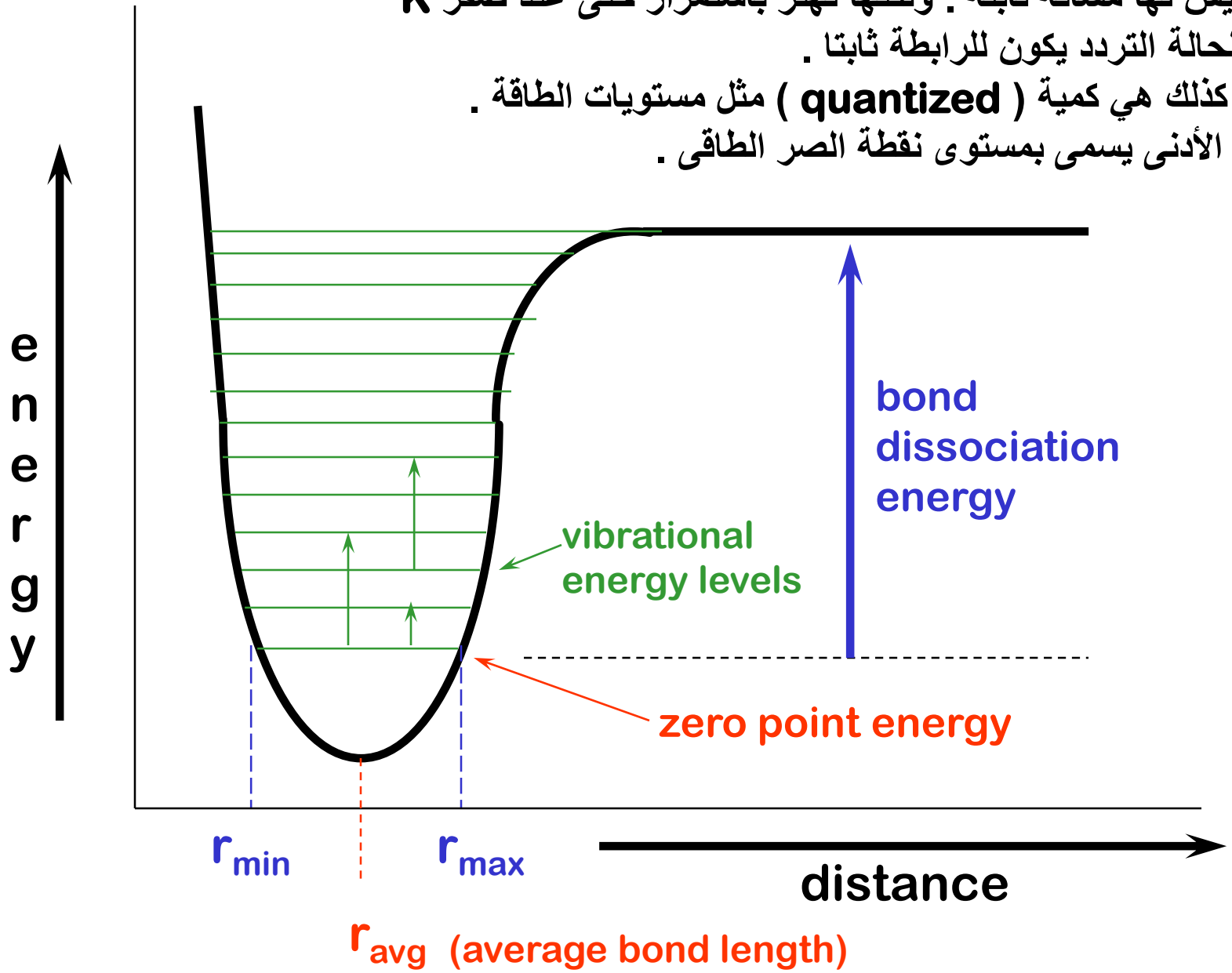
STRETCHING

مستويات الطاقة لإهتزازات الرابطة

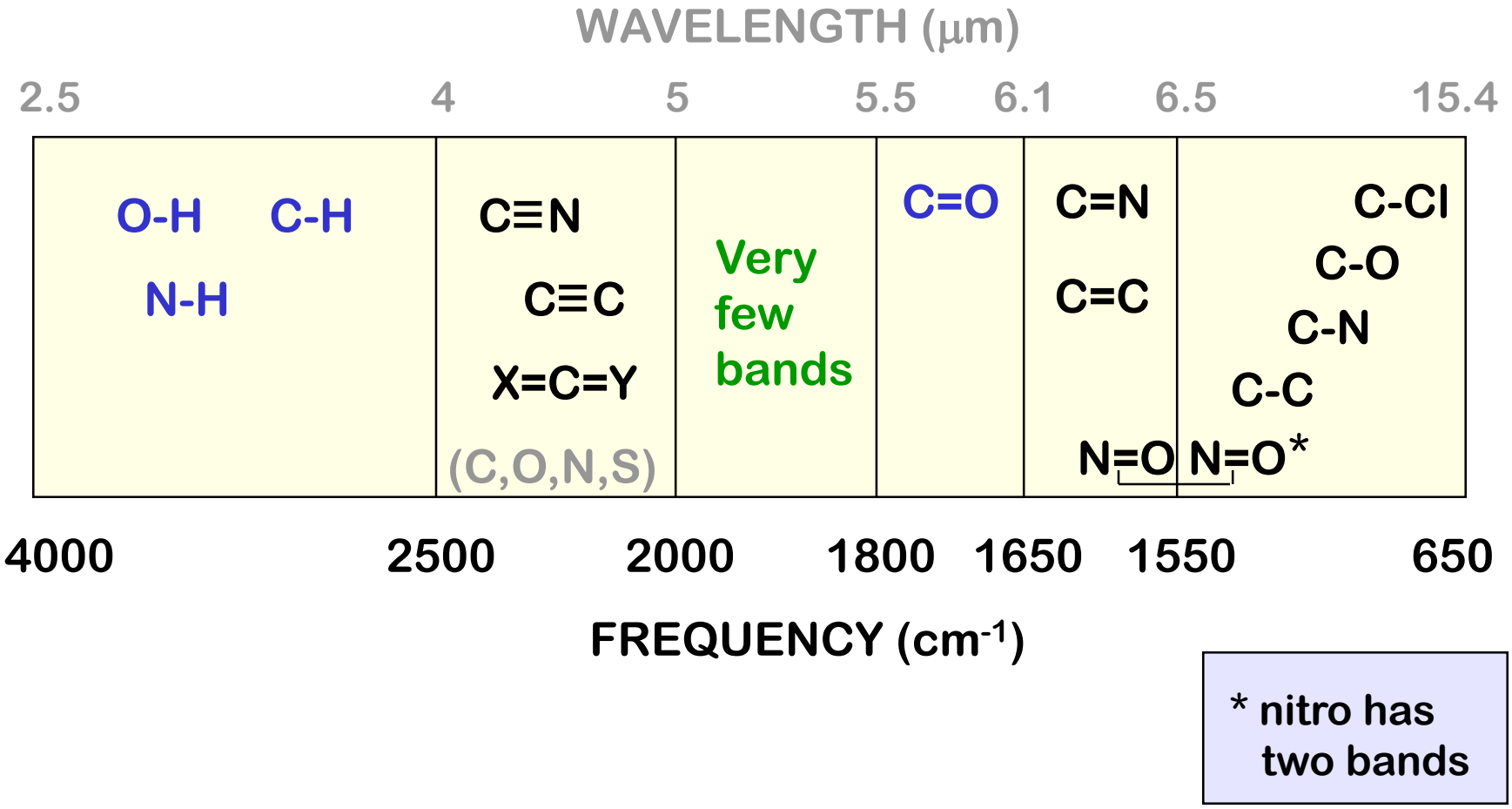


مستويات الطاقة لإهتزازات الرابطة

الروابط ليس لها مسافة ثابتة . ولكنها تهتز باستمرار حتى عند صفر K
في هذه الحالة التردد يكون للرابطة ثابتا .
الترددات كذلك هي كمية (quantized) مثل مستويات الطاقة .
المستوى الأدنى يسمى بمستوى نقطة الصر الطاقى .



مناطق الإمتصاص لطيف الإشعة تحت الحمراء
الأهتزازات التمددية
(stretching vibrations)

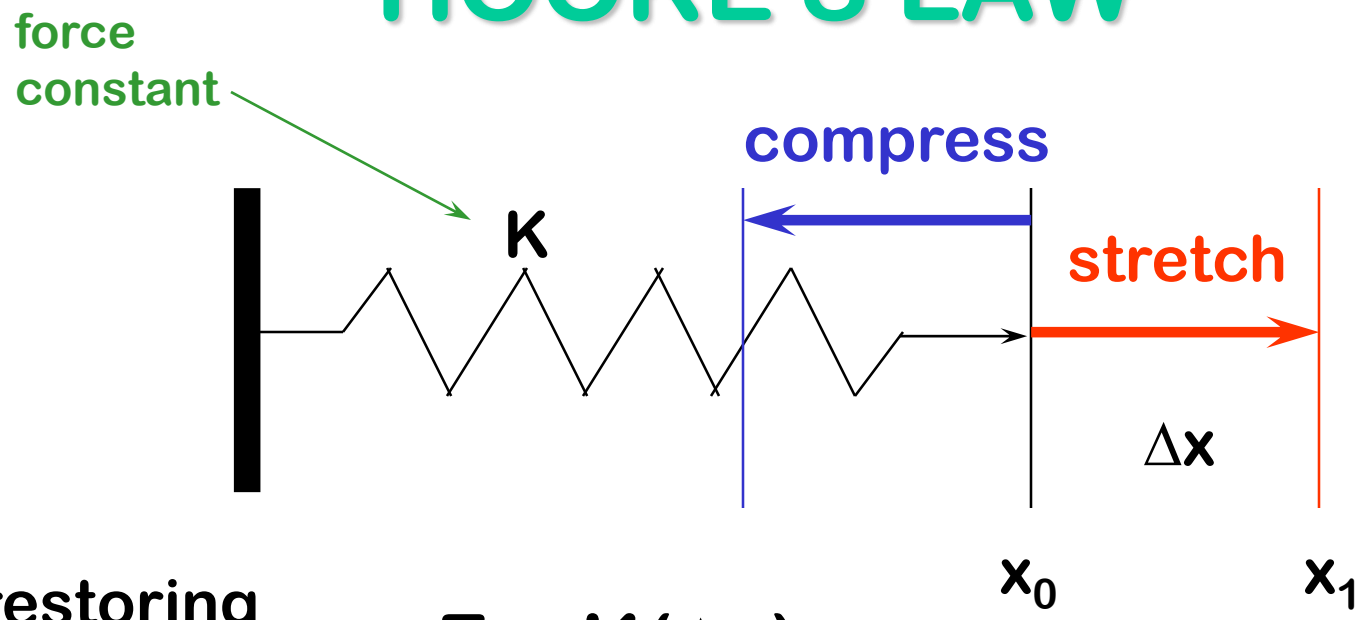


HARMONIC OSCILLATOR

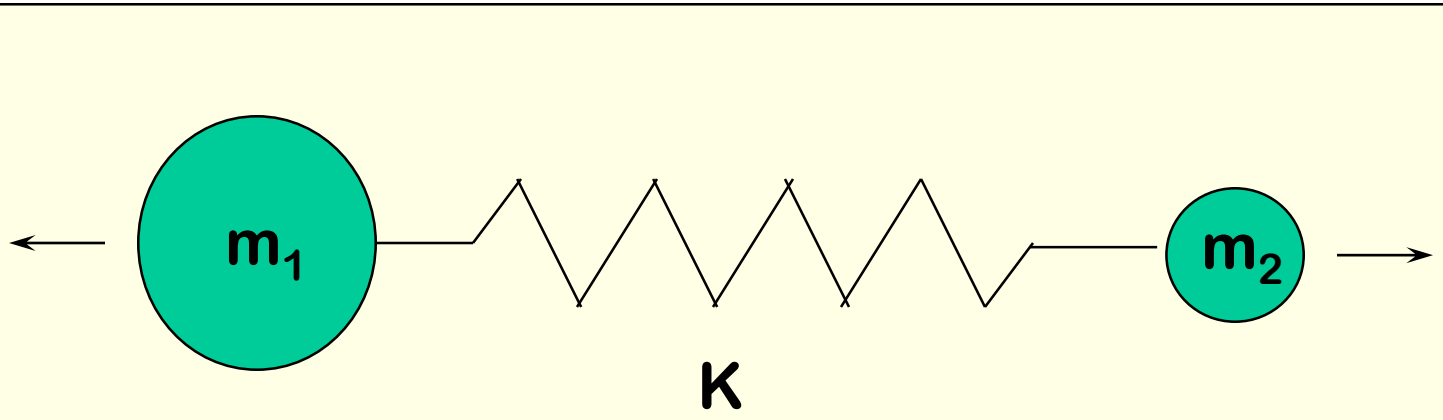
MATHEMATICAL DESCRIPTION OF THE VIBRATION IN A BOND

…. assumes a bond is like a spring

HOOKE'S LAW

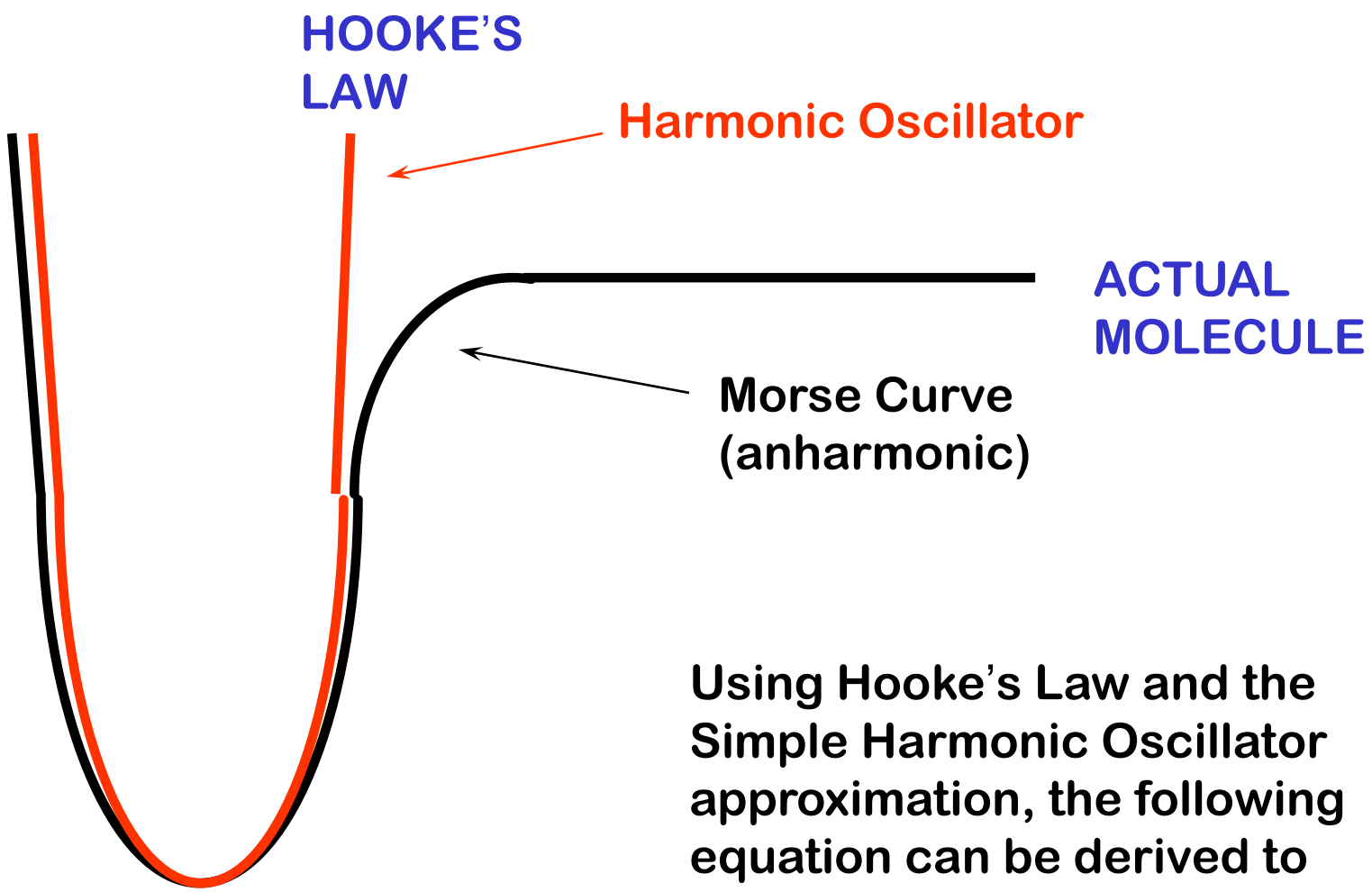


restoring force = $-F = K(\Delta x)$



Molecule as a Hooke's Law device

THE MORSE CURVE APPROXIMATES AN HARMONIC OSCILLATOR



Using Hooke's Law and the Simple Harmonic Oscillator approximation, the following equation can be derived to describe the motion of a bond…..

THE EQUATION OF A SIMPLE HARMONIC OSCILLATOR

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

This equation describes the vibrations of a bond.

$\bar{\nu}$ = frequency in cm^{-1}

c = velocity of light (3×10^{10} cm/sec)

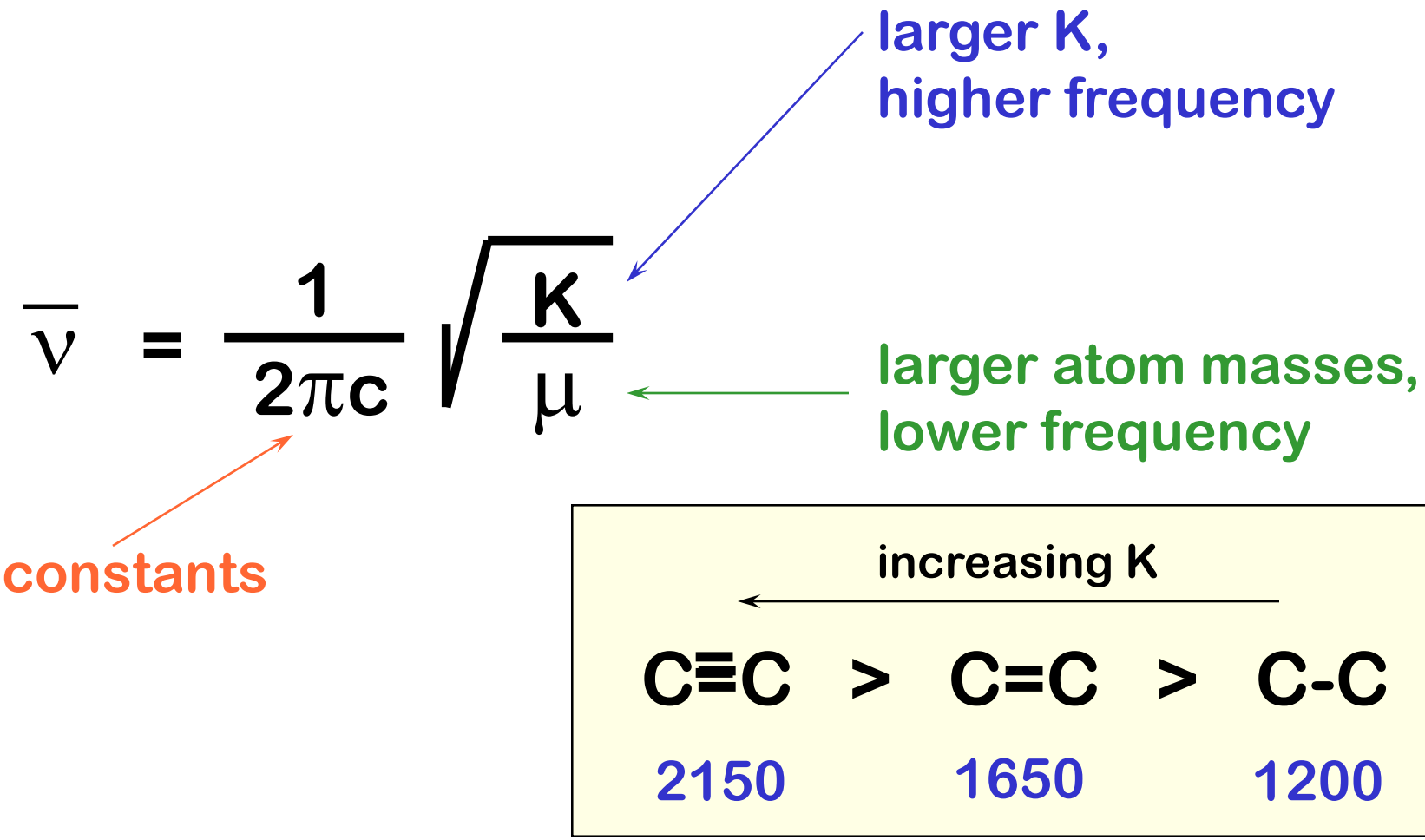
K = force constant in dynes/cm

C≡C > C=C > C—C

multiple bonds have higher K's

m = atomic masses

μ = reduced mass


larger K,
higher frequency
$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$
larger atom masses,
lower frequency
constants
increasing K
C≡C > C=C > C-C
2150 1650 1200
increasing μ
C-H > C-C > C-O > C-Cl > C-Br
3000 1200 1100 750 650

العزم القطبي

DIPOLE MOMENTS

العزم القطبي

فقط الروابط والتي لها عزم قطبي ملحوظ تستطيع امتصاص الأشعة تحت الحمراء

الروابط والتي لا تمتص الشعة تحت الحمراء تتكون من :

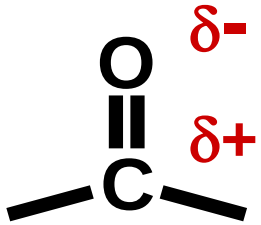
- **Symmetrically substituted alkenes and alkynes**

- **Many types of C-C Bonds**
- **Symmetric diatomic molecules**

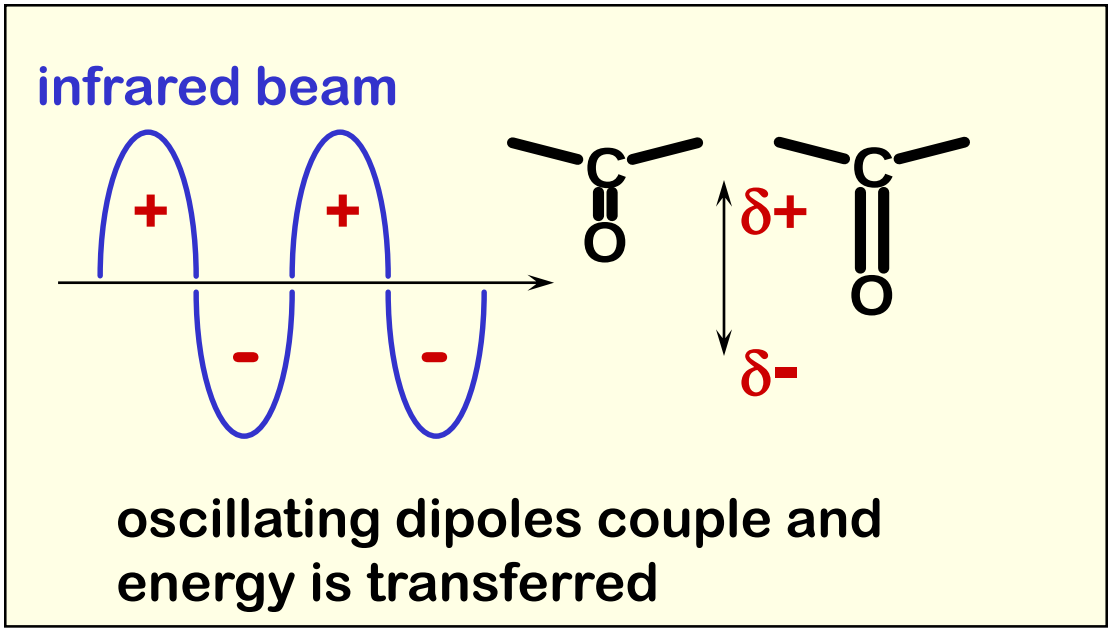
H-H Cl-Cl

STRONG ABSORBERS

The carbonyl group is one of the strongest absorbers



Also O-H and C-O bonds



RAMAN SPECTROSCOPY

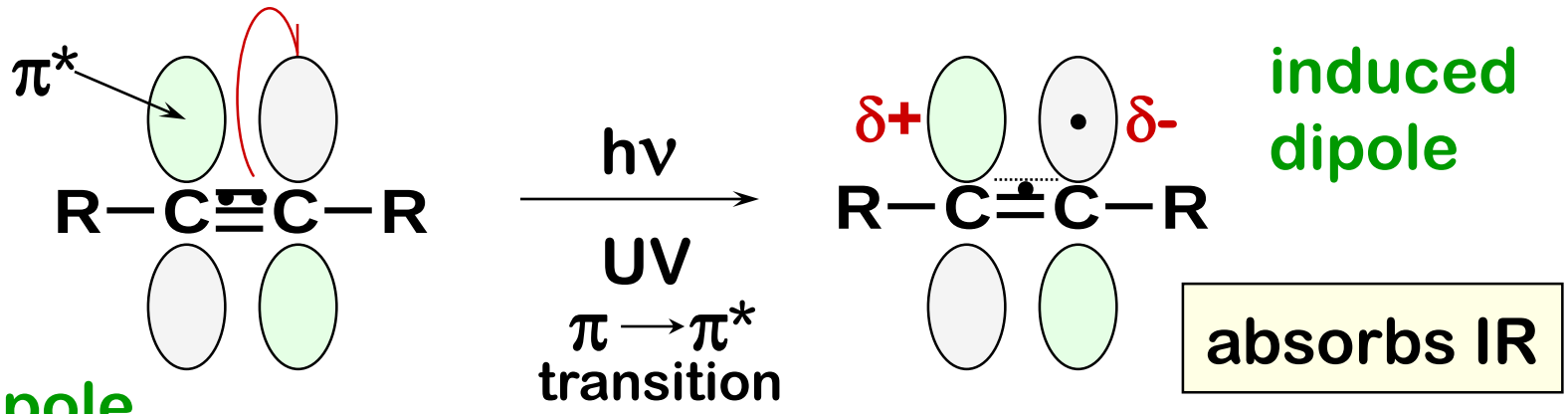
Another kind of vibrational spectroscopy that can detect symmetric bonds.

Infrared spectroscopy and Raman spectroscopy complement each other.

RAMAN SPECTROSCOPY

في هذا النوع يتم تعريض المركب لإشعاع من نوع فوق البنفسجي قوي
في نفس الوقت يتم نعريضه للأشعة تحت الحمراء والتي يتم فيها الأمتصاص

Ultraviolet light promotes electrons from bonding orbitals into antibonding orbitals. This causes formation of a dipole in groups that were formerly IR inactive and they will absorb infrared radiation.



….. we will not talk further about this technique

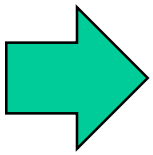
SUGGESTED SOFTWARE

IR TUTOR

- Select *ChemApps* folder
- Select *Spectroscopy* icon
- Select *IR Tutor* icon

IR TUTOR ACTUALLY ILLUSTRATES INFRARED VIBRATIONS AND THEORY WITH ANIMATIONS

HYDROCARBONS
(C-H ABSORPTIONS)
ALCOHOLS
ACIDS
(O-H ABSORPTIONS)
AMINES
(N-H ABSORPTIONS)



O-H 3600
N-H 3400
C-H 3000

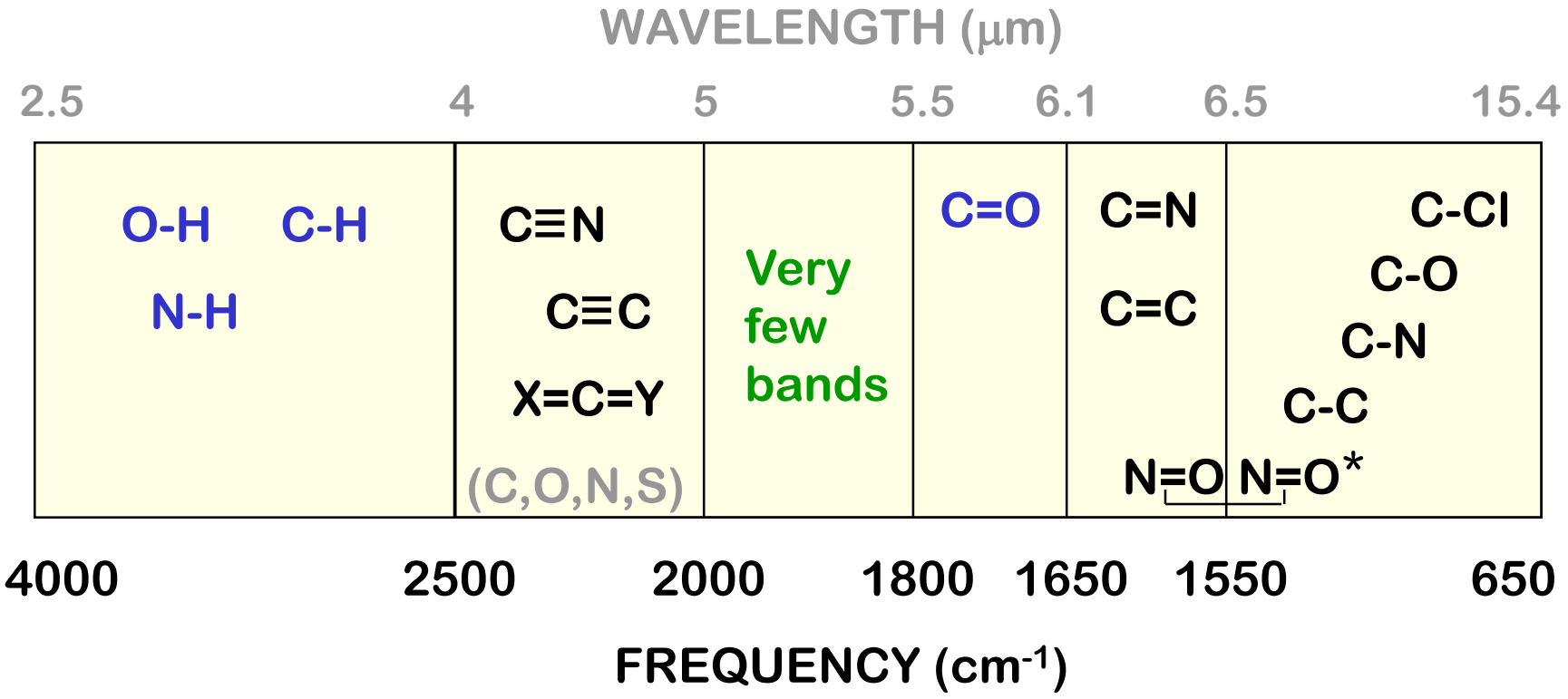
C≡N 2250
C≡C 2150

C=O 1715
C=C 1650

C-O 1100

SURVEY OF SPECTRA

Typical Infrared Absorption Regions



BASE VALUES

Guideposts for you to memorize.

BASE VALUES

(+/- 10 cm^{-1})

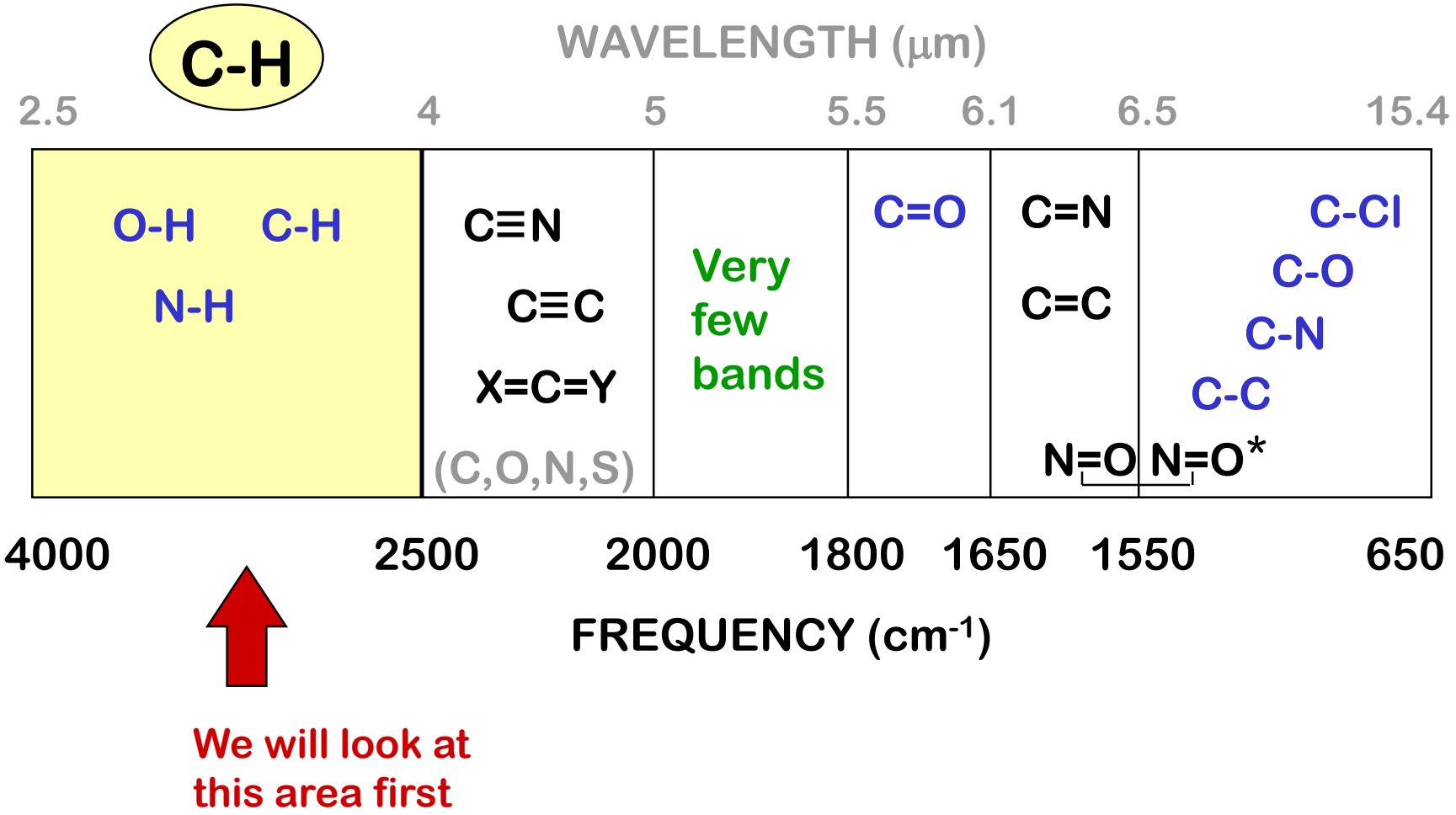
These are the minimum number of values to memorize.

O-H	3600
N-H	3400
C-H	3000
C≡N	2250
C≡C	2150
C=O	1715
C=C	1650
C−O	~1100

large range

C-H STRETCH

Typical Infrared Absorption Regions



The C-H stretching region

BASE VALUE = 3000 cm^{-1}

- **C-H sp stretch ~ 3300 cm^{-1}**
- **C-H sp^2 stretch > 3000 cm^{-1}**

UNSATURATED

3000 divides

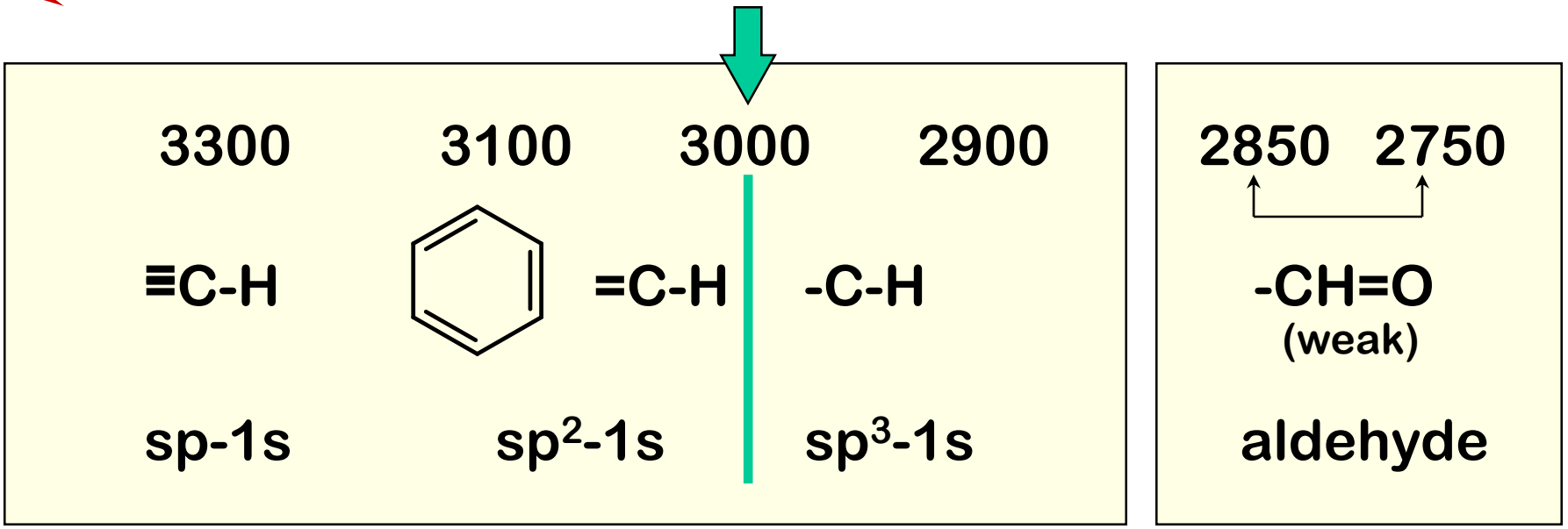
- **C-H sp^3 stretch < 3000 cm^{-1}**

SATURATED

- **C-H aldehyde, two peaks (both weak) ~ 2850 and 2750 cm^{-1}**

STRONGER BONDS HAVE LARGER FORCE CONSTANTS AND ABSORB AT HIGHER FREQUENCIES

increasing frequency (cm^{-1})



increasing s character in bond

increasing CH Bond Strength

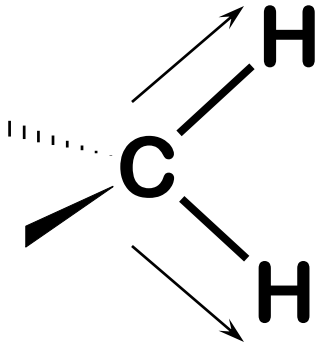
increasing force constant K

CH BASE VALUE = 3000 cm^{-1}

METHYLENE GROUP STRETCHING VIBRATIONS

Two C-H bonds share a central carbon
(hydrogens attached to the same carbon)

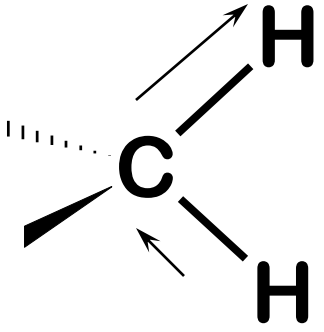
in-phase



Symmetric Stretch

~2853 cm^{-1}

out-of-phase



Asymmetric Stretch

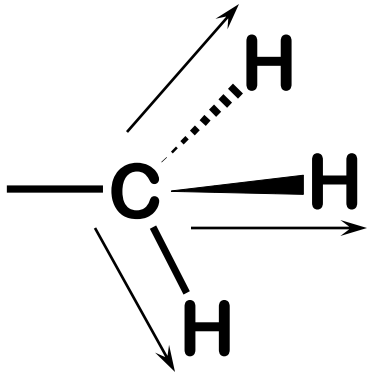
~2926 cm^{-1}

Any time you have two or more of the same kind of bond sharing a central atom you will have symmetric and asymmetric modes.

METHYL GROUP STRETCHING VIBRATIONS

Three C-H bonds share a central carbon
(hydrogens attached to the same carbon)

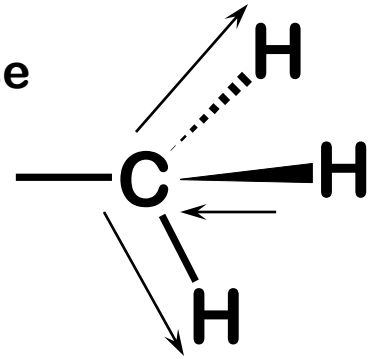
in-phase



Symmetric Stretch

~2872 cm^{-1}

out-of-phase

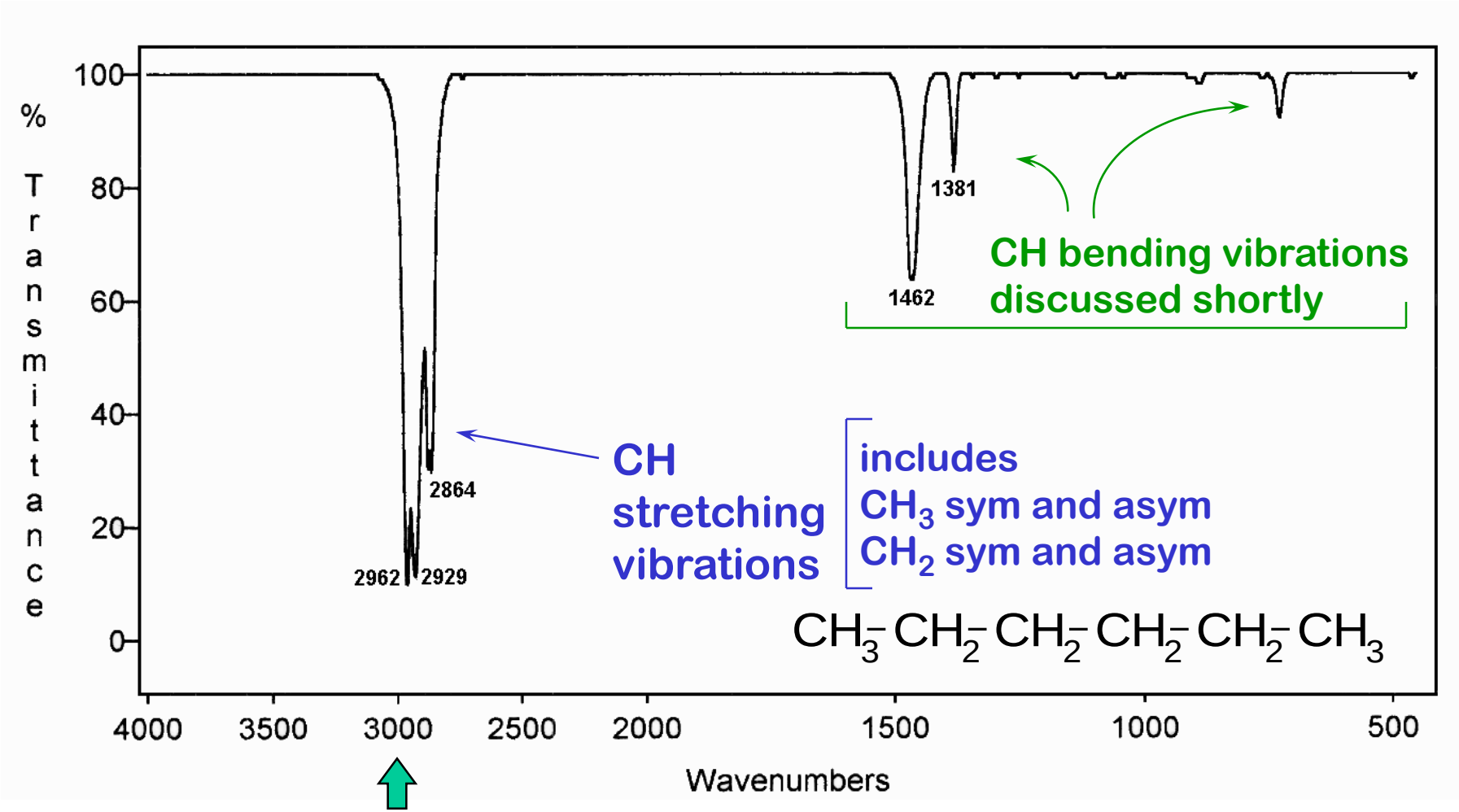


Asymmetric Stretch

~2962 cm^{-1}

ALKANE

Hexane



C-H BENDING

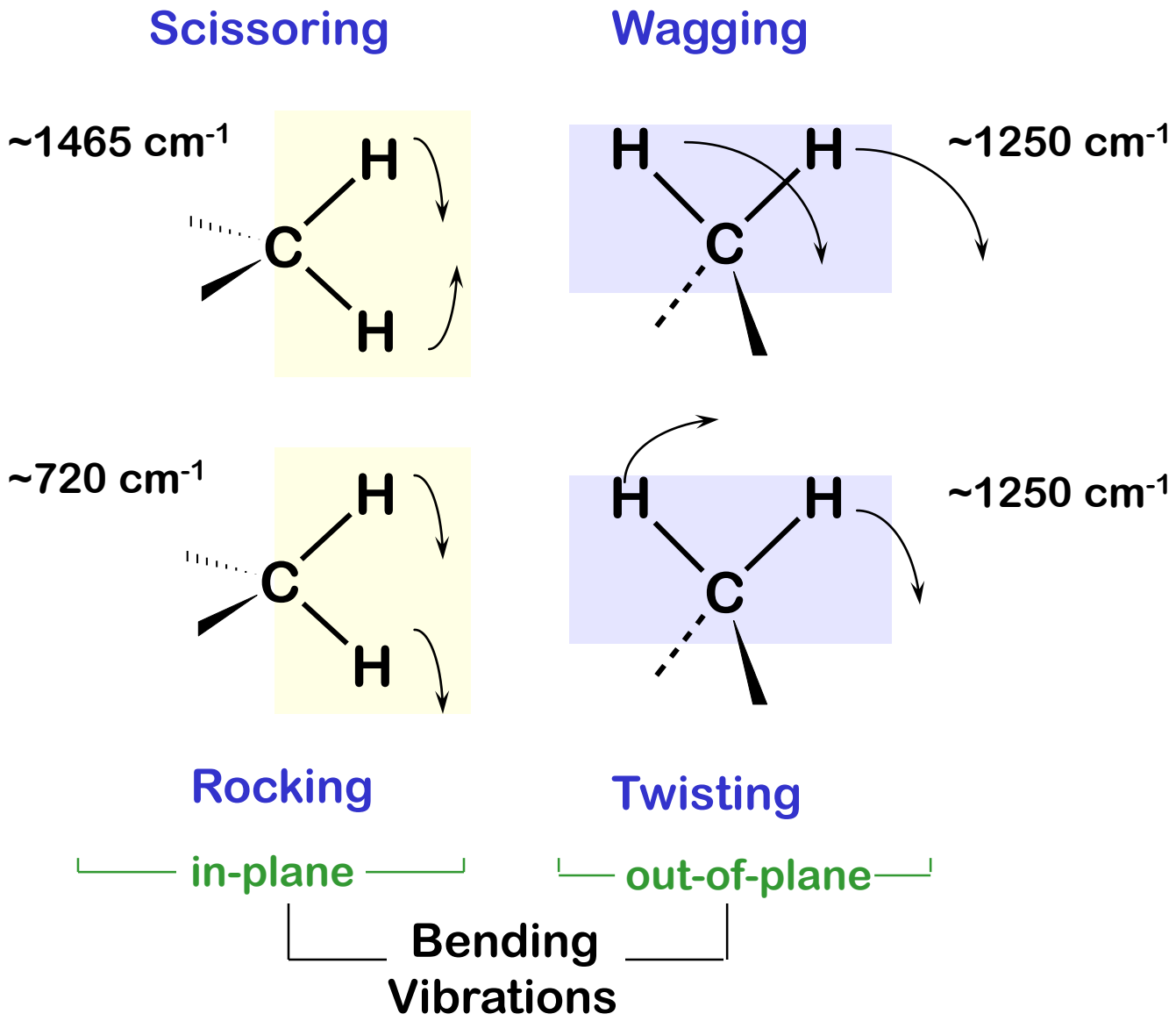
THE C-H BENDING REGION

- CH_2 bending ~ 1465 cm^{-1}

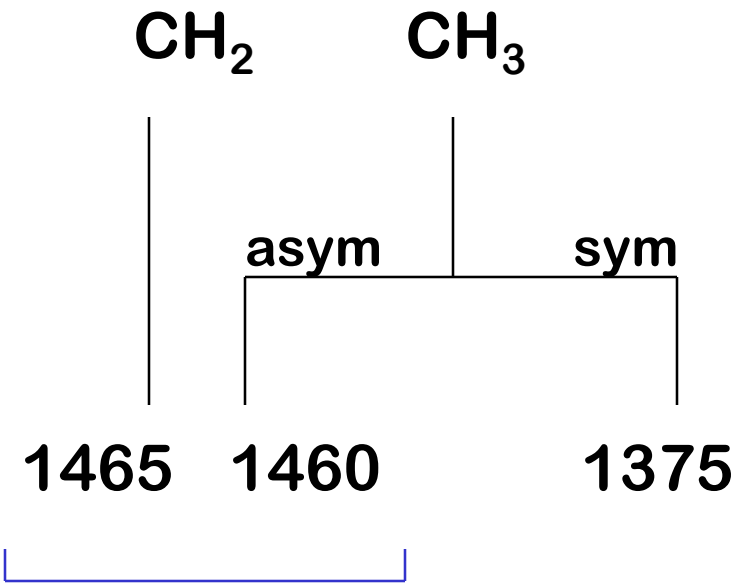
- CH_3 bending (asym) appears near the CH_2 value ~ 1460 cm^{-1}

- CH_3 bending (sym) ~ 1375 cm^{-1}

METHYLENE GROUP BENDING VIBRATIONS

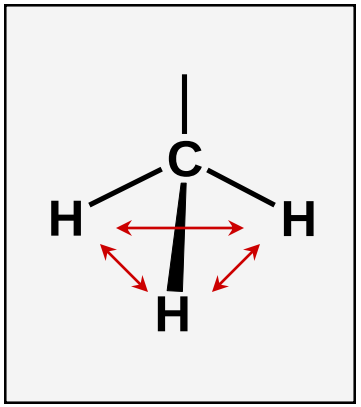


METHYLENE AND METHYL BENDING VIBRATIONS



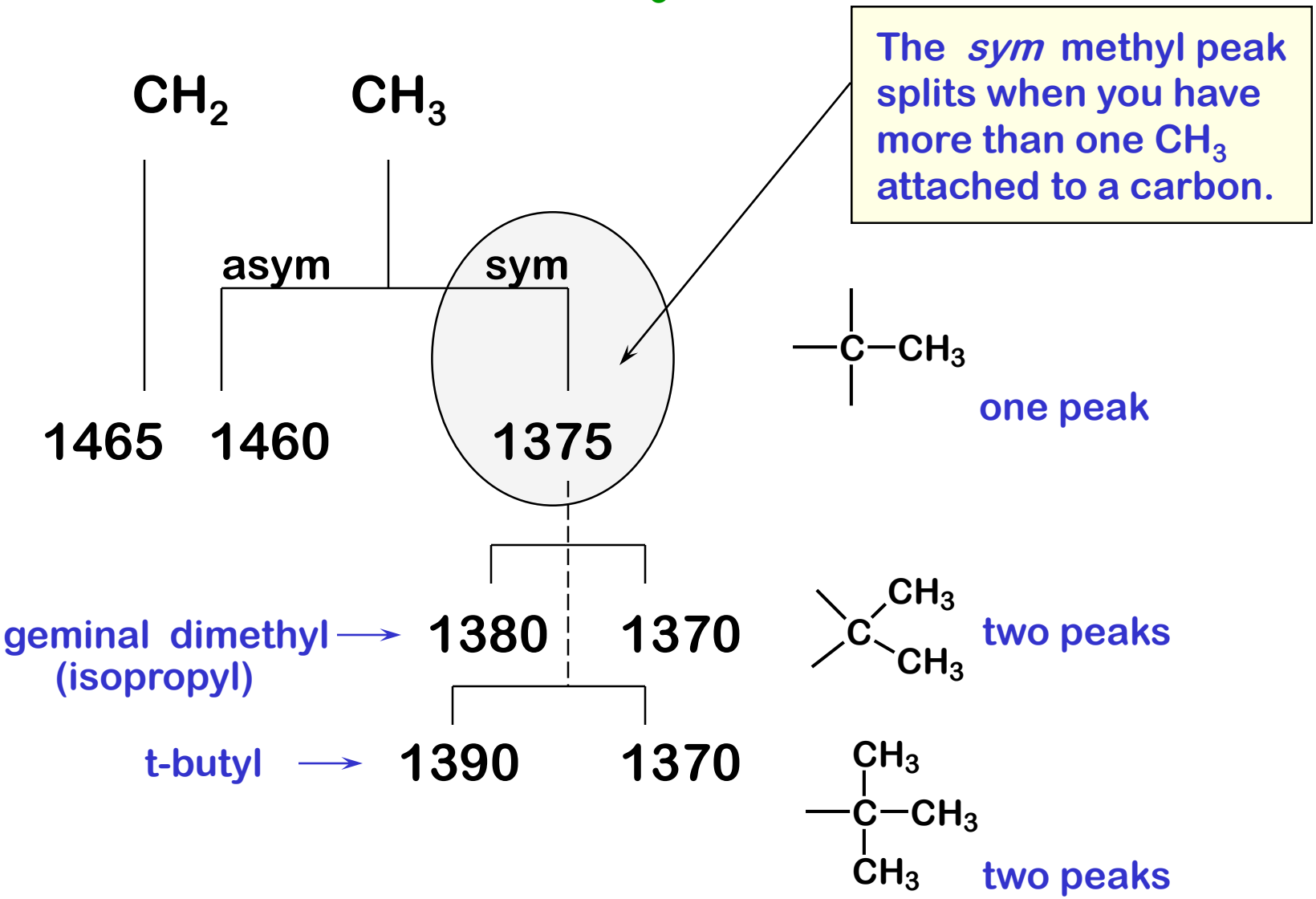
C-H Bending, look near 1465 and 1375 cm^{-1}

these two peaks frequently overlap and are not resolved



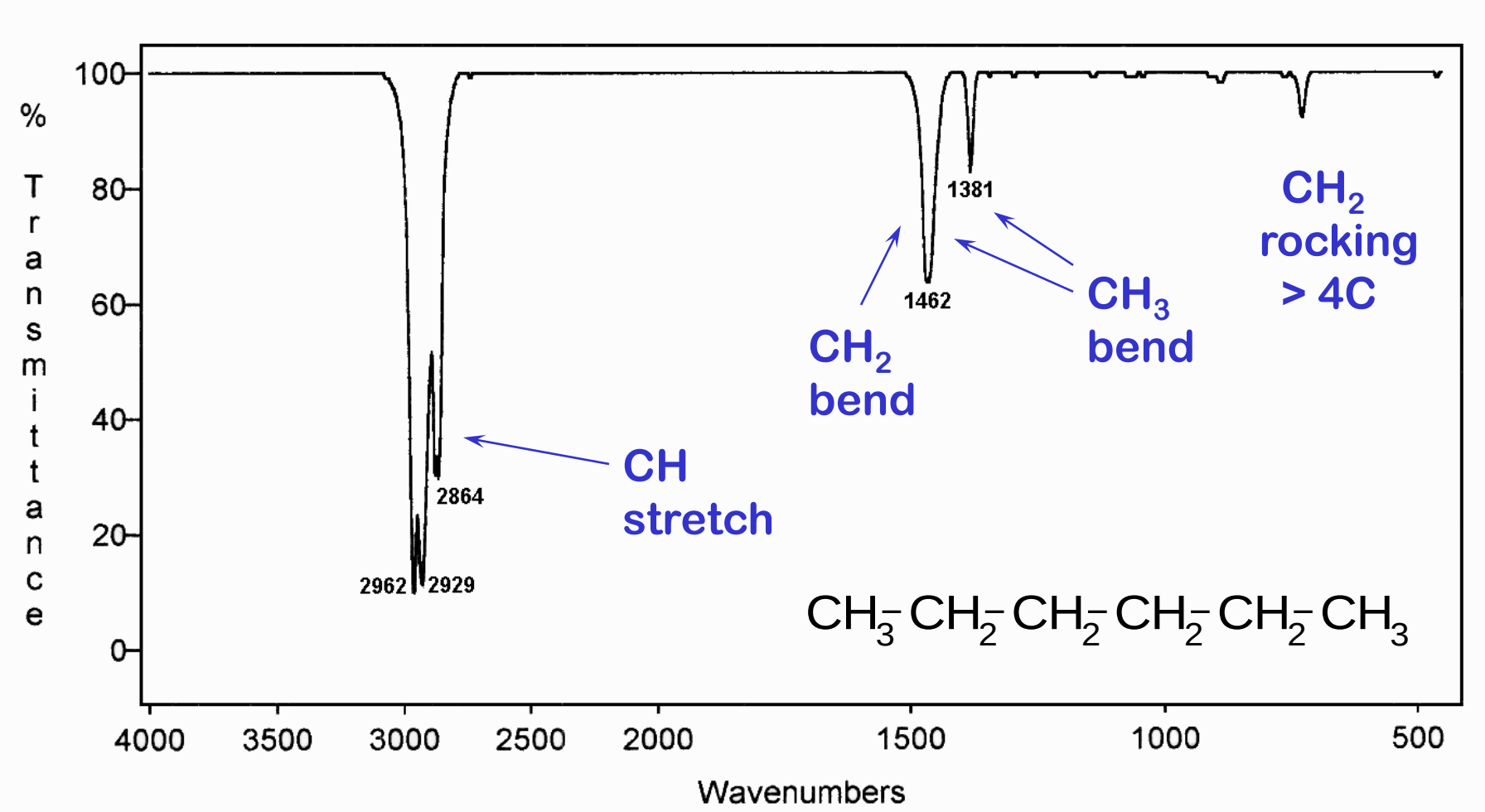
METHYLENE AND METHYL BENDING VIBRATIONS

ADDITIONAL DETAILS FOR SYM CH_3



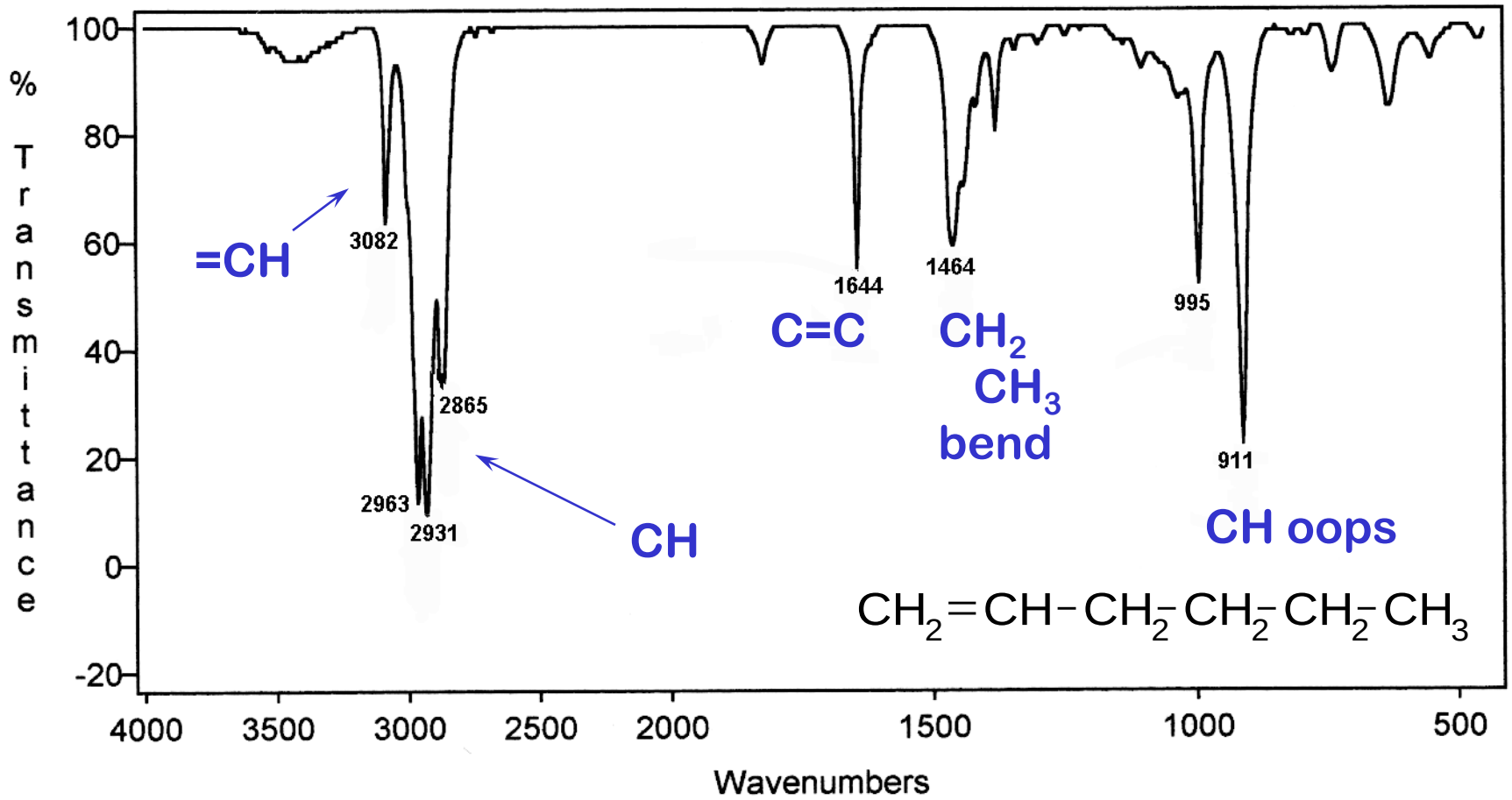
ALKANE

Hexane



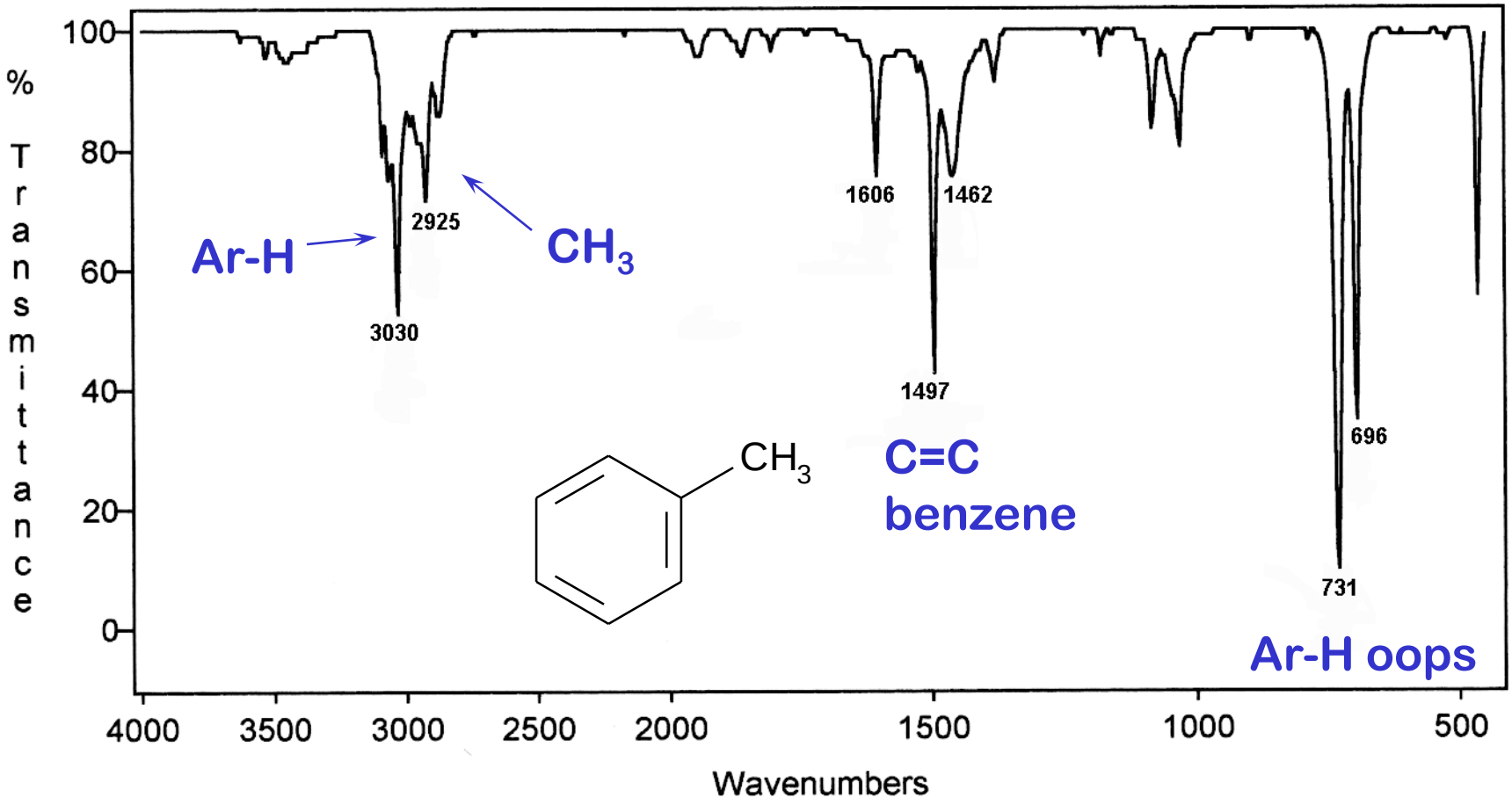
ALKENE

1-Hexene



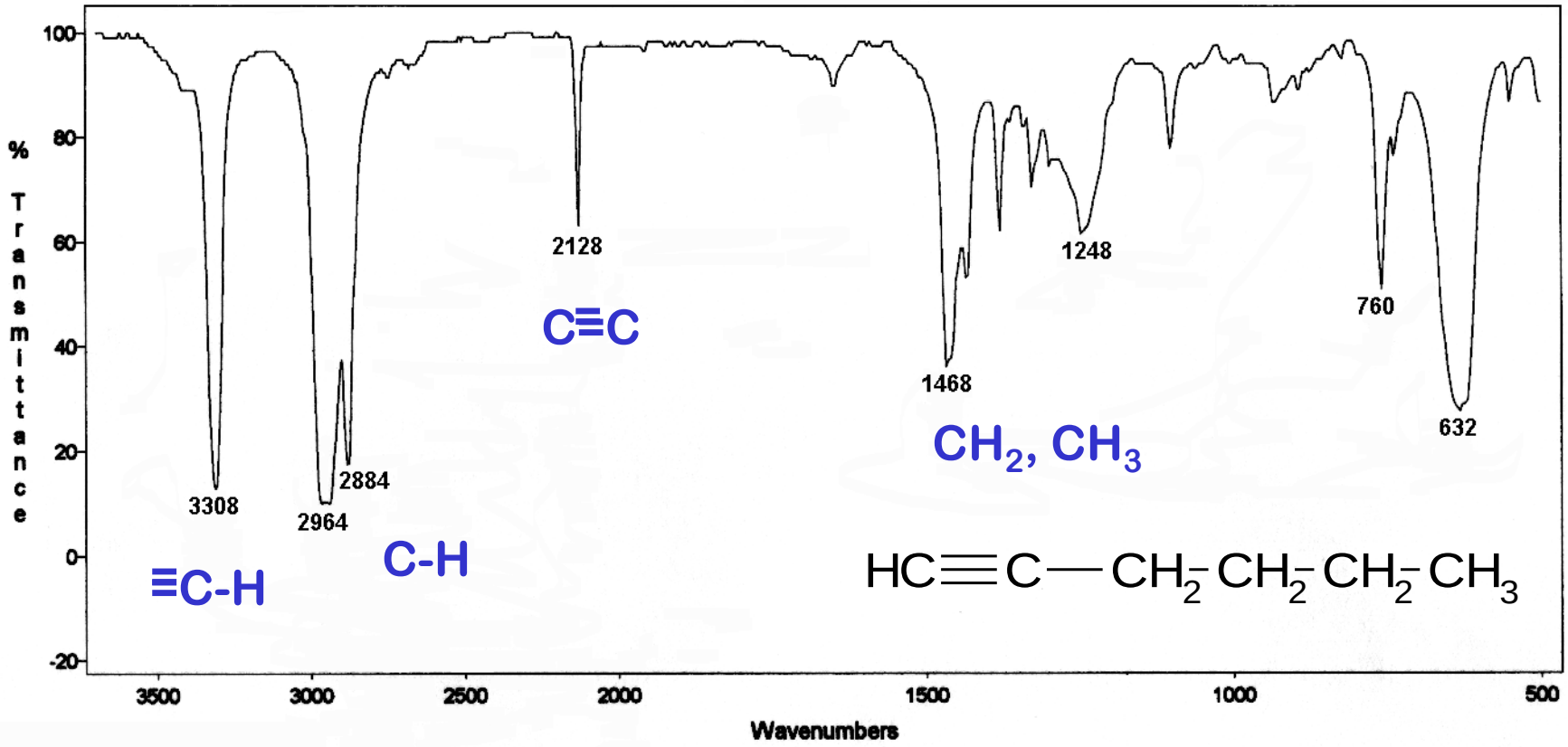
AROMATIC

Toluene



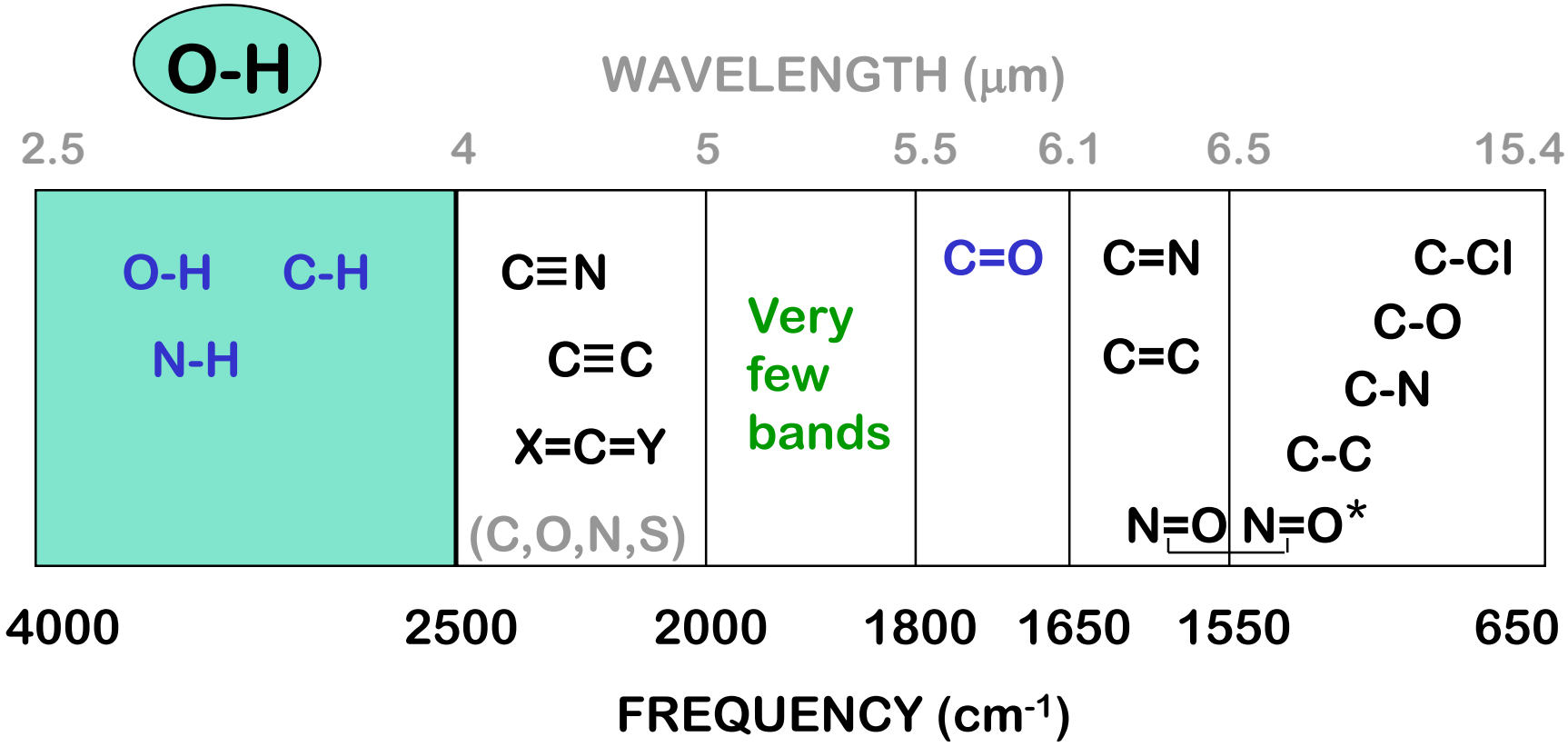
ALKYNE

1-Hexyne



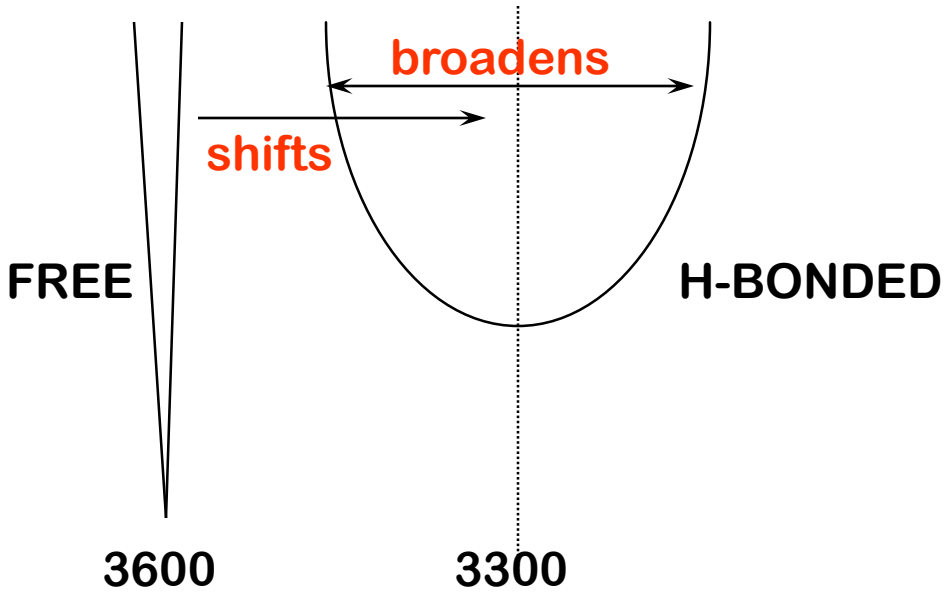
O-H STRETCH

Typical Infrared Absorption Regions

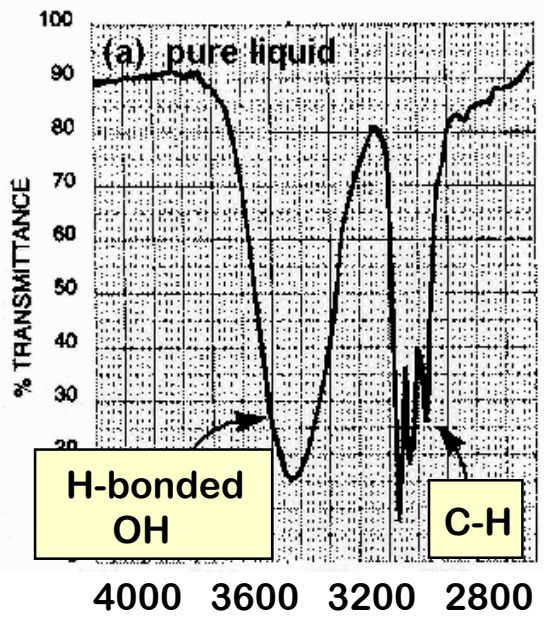


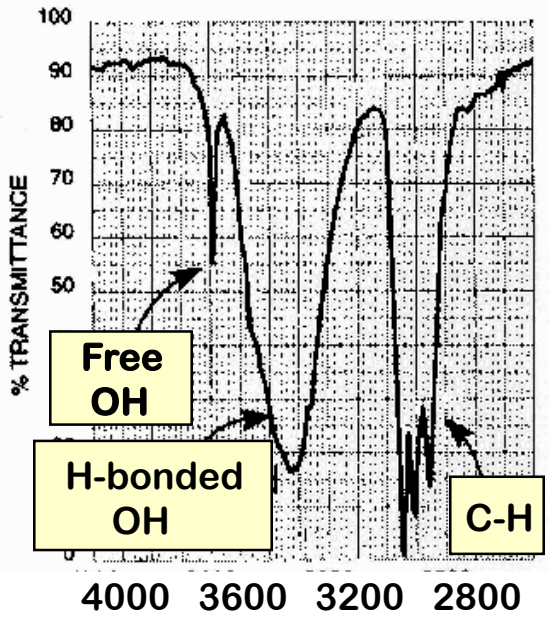
The O-H stretching region

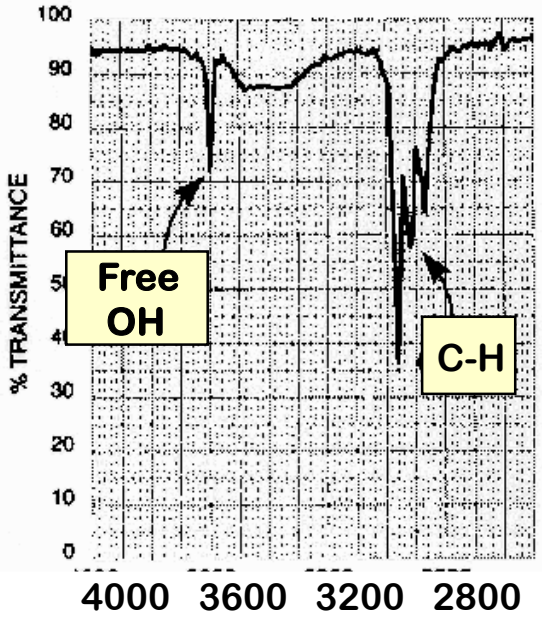
- O-H 3600 cm^{-1} (alcohol, free)
- O-H 3300 cm^{-1} (alcohols & acids, H-bonding)



Effect of Hydrogen-Bonding on O-H Stretching







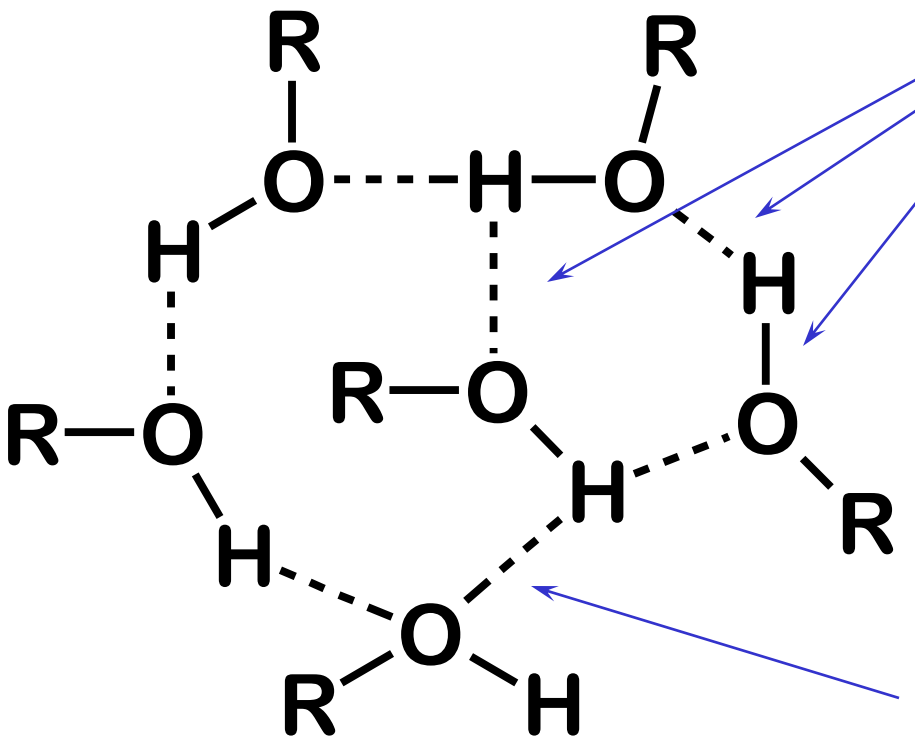
(a) Pure Liquid "neat"

(b) Dilute Solution

(c) Very Dilute Solution

1-Butanol

HYDROGEN-BONDED HYDROXYL



Many kinds of OH bonds of different lengths and strengths This leads to a broad absorption.

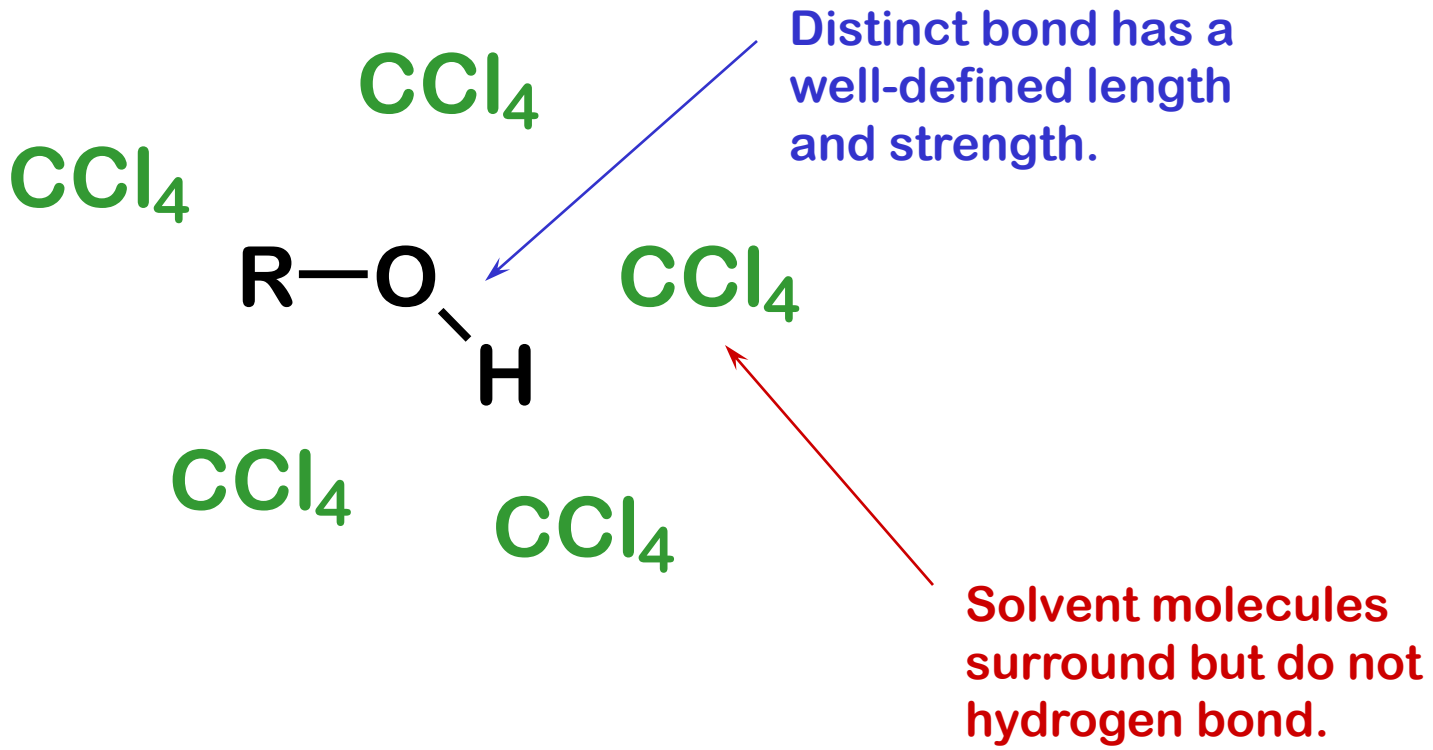
"Neat" solution.

Longer bonds are weaker and lead to lower frequency.

Hydrogen bonding occurs in concentrated solutions (for instance, undiluted alcohol).

"FREE" HYDROXYL

The "free" hydroxyl vibrates without interference from any other molecule.

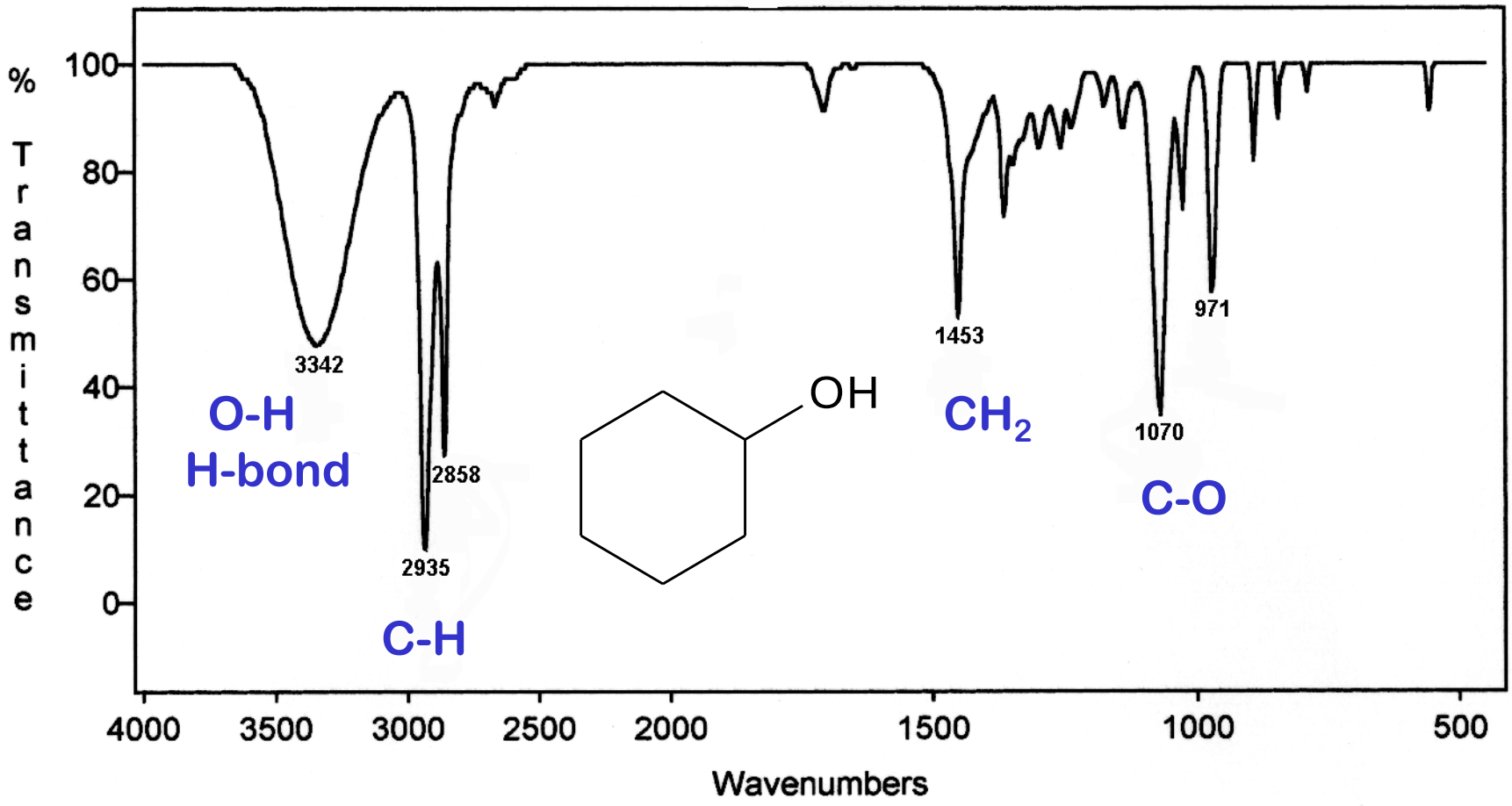


Occurs in dilute solutions of alcohol in an "inert" solvent like CCl_4.

ALCOHOL

Cyclohexanol

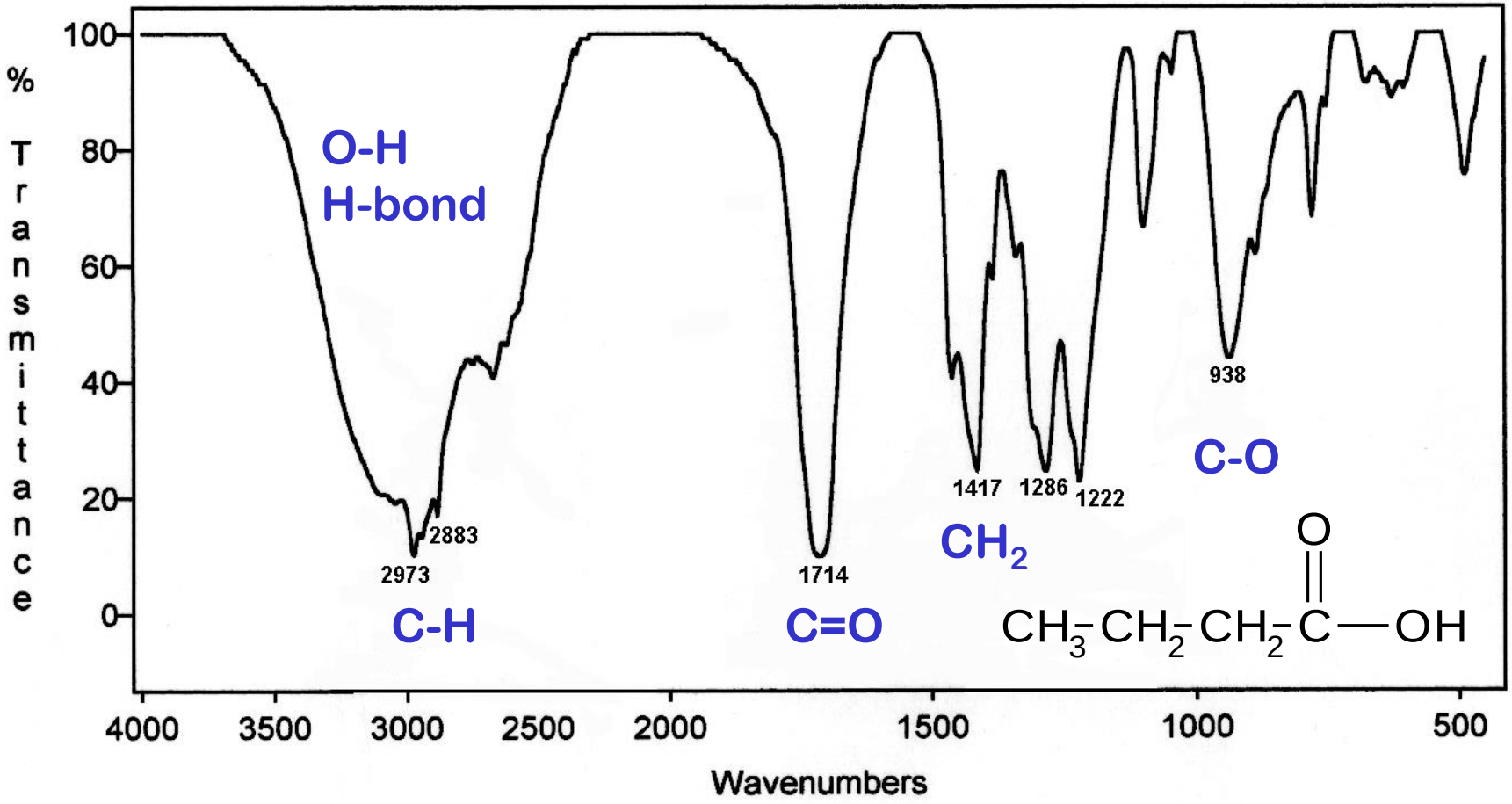
neat solution



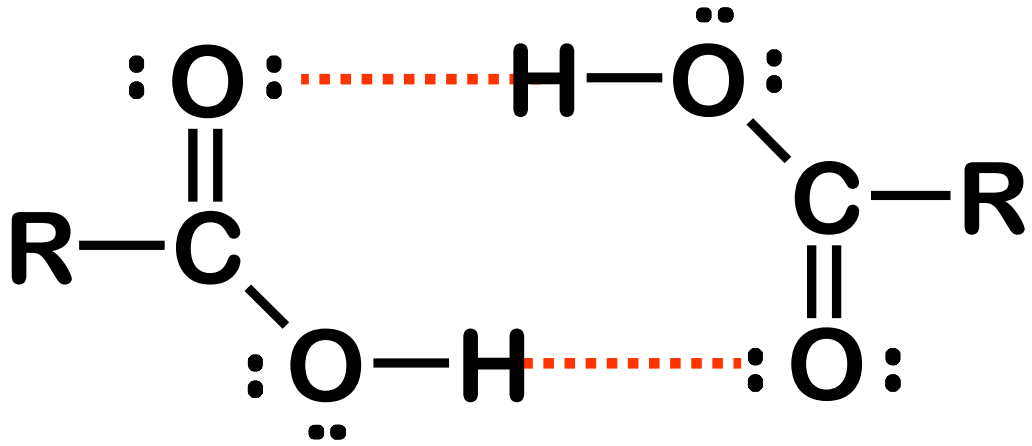
CARBOXYLIC ACID

Butanoic Acid

neat solution



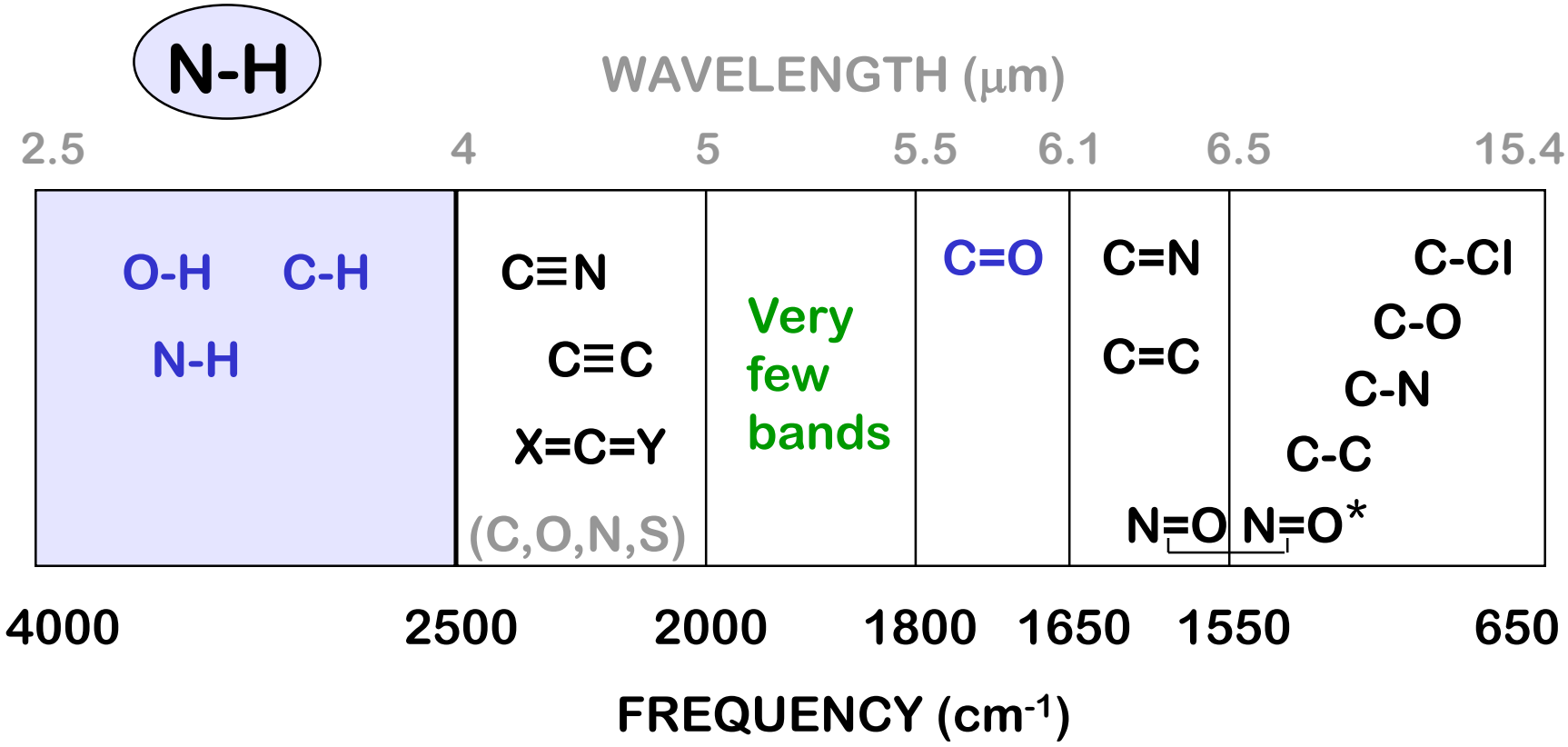
CARBOXYLIC ACID DIMER



Strong hydrogen bonding in the dimer weakens the OH bond and leads to a broad peak at lower frequency.

N-H STRETCH

Typical Infrared Absorption Regions



The N-H stretching region

N-H 3300 - 3400 cm^{-1}

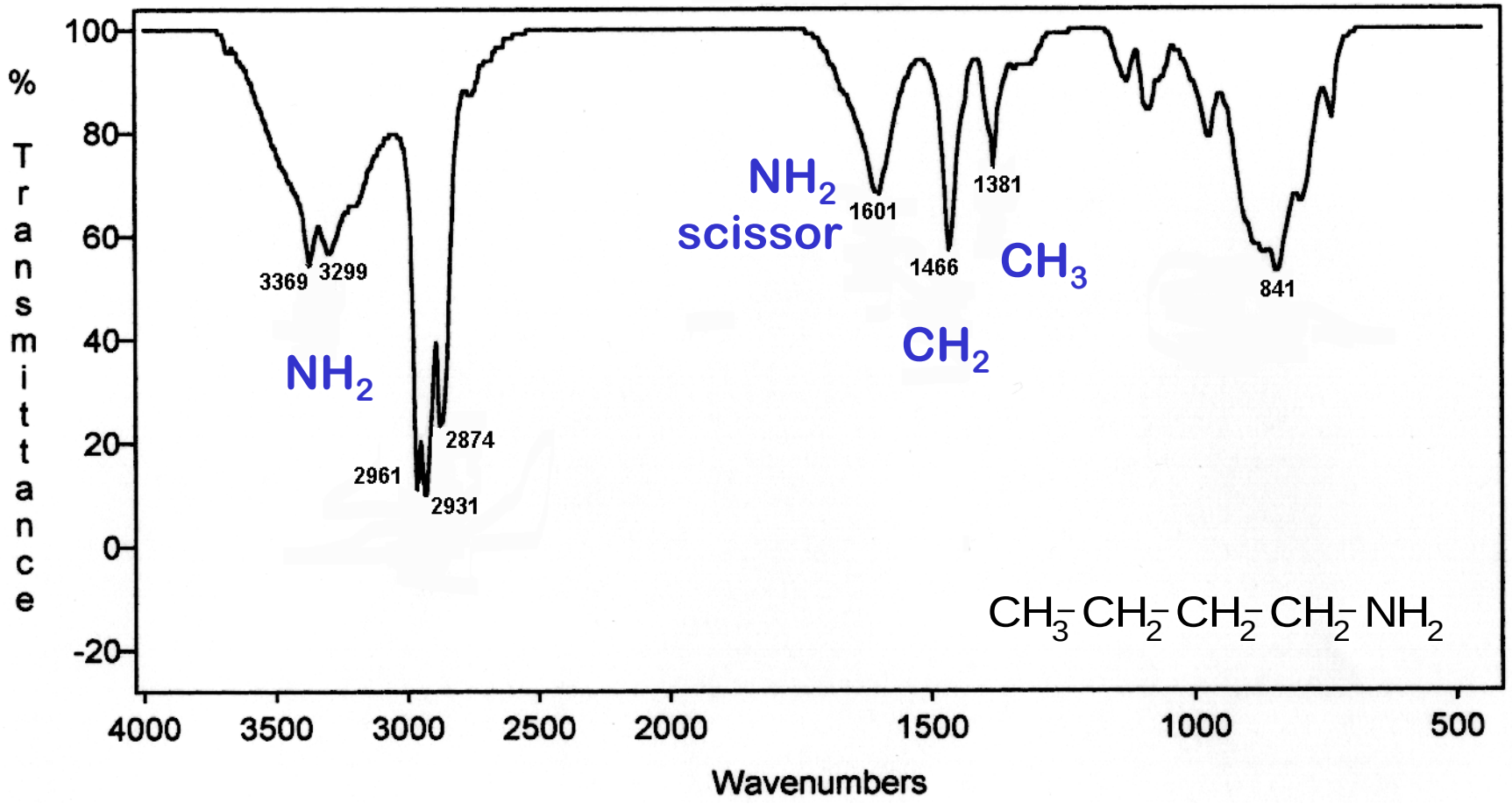
- Primary amines give <u>two</u> peaks

symmetric asymmetric

- Secondary amines give <u>one</u> peak
- Tertiary amines give <u>no peak</u>

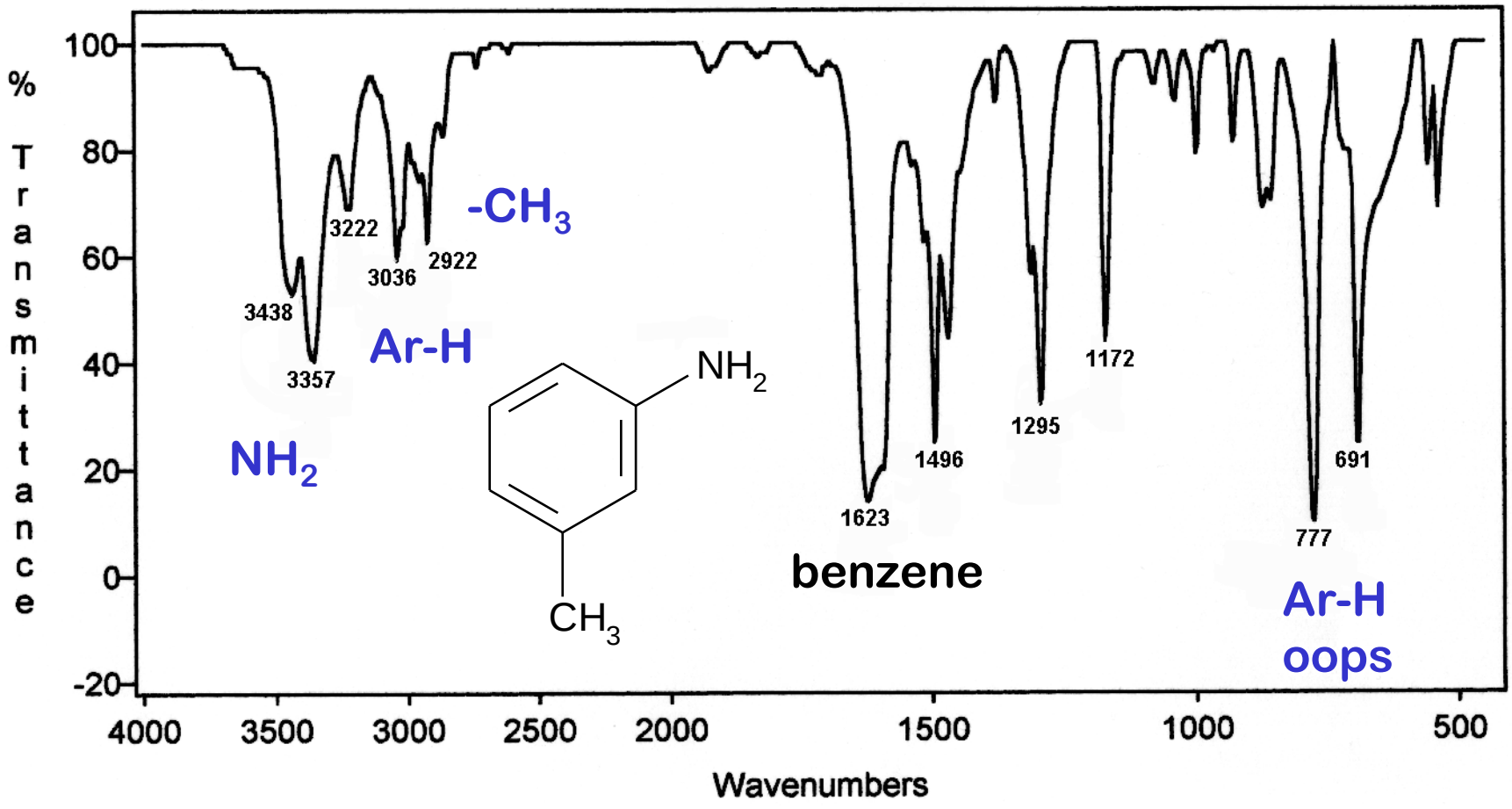
PRIMARY AMINE
aliphatic

1-Butanamine



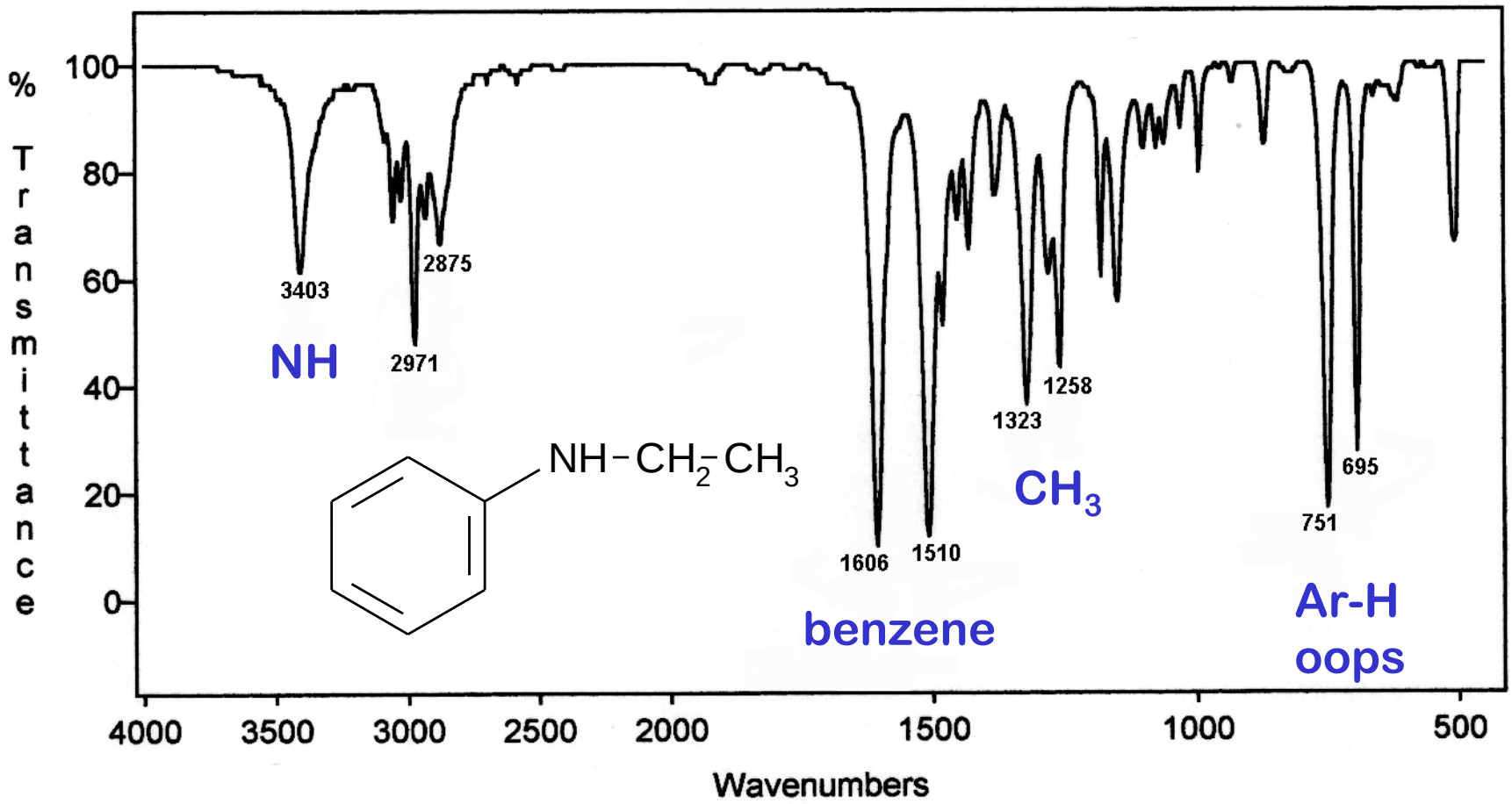
PRIMARY AMINE
aromatic

3-Methylbenzenamine



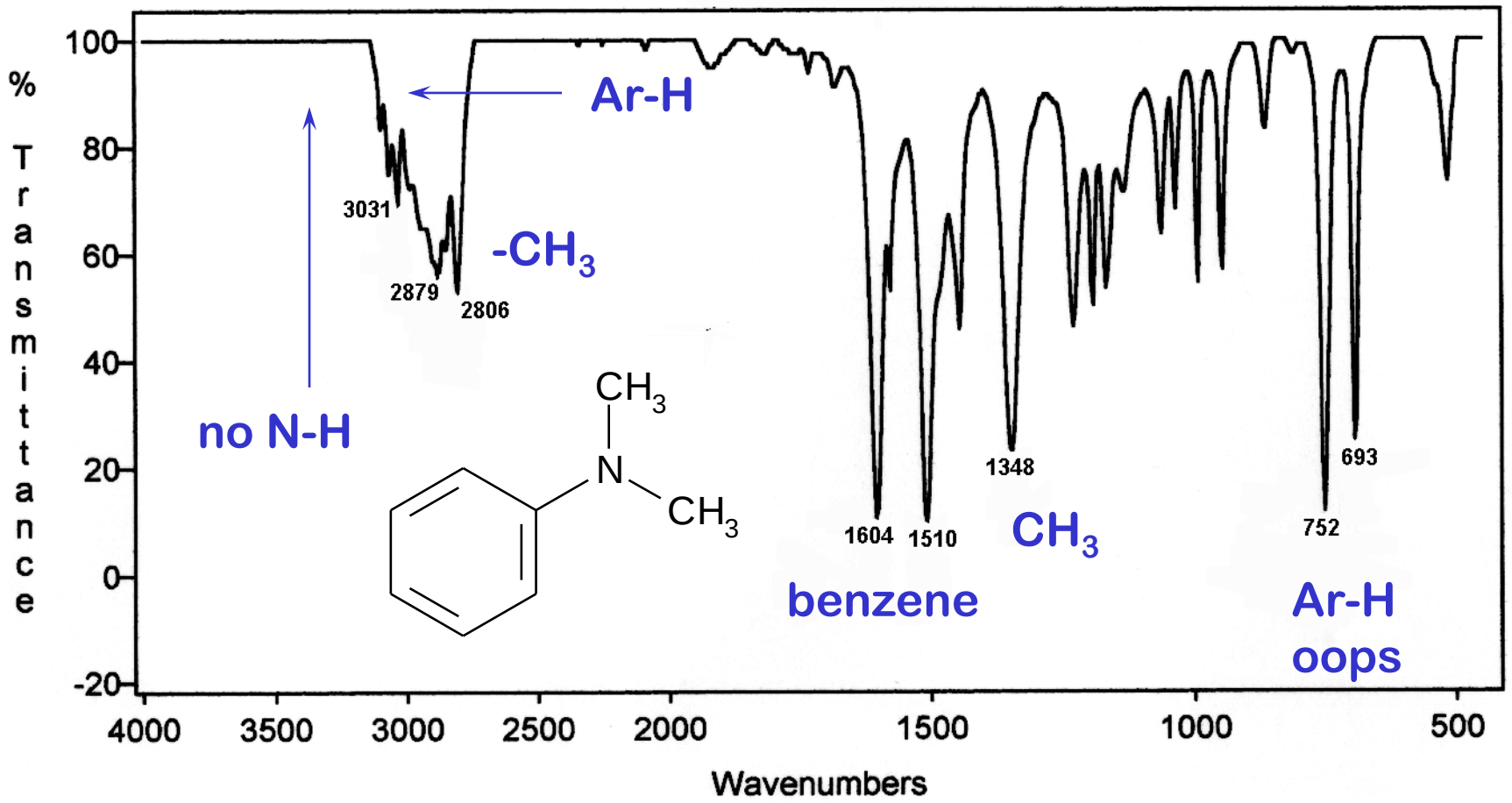
SECONDARY AMINE

N-Ethylbenzenamine

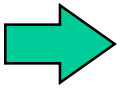


TERTIARY AMINE

N,N-Dimethylaniline



NITRILES
ALKYNES



O-H 3600
N-H 3400
C-H 3000

C≡N 2250
C≡C 2150

C=O 1715
C=C 1650

C-O 1100

SURVEY OF SPECTRA

BASE VALUES

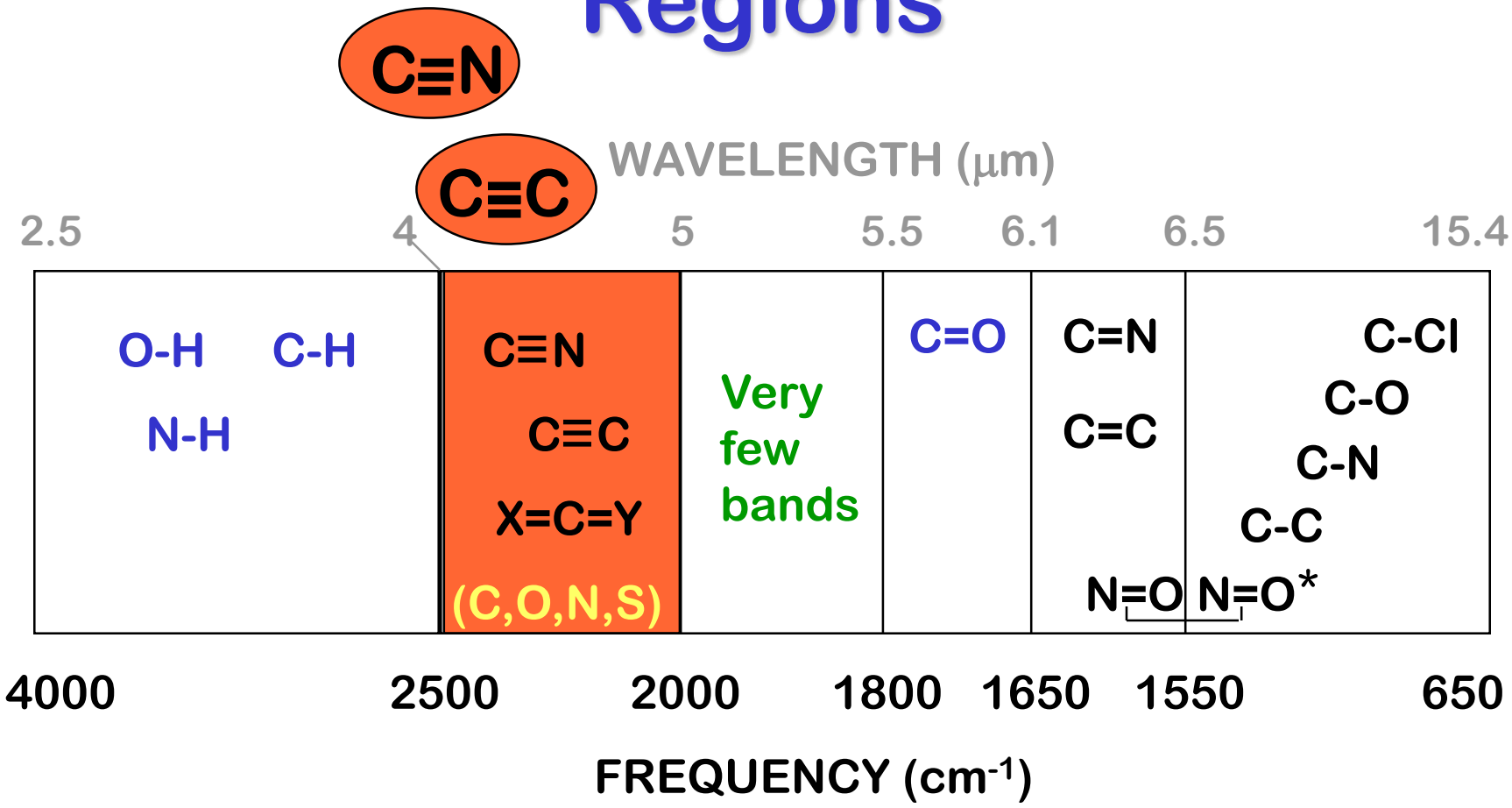
(+/- 10 cm^{-1})

REMEMBER THESE ?

O-H	3600
N-H	3400
C-H	3000
C≡N	2250
C≡C	2150
C=O	1715
C=C	1650
C−O	~1100

C≡N AND C≡C STRETCH

Typical Infrared Absorption Regions

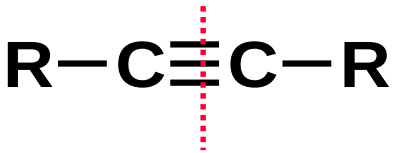


The triple bond stretching region

- C≡N 2250 cm^{-1}
- C≡C 2150 cm^{-1}

The cyano group often gives a strong, sharp peak due to its large dipole moment.

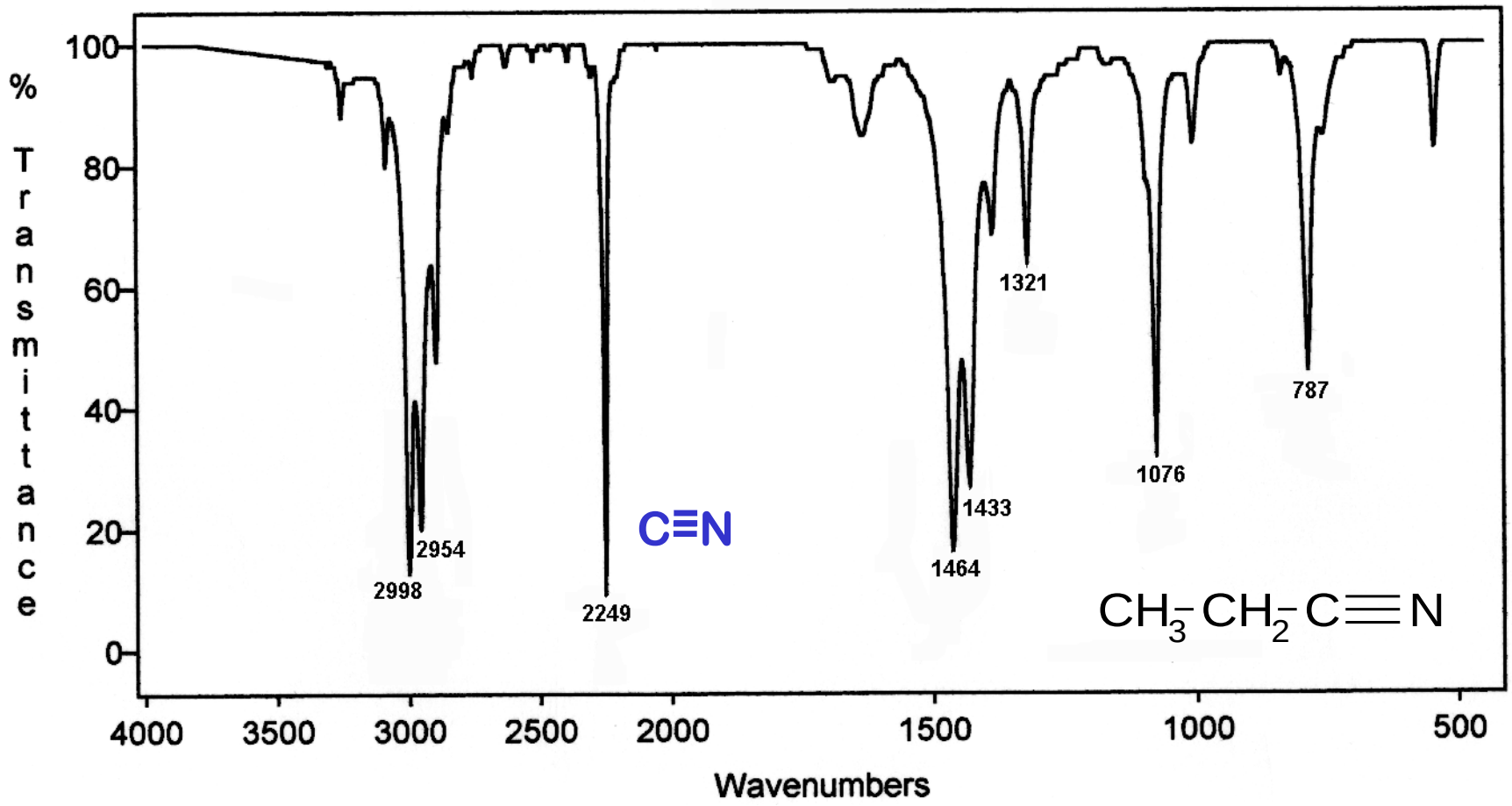
The carbon-carbon triple bond gives a sharp peak, but it is often weak due to a lack of a dipole. This is especially true if it is at the center of a symmetric molecule.



NITRILE

Propanenitrile

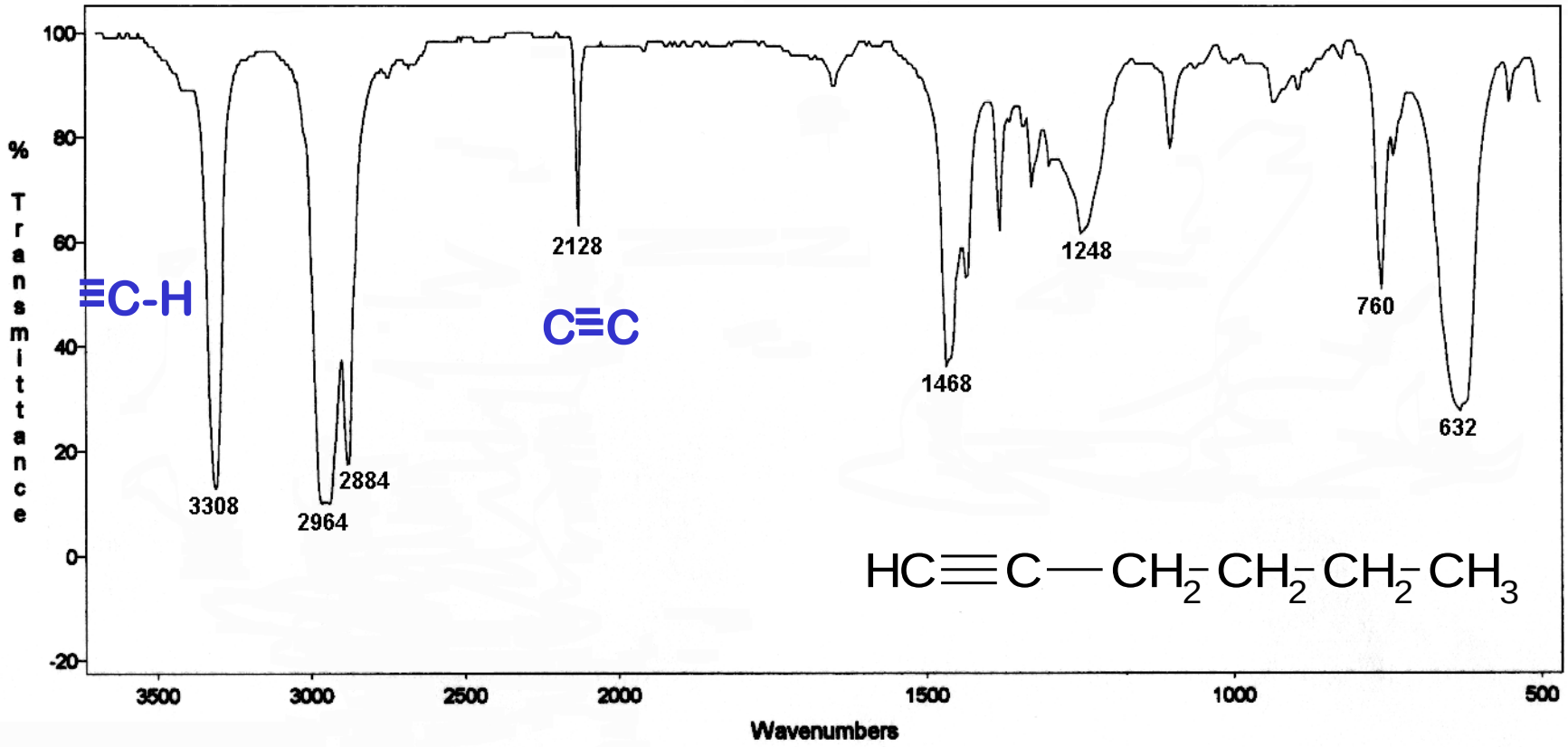
BASE = 2250



ALKYNE

BASE = 2150

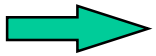
1-Hexyne



CARBONYL COMPOUNDS

(C=O BOND STRETCH)

Aldehydes
Ketones
Esters
Amides
Acid Chlorides



O-H 3600
N-H 3400
C-H 3000

C≡N 2250
C≡C 2150

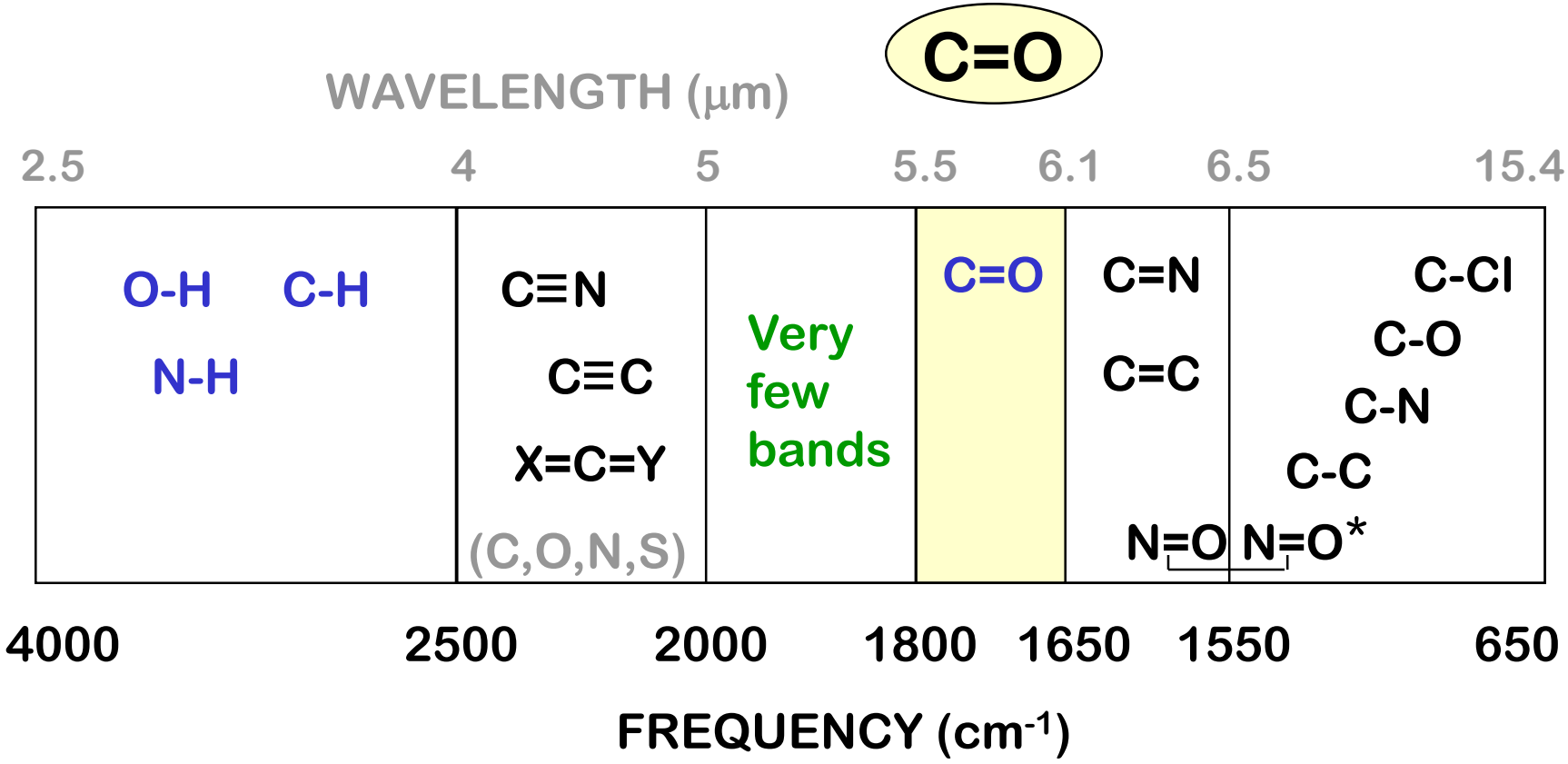
C=O 1715
C=C 1650

C-O 1100

SURVEY OF SPECTRA

C=O STRETCHING

Typical Infrared Absorption Regions



THE CARBONYL STRETCHING REGION

- This region stretches from about 1800 to 1650 cm^{-1} - RIGHT IN THE MIDDLE OF THE SPECTRUM

- The base value is 1715 cm^{-1} (ketone)

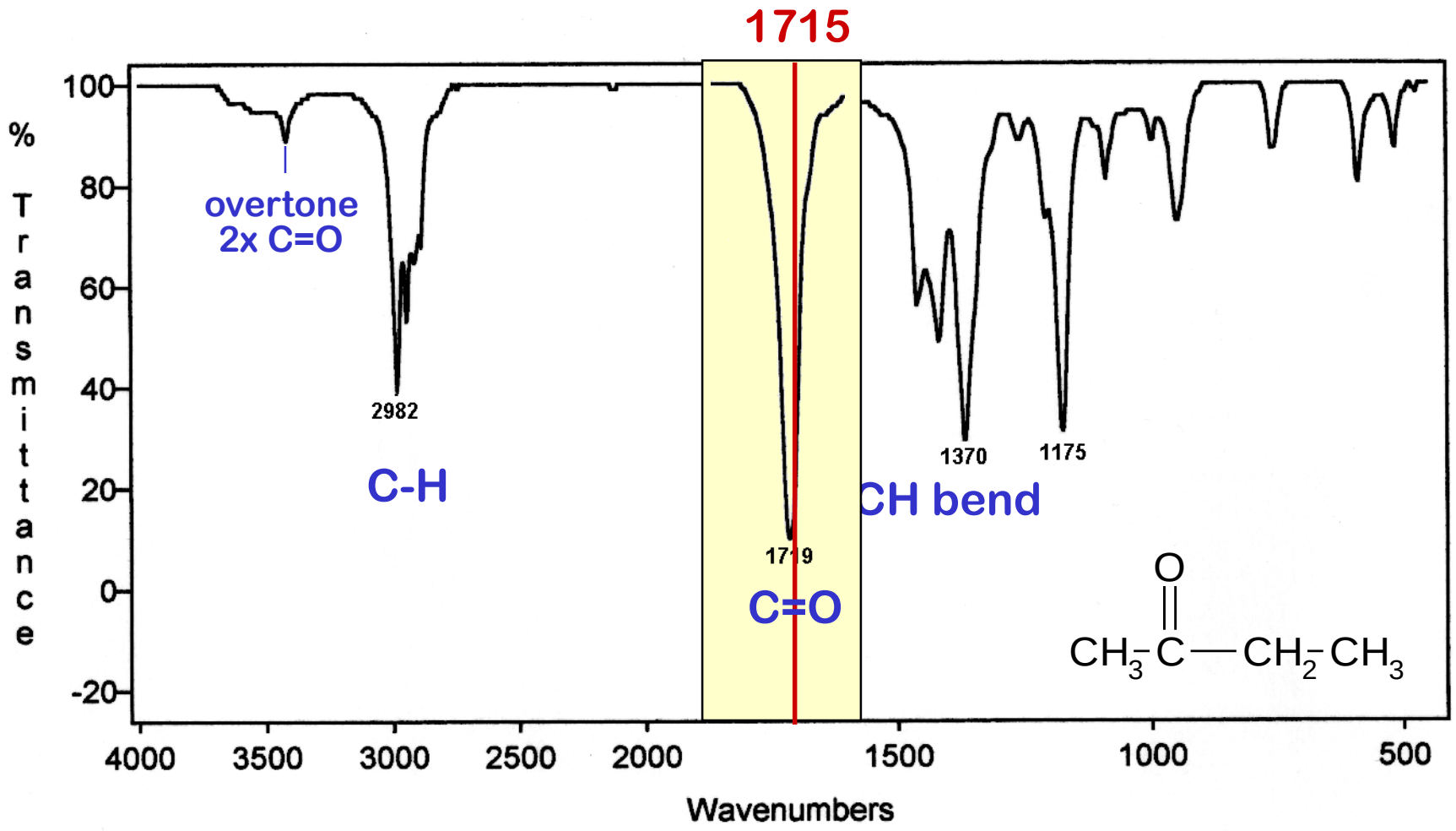
- The bands are very strong !!! due to the large C=O dipole moment.

- C=O is often one of the strongest peaks in the spectrum

KETONE

BASE = 1715

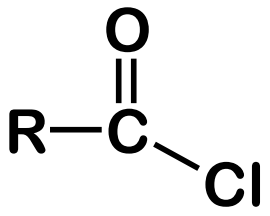
2-Butanone



C=O IS SENSITIVE TO ITS ENVIRONMENT

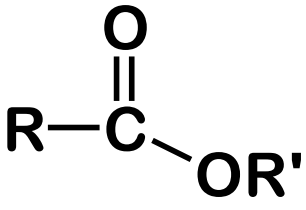
EACH DIFFERENT KIND OF C=O COMES AT A DIFFERENT FREQUENCY

acid chloride



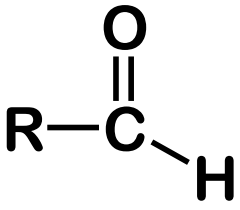
1800

ester



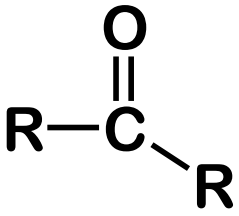
1735

aldehyde



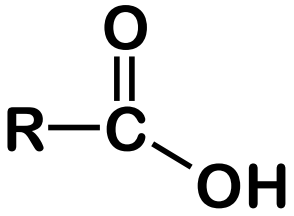
1725

ketone



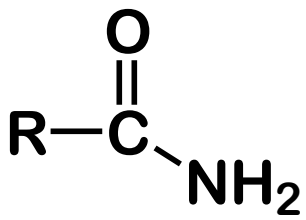
1715

carboxylic acid



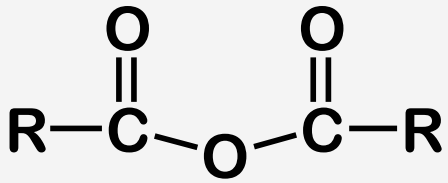
1710

amide



1690

anhydride



1810 and 1760

(two peaks)

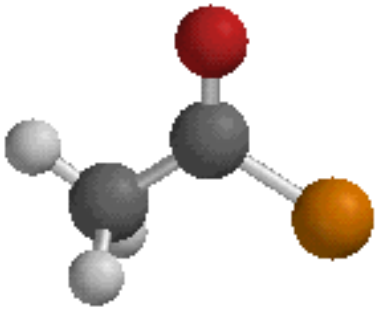
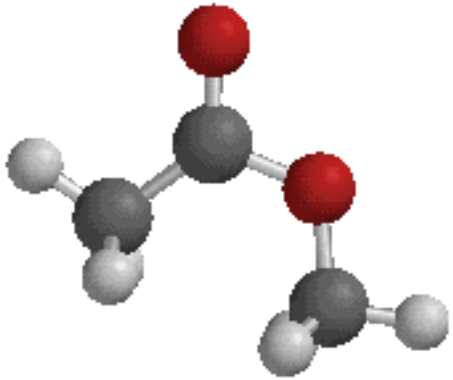
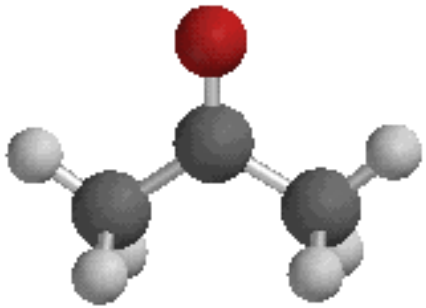
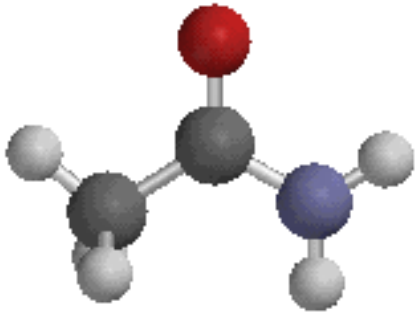
BASE VALUE

THESE VALUES ARE WORTH LEARNING

all are +/- 10 cm^{-1}

C=O BOND LENGTHS IN CARBONYL COMPOUNDS

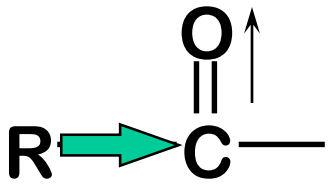
shorter ← | → longer

1.225 A	1.231 A	1.235 A	1.248 A
			
acid chloride	ester	ketone	amide
1780 cm^{-1}	1735 cm^{-1}	1715 cm^{-1}	1680 cm^{-1}

FACTORS THAT INFLUENCE THE C=O ABSORPTION

INDUCTIVE AND RESONANCE EFFECTS ON THE CARBONYL FREQUENCY

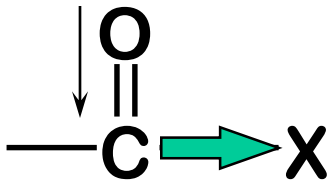
A



R = Me, Et, etc.

Electron-donating groups weaken the carbonyl and lower its absorption frequency

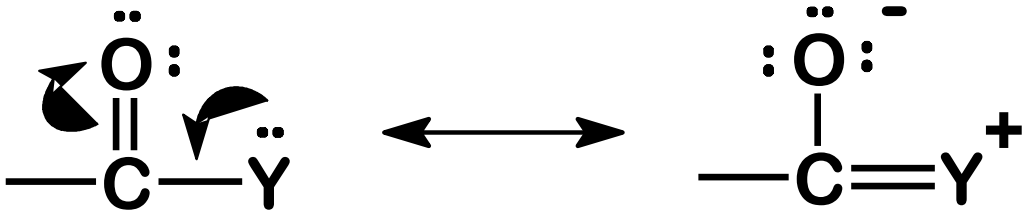
B



X = F, Cl, Br, O

Electron-withdrawing groups strengthen the carbonyl and raise its absorption frequency

INDUCTIVE AND RESONANCE EFFECTS ON THE CARBONYL FREQUENCY



Resonance
weakens the carbonyl and

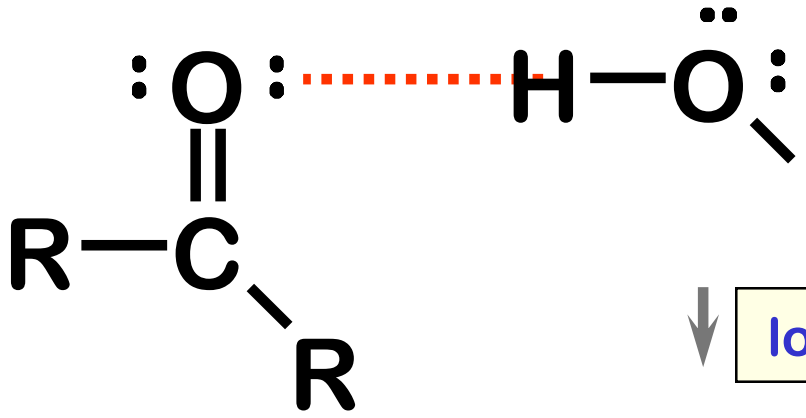
C

Y = N, O, or C=C

lowers its absorption frequency

(Note the lengthening of the C=O bond!)

D



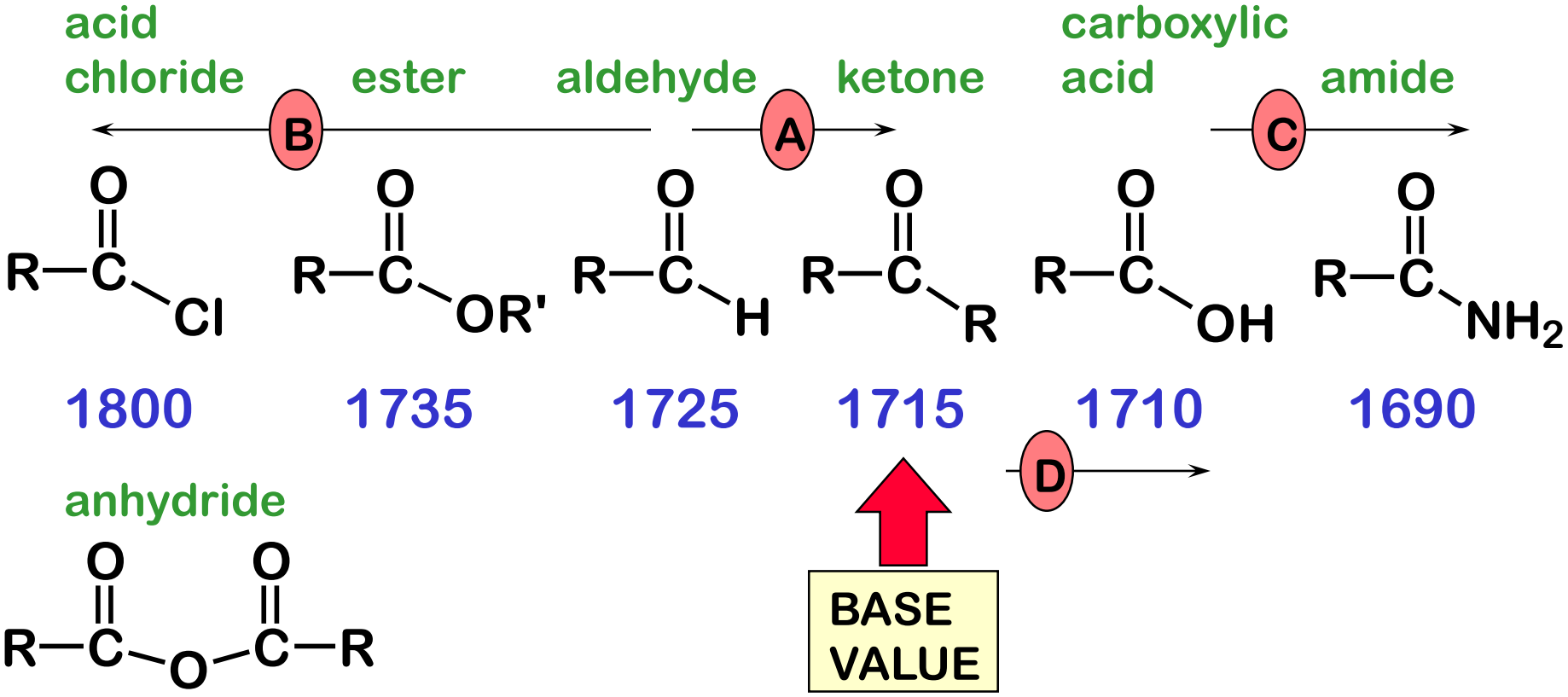
Hydrogen bonding

lengthens and weakens the C=O bond and

lowers its absorption frequency

HOW THE FACTORS AFFECT C=O

STRETCHING VIBRATIONS



SUMMARY

Ketones are at lower frequency than **Aldehydes** because of the second electron-donating alkyl group.

Acid chlorides are at higher frequency than ketones because of the electron-withdrawing halide.

Esters are at higher frequencies than ketones due to the electron-withdrawing oxygen atom. This is more important than resonance with the electron pair on the oxygen.

Amides are at lower frequencies than ketones due to resonance involving the unshared pair on nitrogen. The electron-withdrawing effect of nitrogen is less important than the resonance.

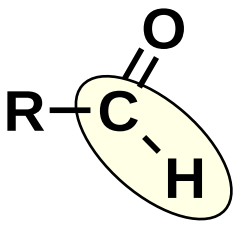
Note the electronegativity difference, O versus N, weights the two factors (resonance/ e-withdrawal) differently in esters than in amides.

Acids are at lower frequency than ketones due to H-bonding.

CONFIRMING PEAKS

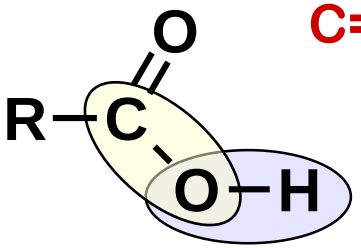
CONFIRMATION OF FUNCTIONAL GROUP

Every type of carbonyl compound has other places you can look to confirm your conclusion based on frequency alone.



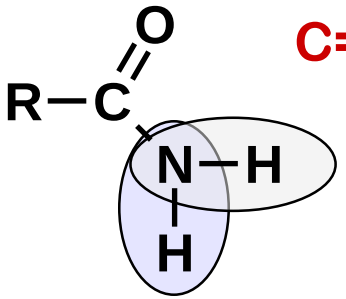
C=O at 1725 cm^{-1}

also look for aldehyde CH 2850 and 2750 cm-1



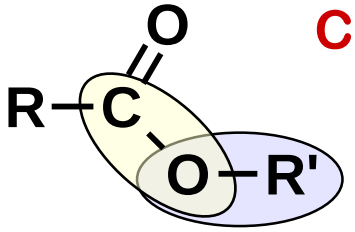
C=O at 1710 cm^{-1}

also look for OH (H-bonded) and C-O ~1200 cm-1



C=O at 1690 cm^{-1}

also look for two NH peaks at 3400 cm-1



C=O at 1735 cm^{-1}

also look for two C-O at 1200 and 1000 cm-1

Ketones have C=O at 1715 cm^{-1} and no NH, OH, C-O or -CHO

Anhydrides have <u>two</u> C=O peaks near 1800 cm^{-1} and two C-O

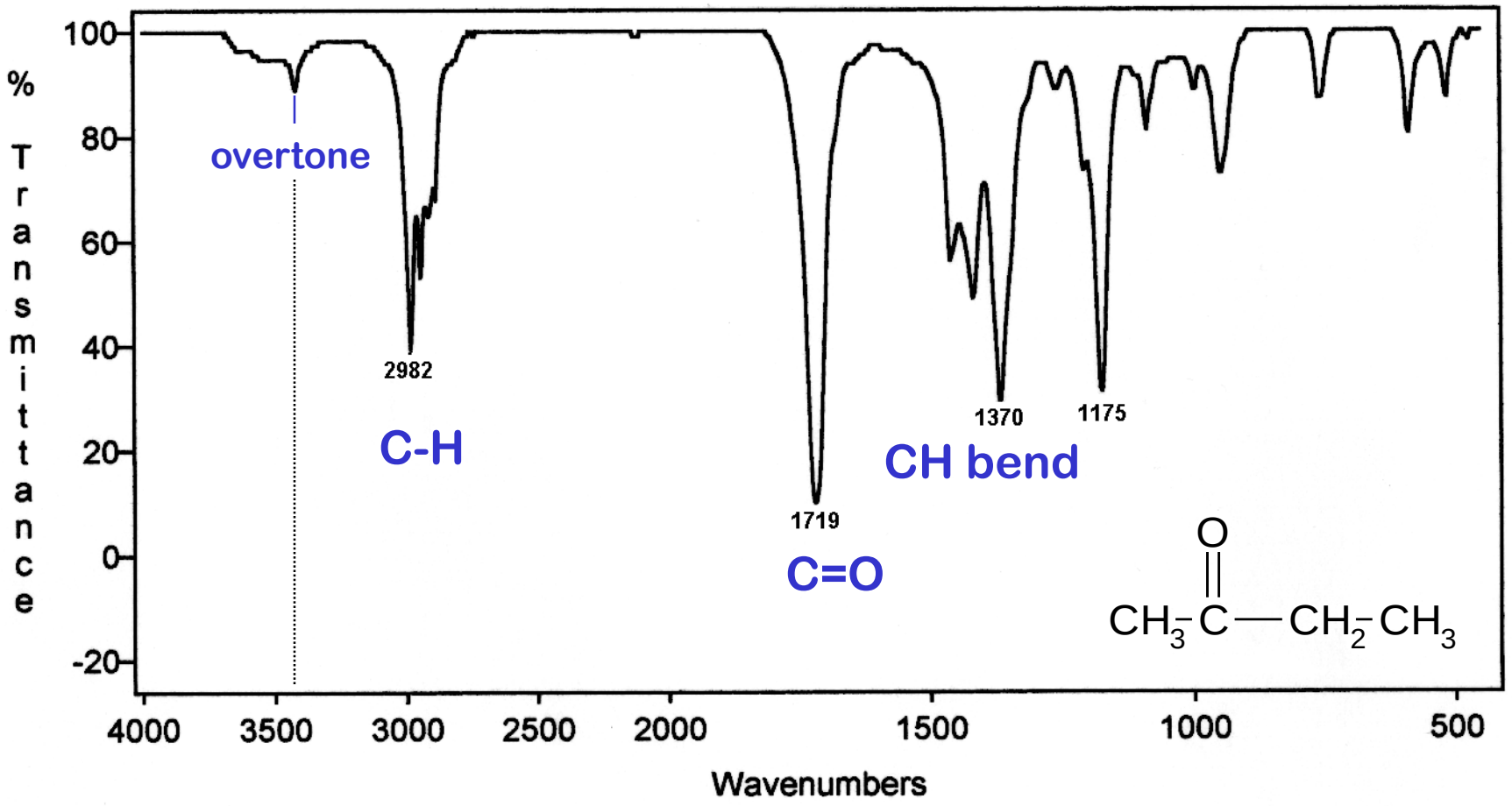
SELECTED SPECTRA

KETONE

BASE = 1715

overtone of strong C=O peak
1719 x 2 = 3438

2-Butanone

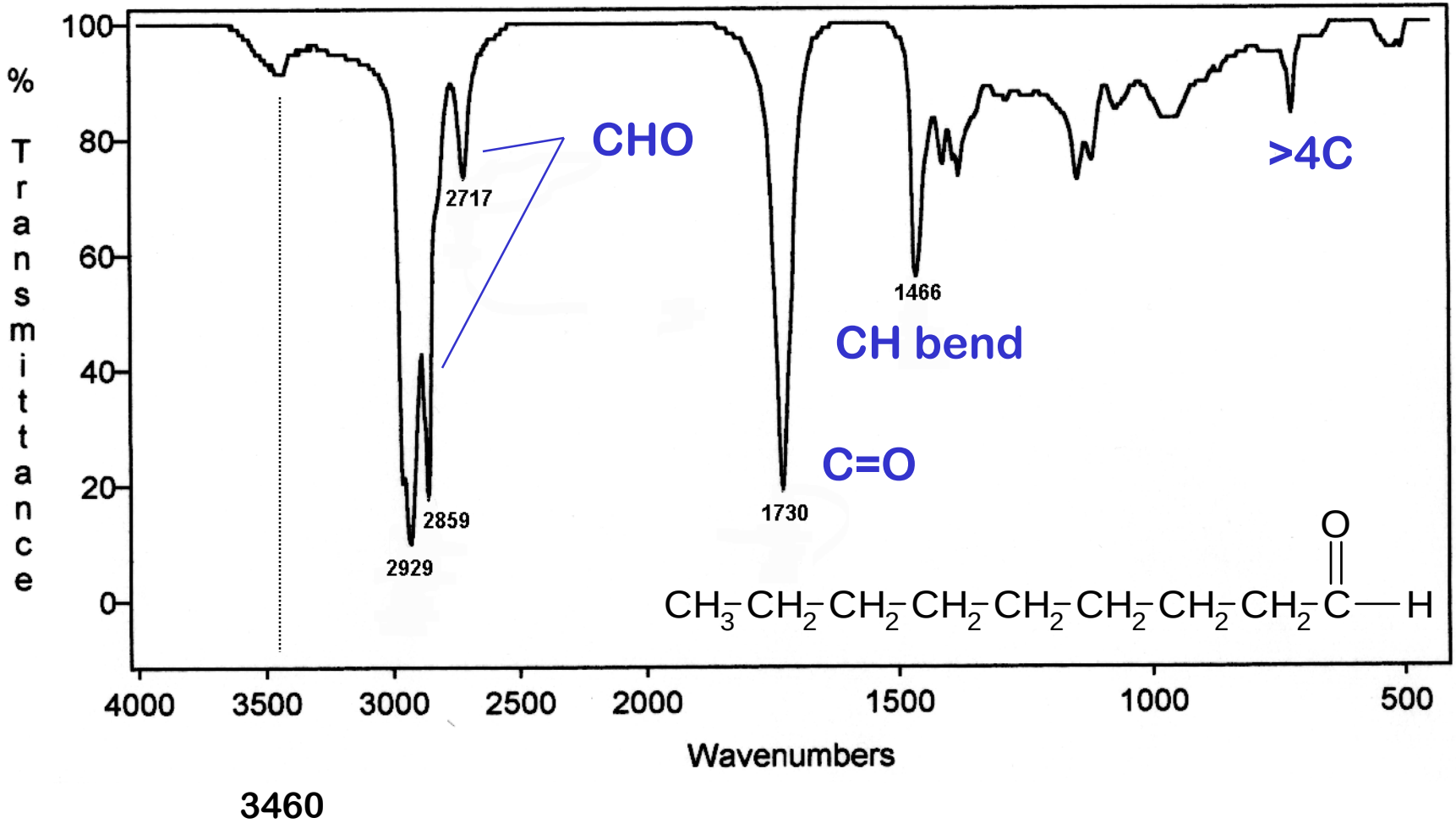


3438

ALDEHYDE

BASE = 1725

Nonanal

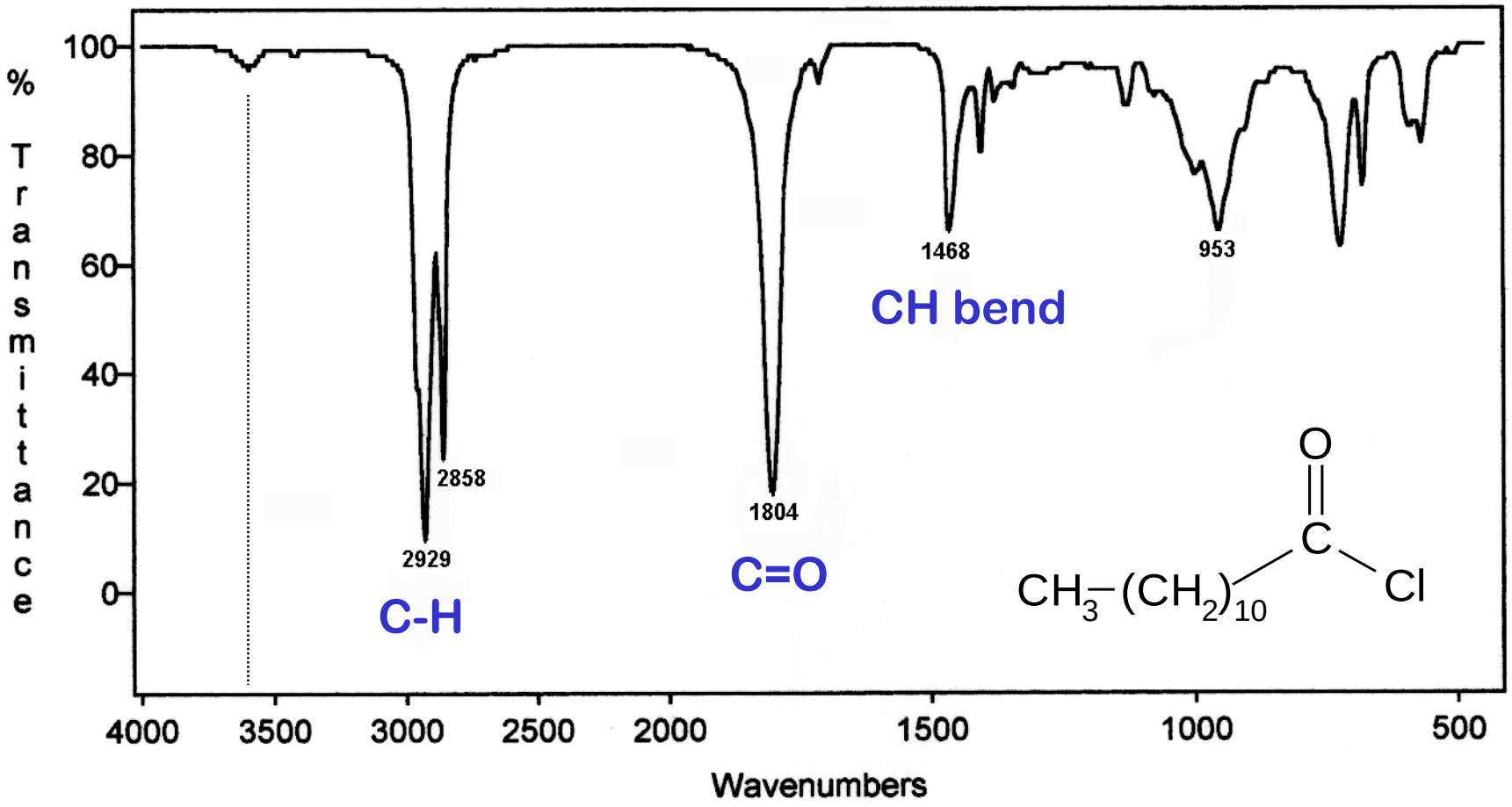


3460

ACID CHLORIDE

BASE = 1800

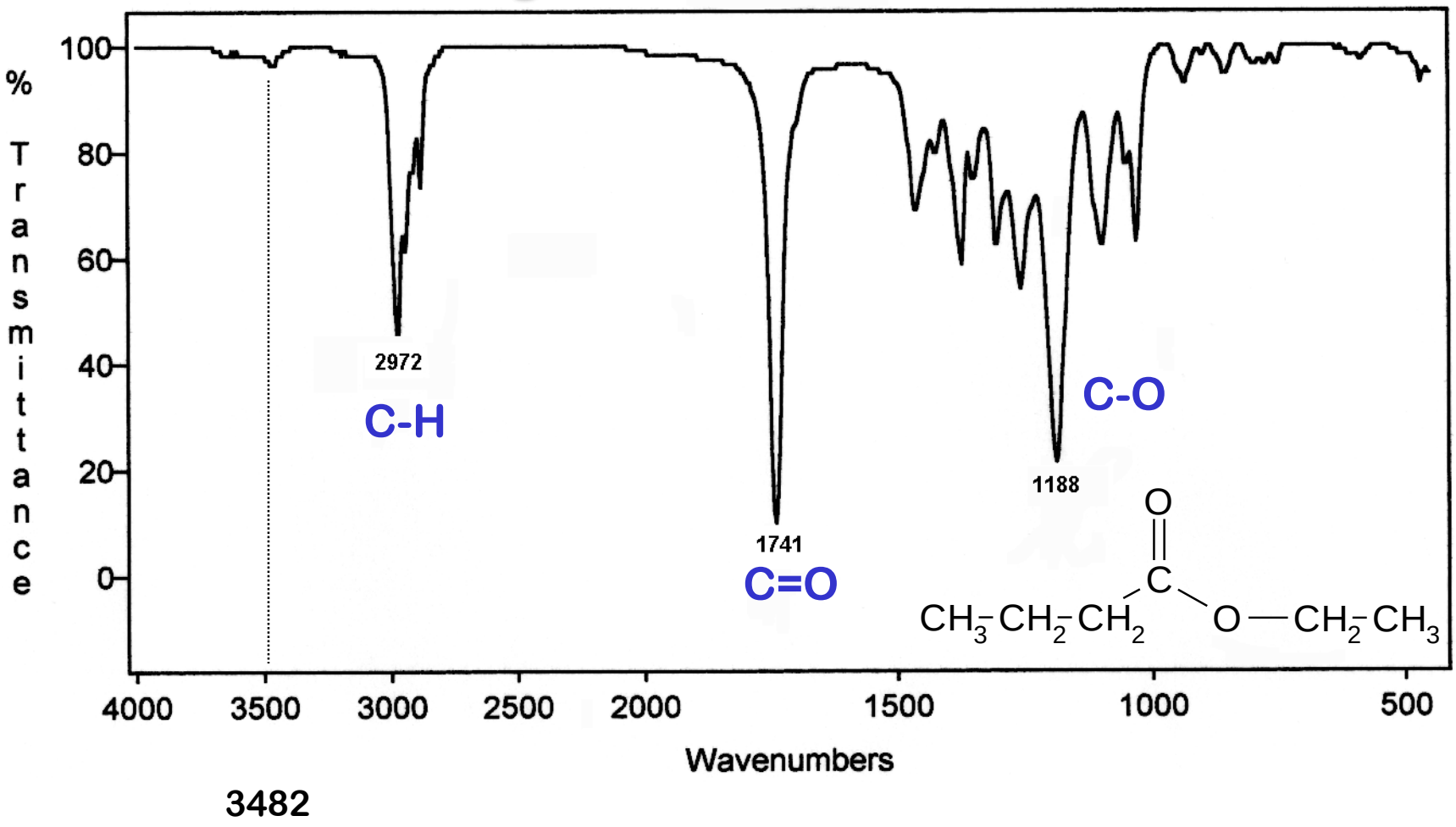
Dodecanoyl Chloride



ESTER

BASE = 1735

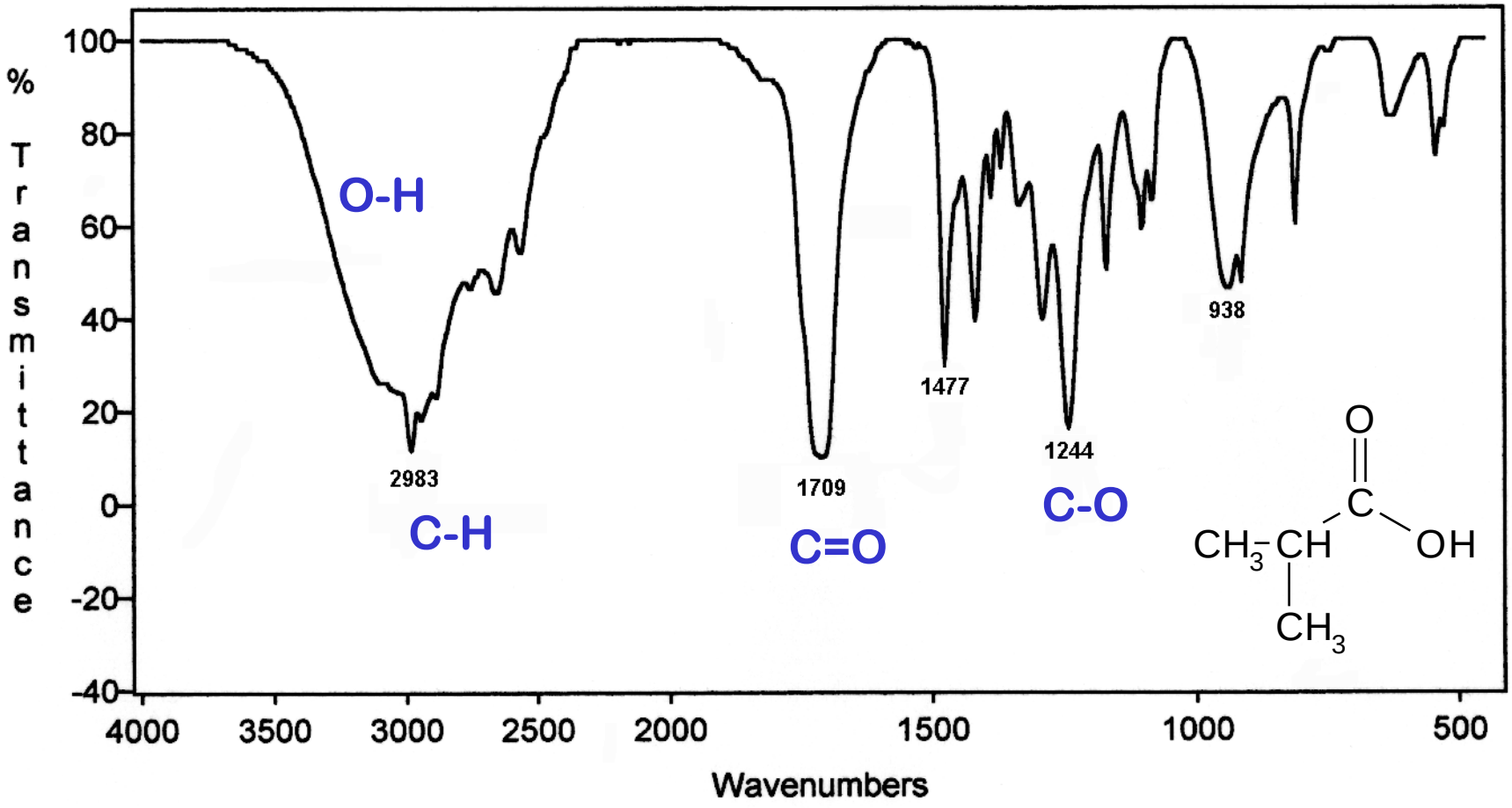
Ethyl Butanoate



CARBOXYLIC ACID

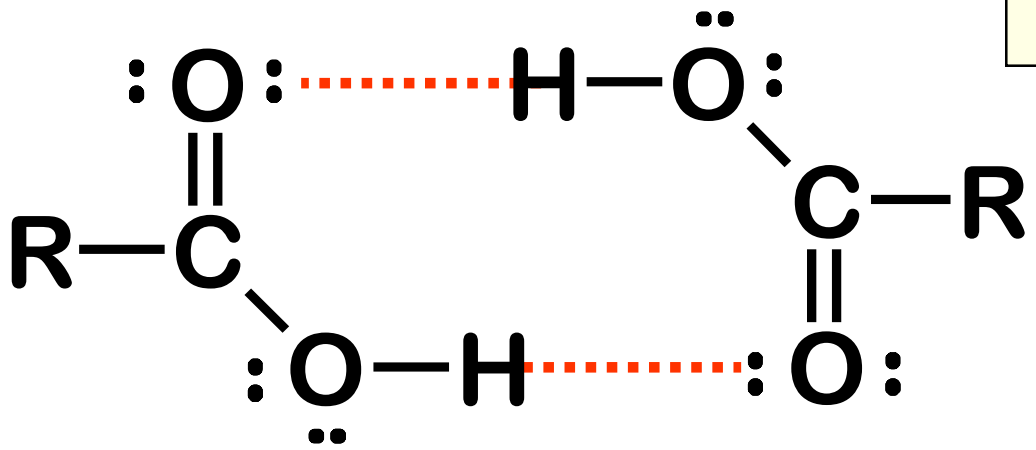
BASE = 1710

2-Methylpropanoic Acid



CARBOXYLIC ACID DIMER

RECALL



lowers frequency of C=O

and also of O-H

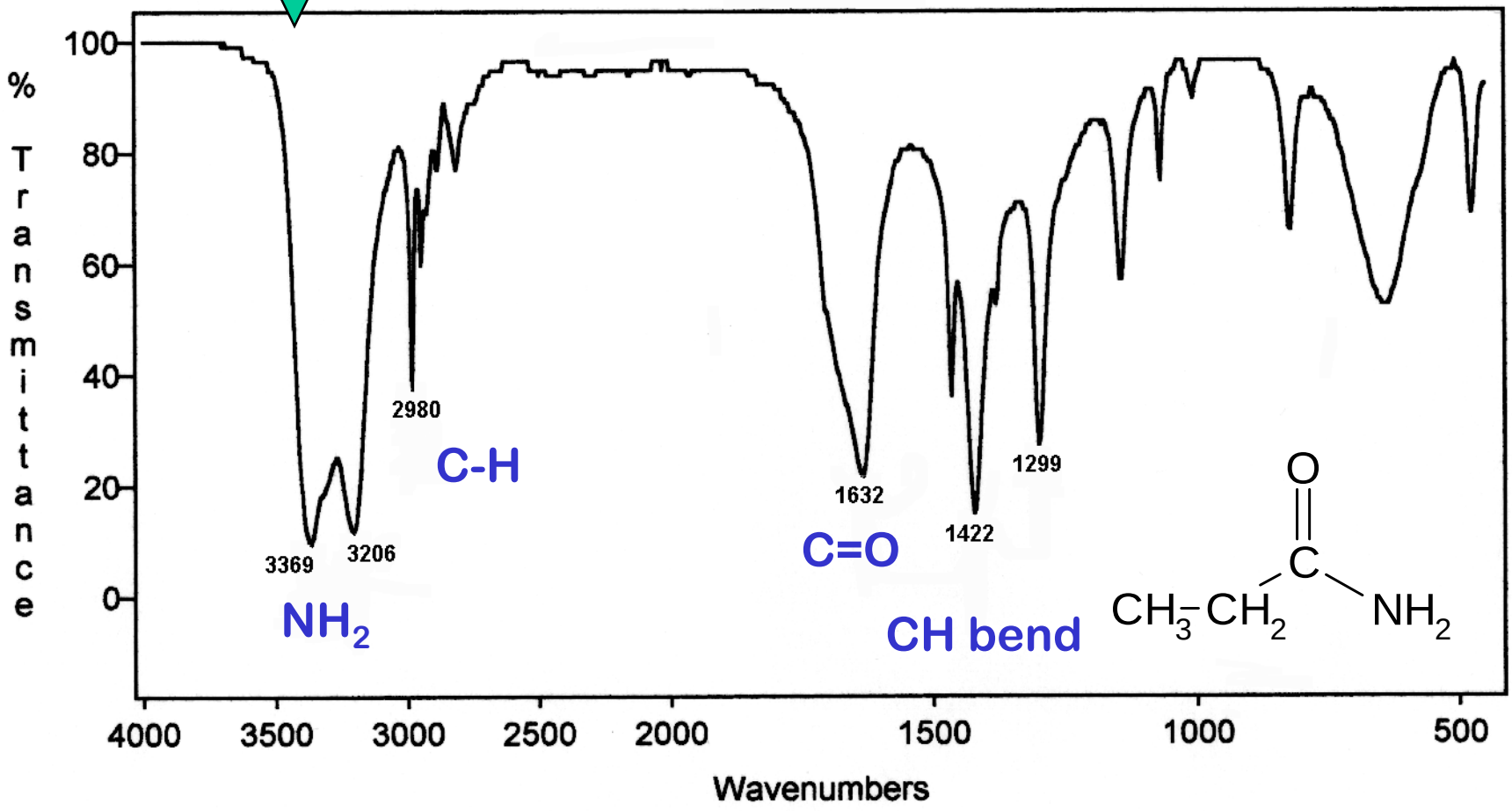
Strong hydrogen-bonding in the dimer weakens the O-H and C=O bonds and leads to broad peaks at lower frequencies.

AMIDE

BASE = 1690

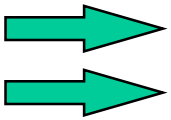
two peaks
sym / asym

Propanamide



EFFECTS OF CONJUGATION
AND RING SIZE ON C=O

ALKENES AND AROMATICS
(C=C STRETCHING)



O-H 3600
N-H 3400
C-H 3000

C≡N 2250
C≡C 2150

C=O 1715
C=C 1650

C-O 1100

SURVEY OF SPECTRA

CONJUGATION

Conjugation of C=O with C=C

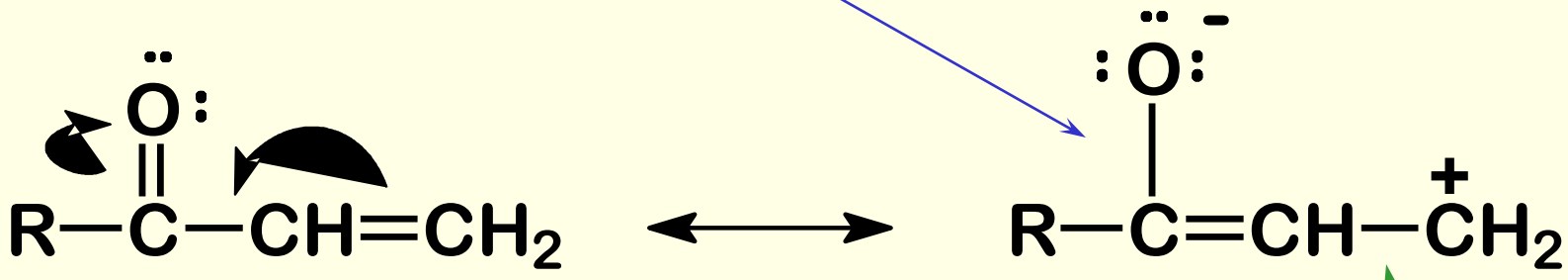
- Conjugation of a carbonyl with a C=C bond shifts values to lower frequencies

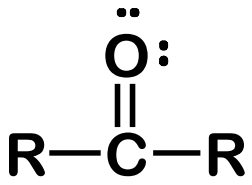
- For aldehydes, ketones and esters, subtract about 25-30 cm^{-1} for conjugation with C=O

- Conjugated ketone = 1690 to 1680 cm^{-1}
- Conjugated ester = 1710 to 1700 cm^{-1}
- C=C becomes quite strong!!

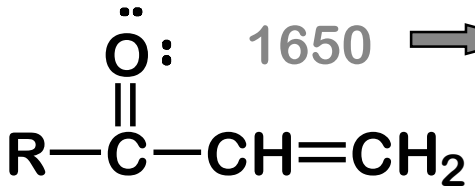
CONJUGATION LOWERS THE FREQUENCY OF C=O AND ALSO OF C=C (WHICH IS STRENGTHENED)

resonance lengthens (weakens) C=O





1715 → 1690 cm^{-1} lowered



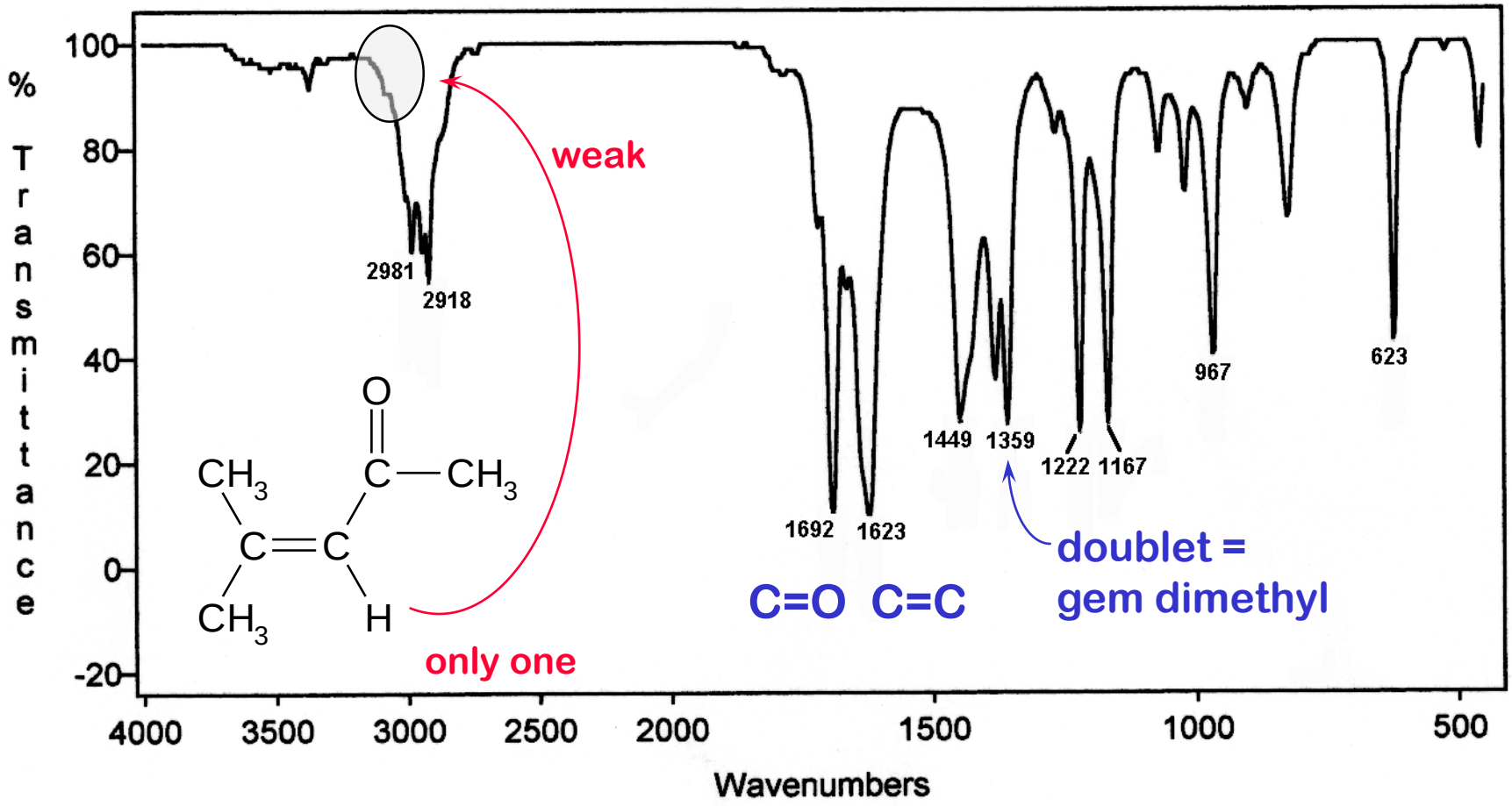
1650 → 1625 cm^{-1}

C=C is also lengthened (weakened) ….. and polarized !

C=O : 1715 - 30 = 1685
C=C : 1650 - 25 = 1625

KETONE conjugated

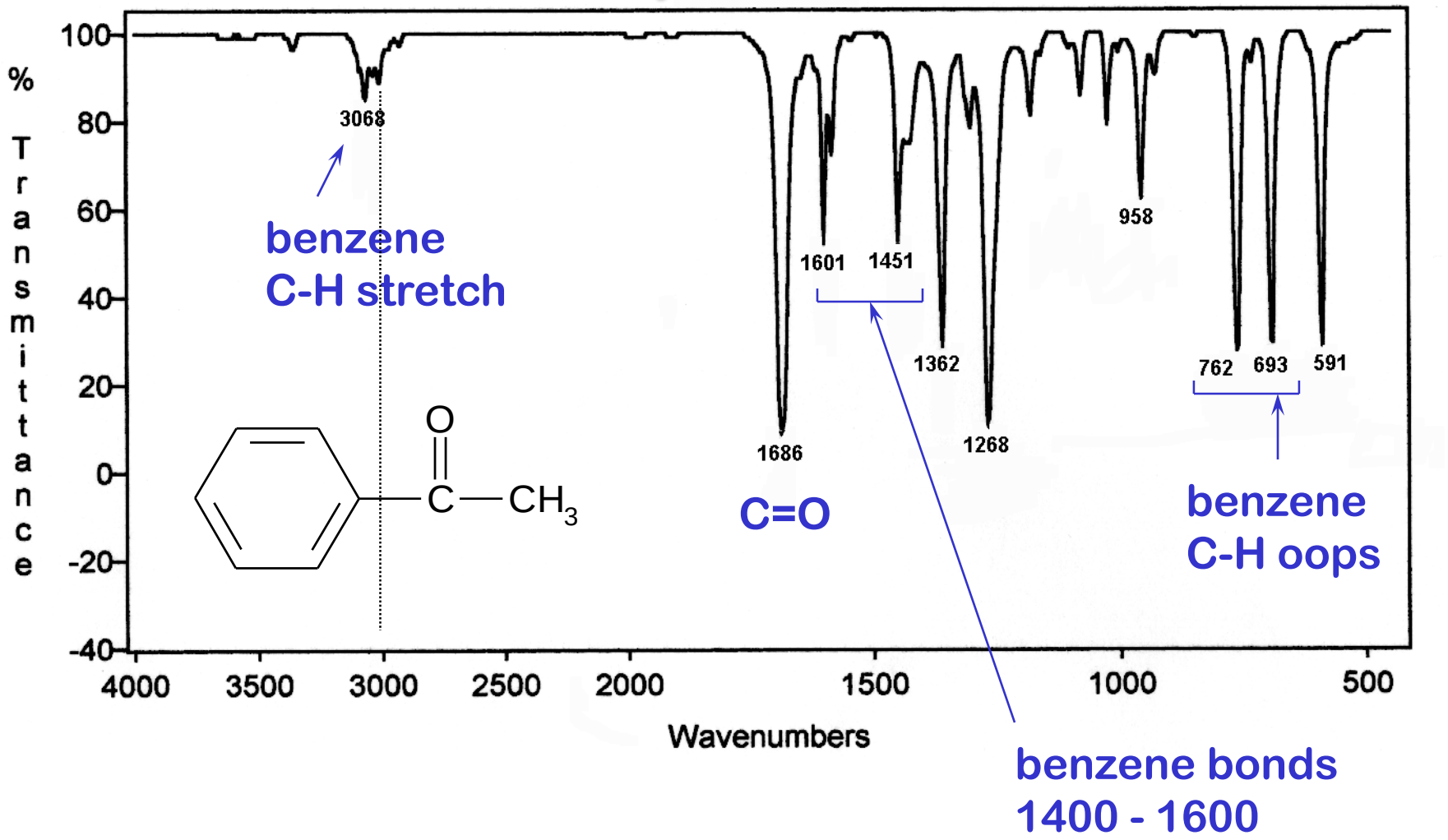
4-Methyl-3-penten-2-one



C=O : 1715 - 30 = 1685

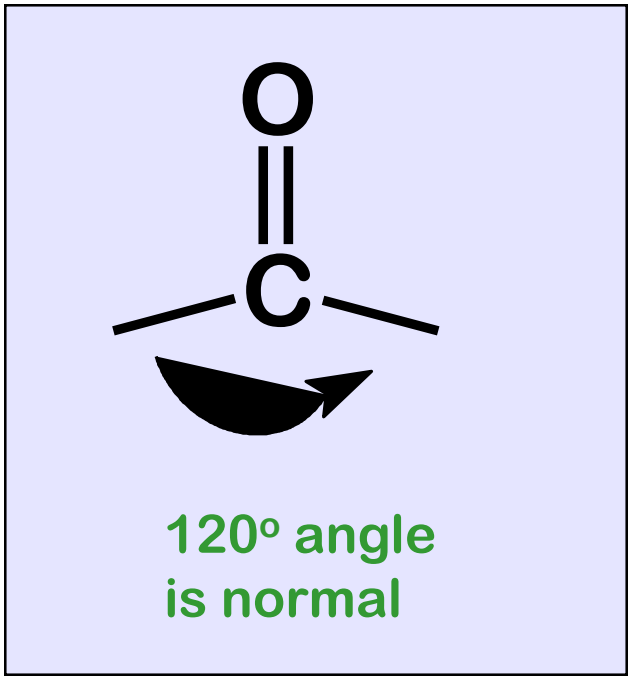
AROMATIC KETONE
conjugated

Acetophenone

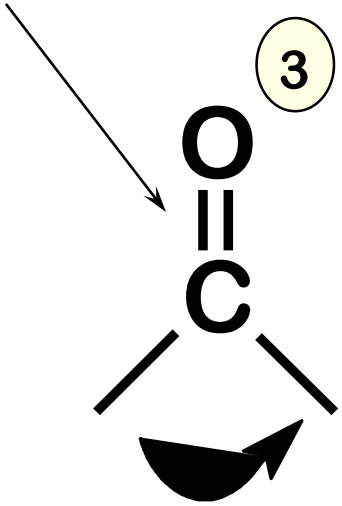


RING SIZE / ANGLE STRAIN

ANGLE STRAIN RAISES THE CARBONYL FREQUENCY



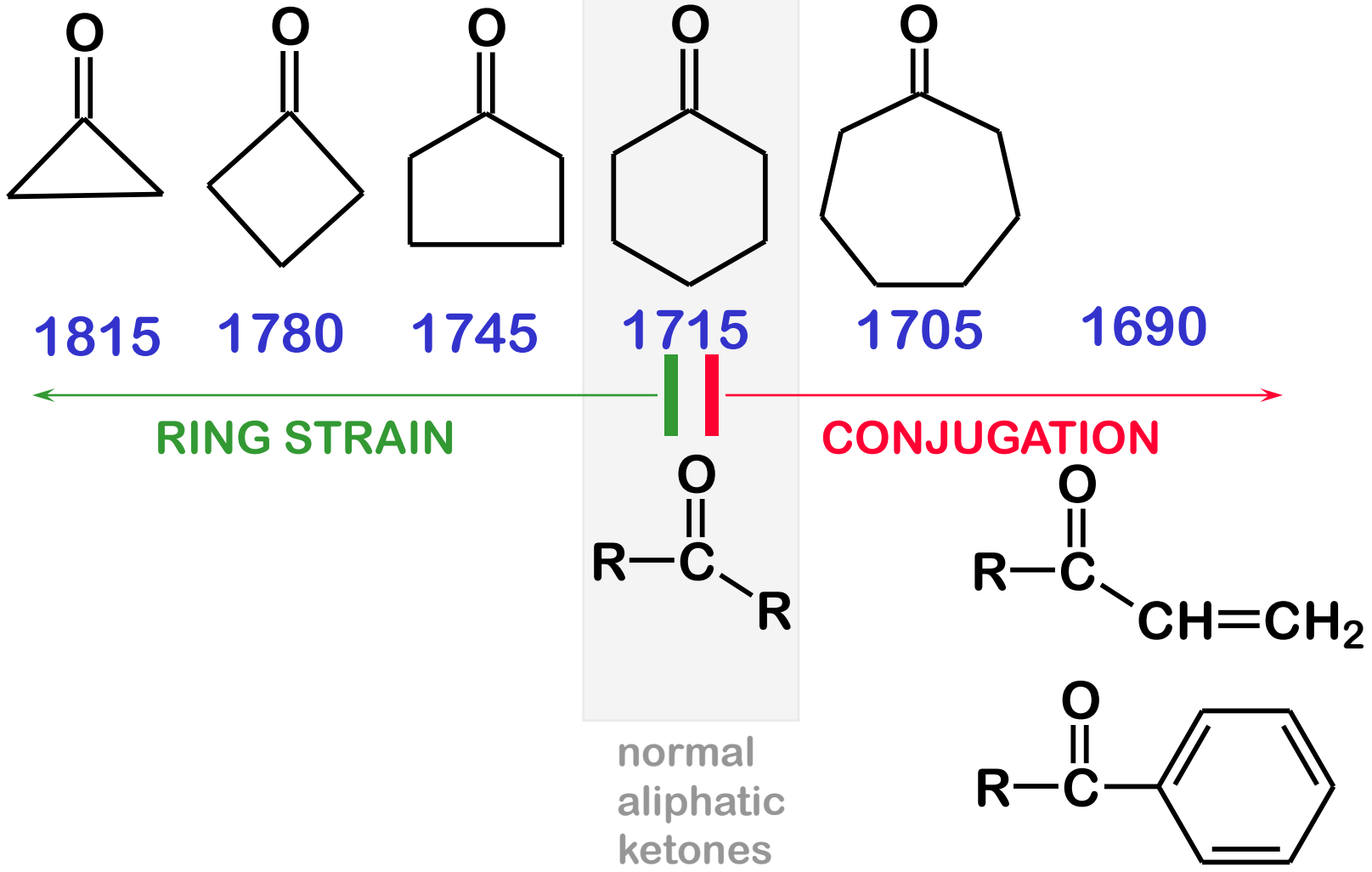
2 In response to more p in the ring bonds, there is more s character in the bonds to C=O.



3 More s character leads to a shorter and stronger bond and a higher frequency.

1 A smaller angle requires more p character in the hybrids forming the ring.

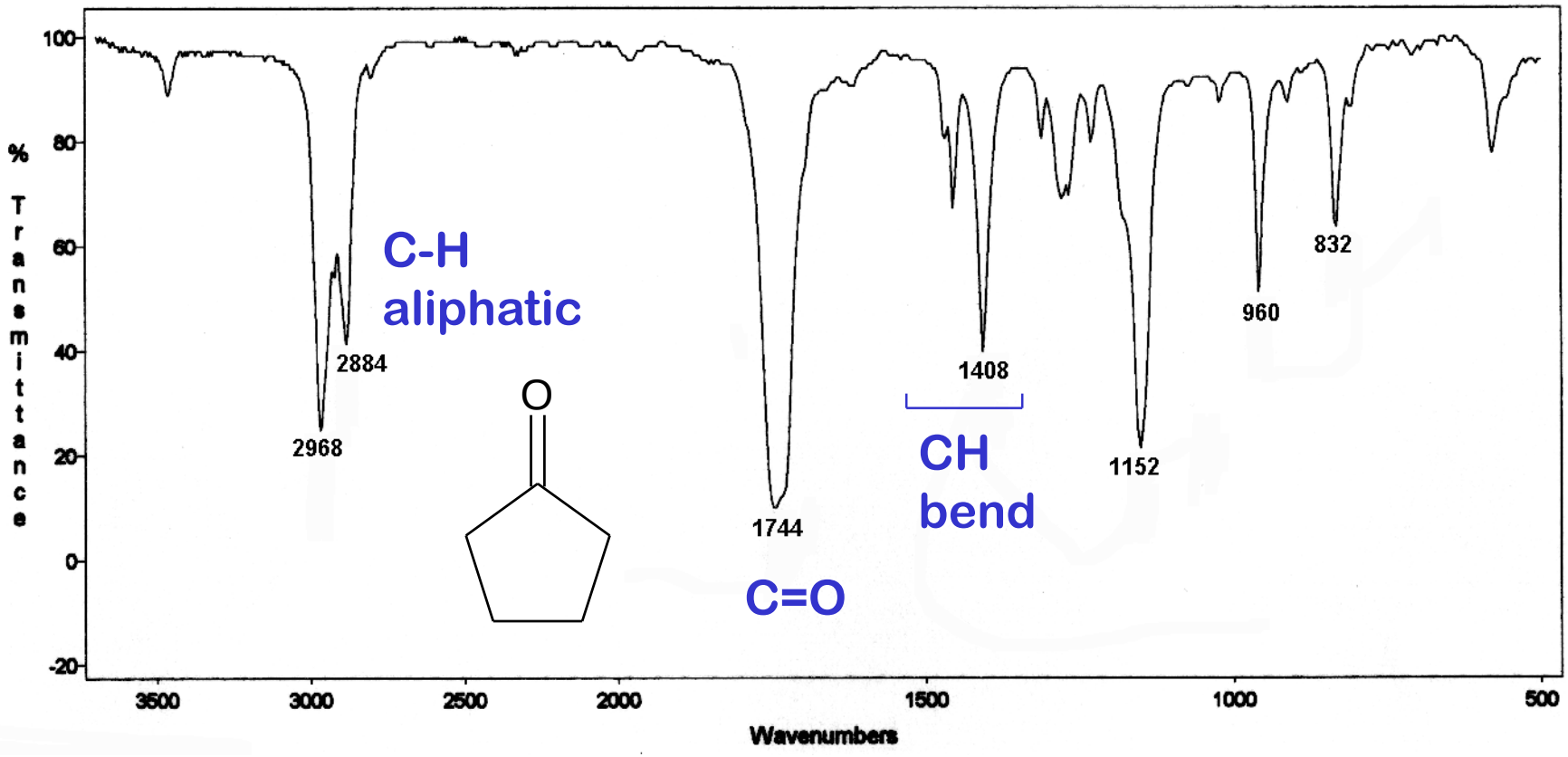
CONJUGATION AND RING SIZE EFFECTS



CYCLIC KETONE
5-ring

expected = 1740

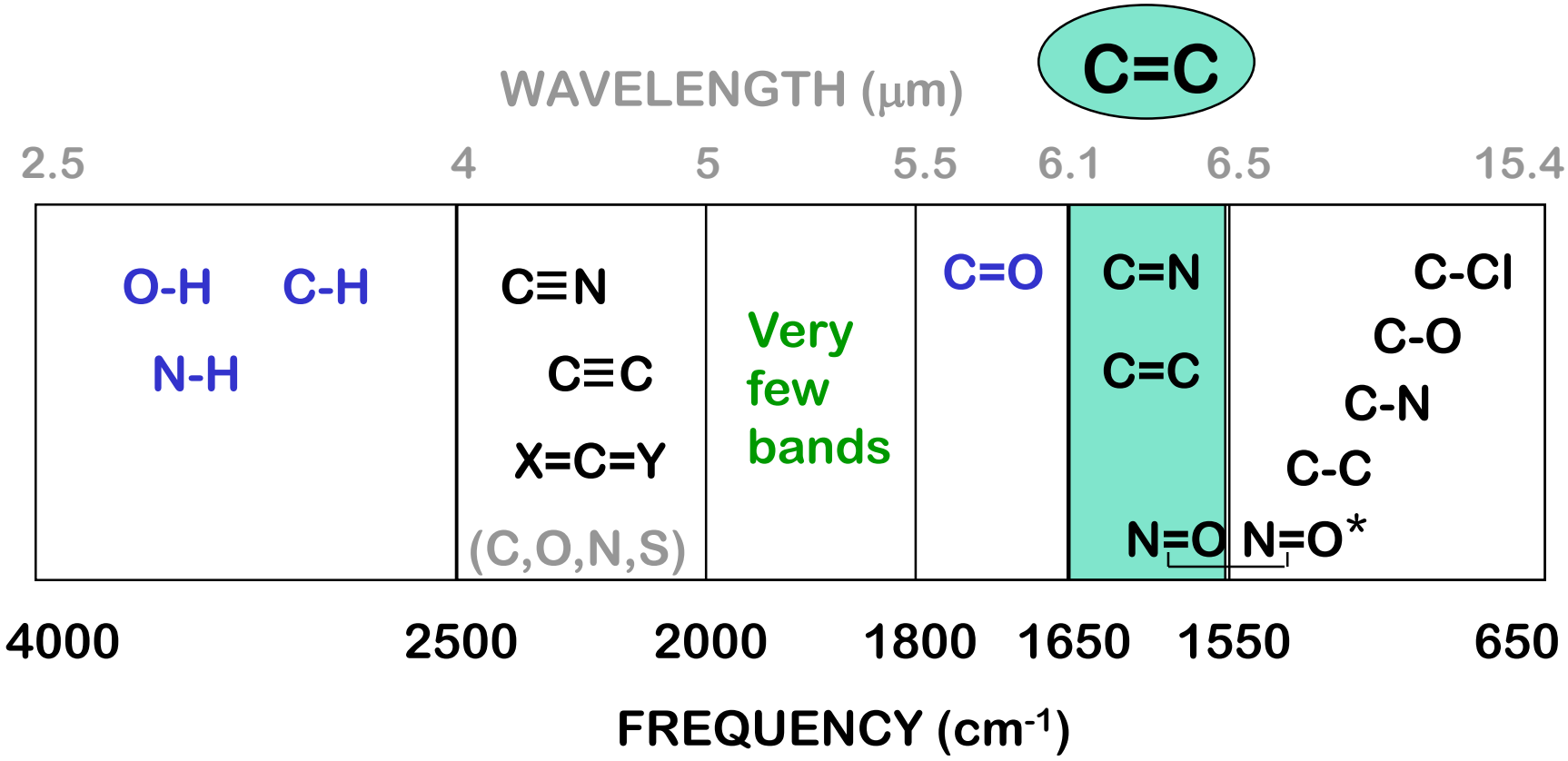
Cyclopentanone



ALKENES
AROMATICS

C=C STRETCHING

Typical Infrared Absorption Regions



The C=C stretching region

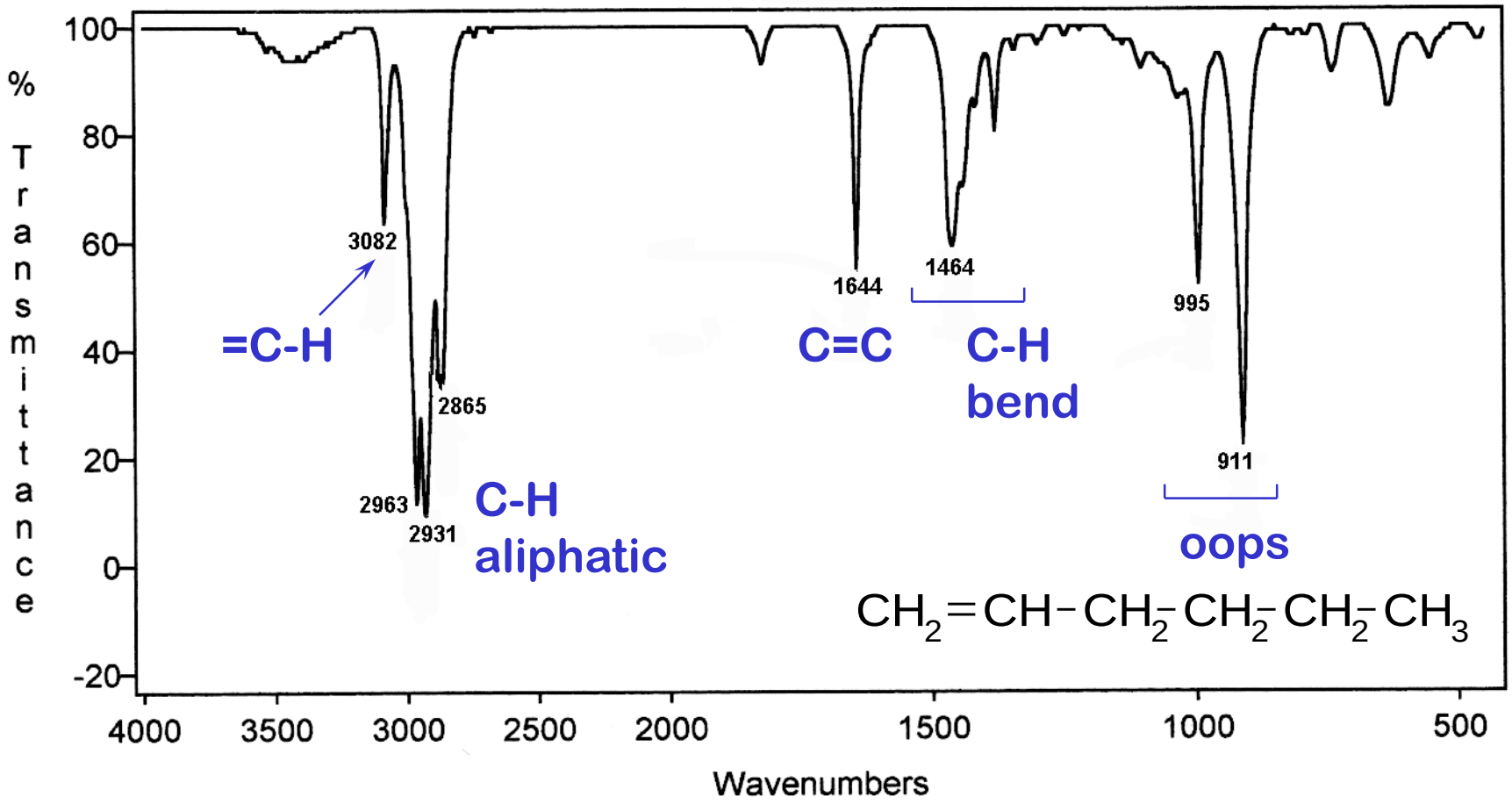
- C=C double bond at 1650 cm^{-1} is often weak or not even seen.

- C=C benzene ring shows peak(s) near 1600 and 1400 cm^{-1} , one or two at each value - CONJUGATION LOWERS THE VALUE.

- When C=C is conjugated with C=O it is stronger and comes at a lower frequency.

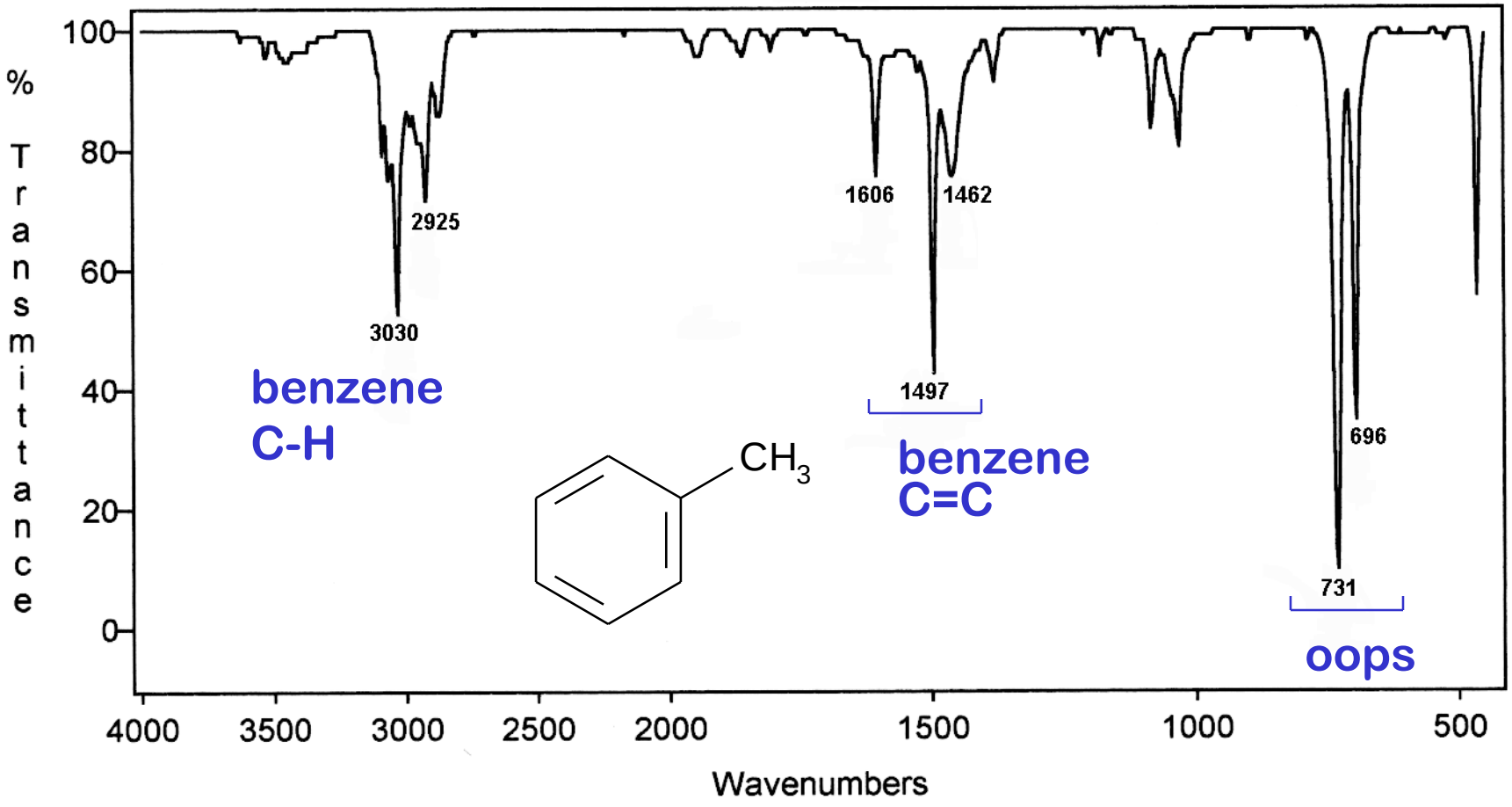
ALKENE

1-Hexene

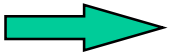


AROMATIC

Toluene



ALCOHOLS
ETHERS
(C-O STRETCHING)



O-H 3600
N-H 3400
C-H 3000

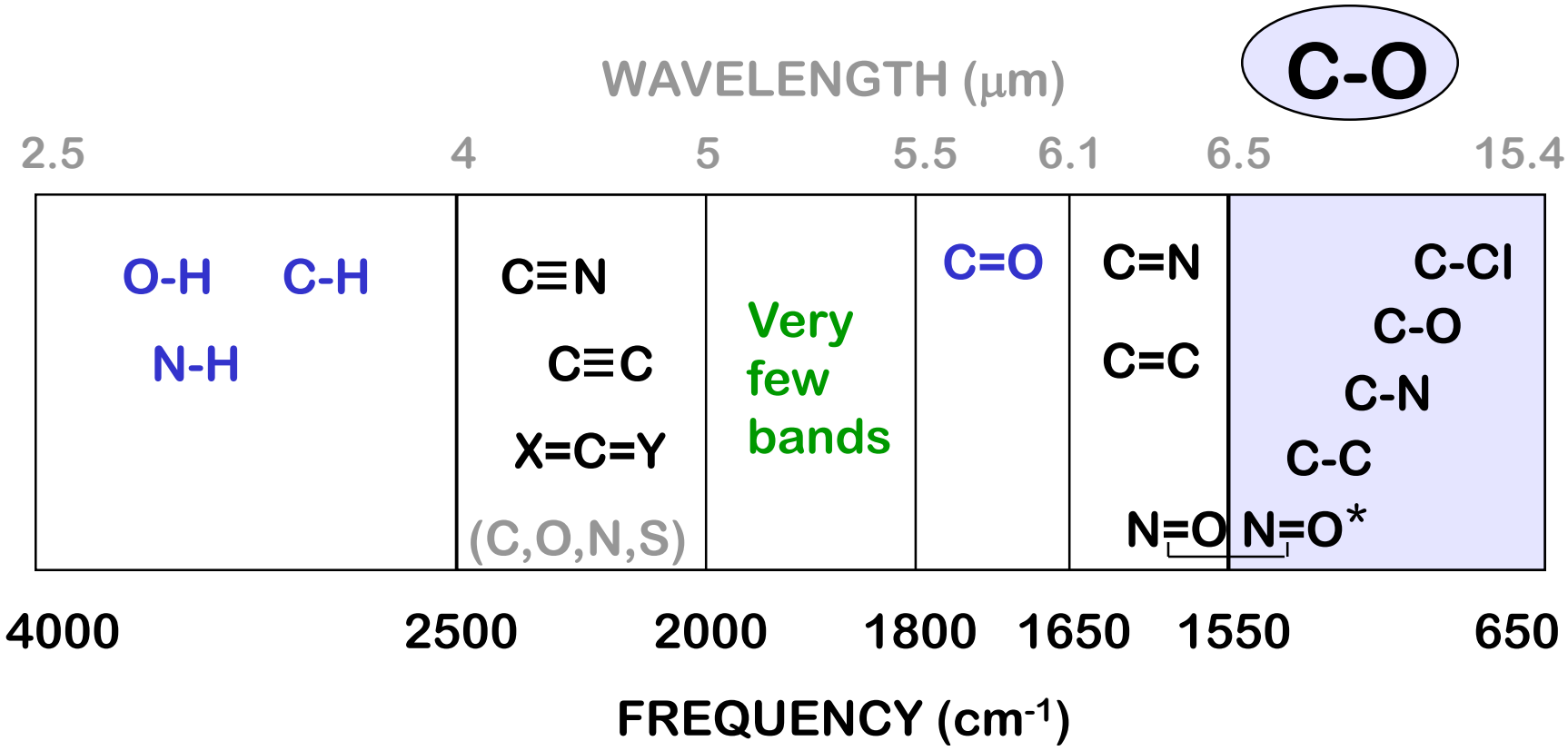
C≡N 2250
C≡C 2150

C=O 1715
C=C 1650

C-O 1100

SURVEY OF SPECTRA

Typical Infrared Absorption Regions



C-O STRETCHING

The C-O stretching region

- The C-O band appears in the range of 1300 to 1000 cm^{-1}

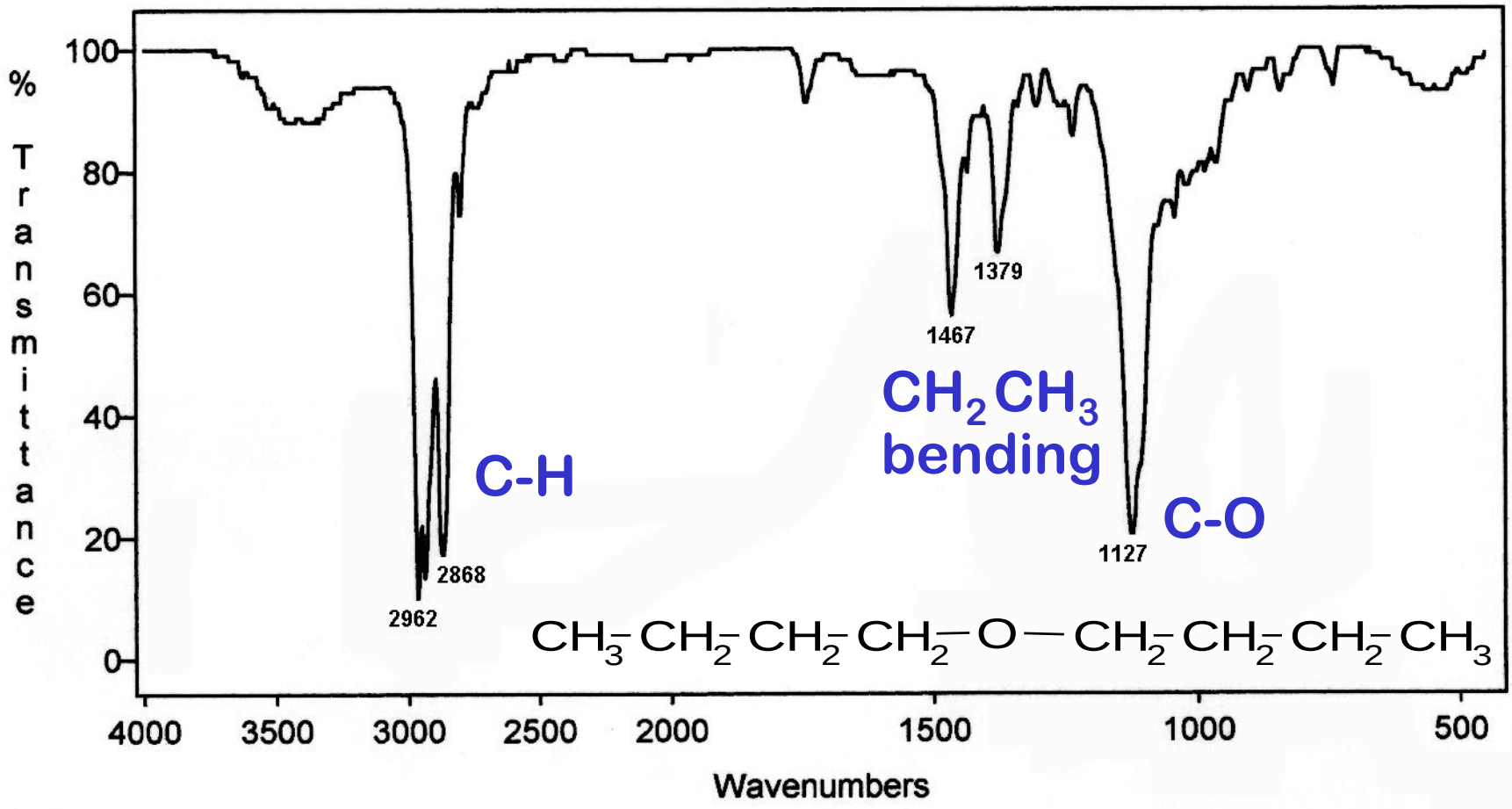
- Look for one or more strong bands appearing in this range!

- Ethers, alcohols, esters and carboxylic acids have C-O bands

ETHER

BASE = 1100

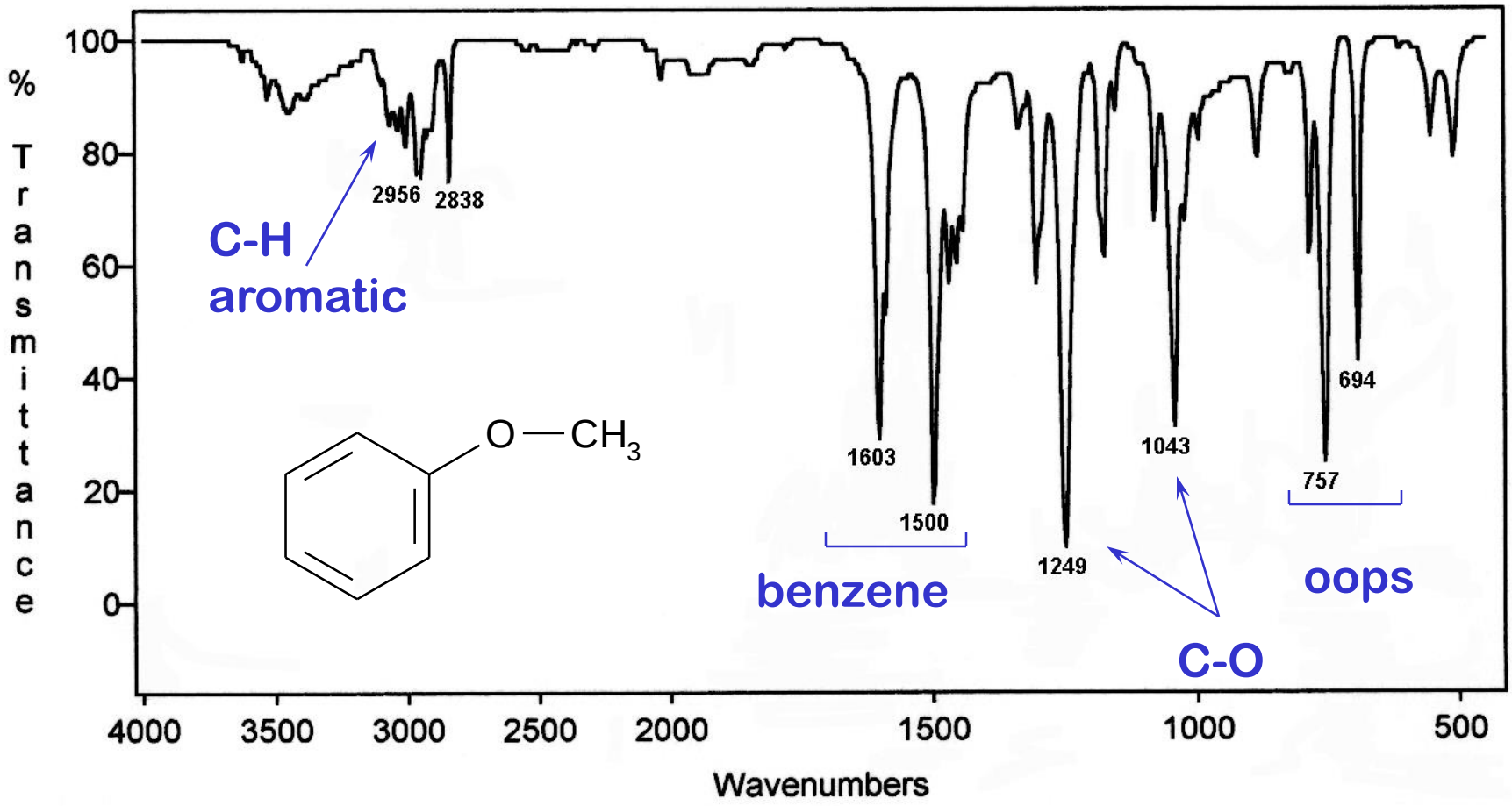
Dibutyl Ether



AROMATIC ETHER

BASE = 1100

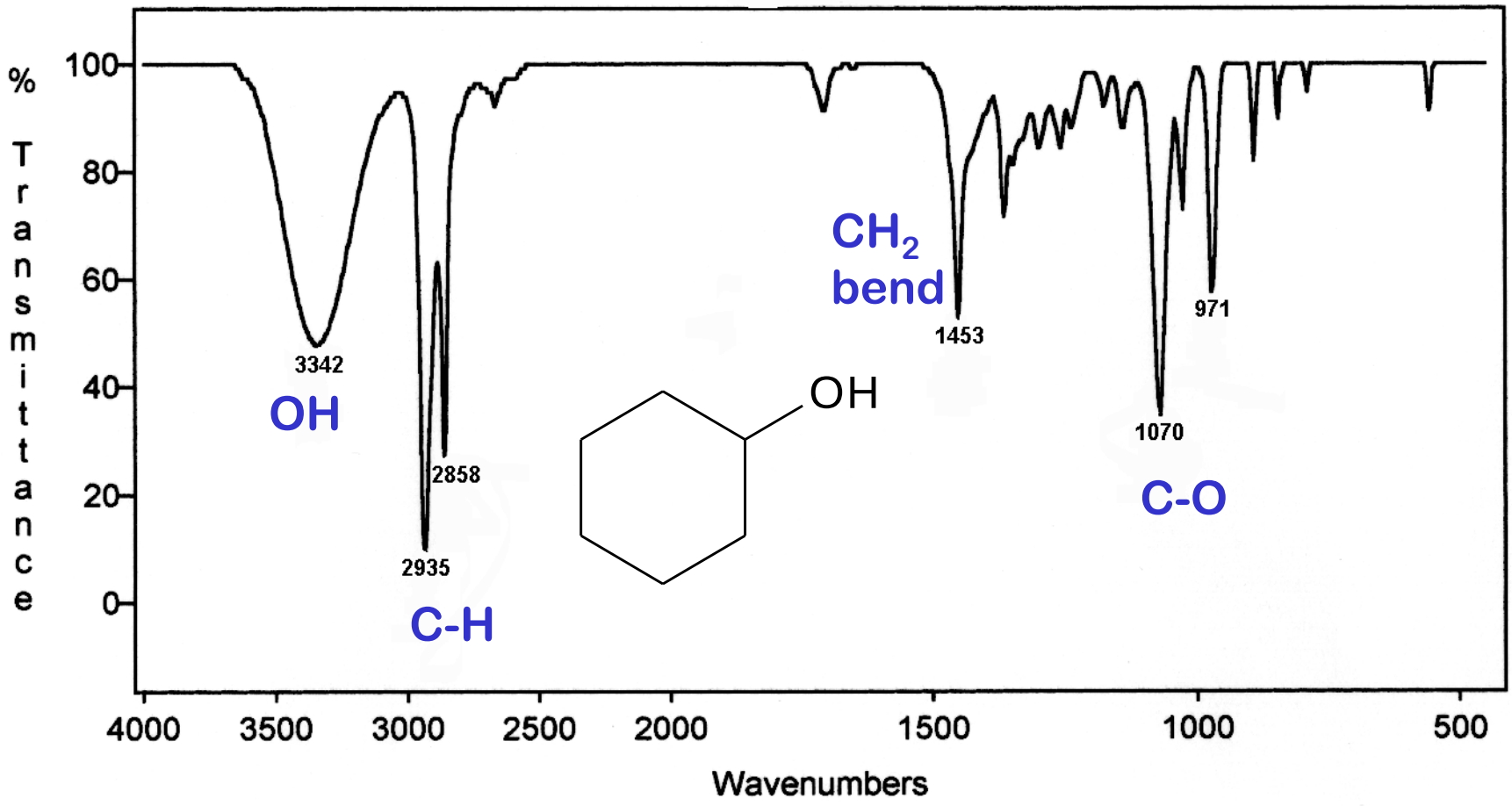
Anisole



ALCOHOL

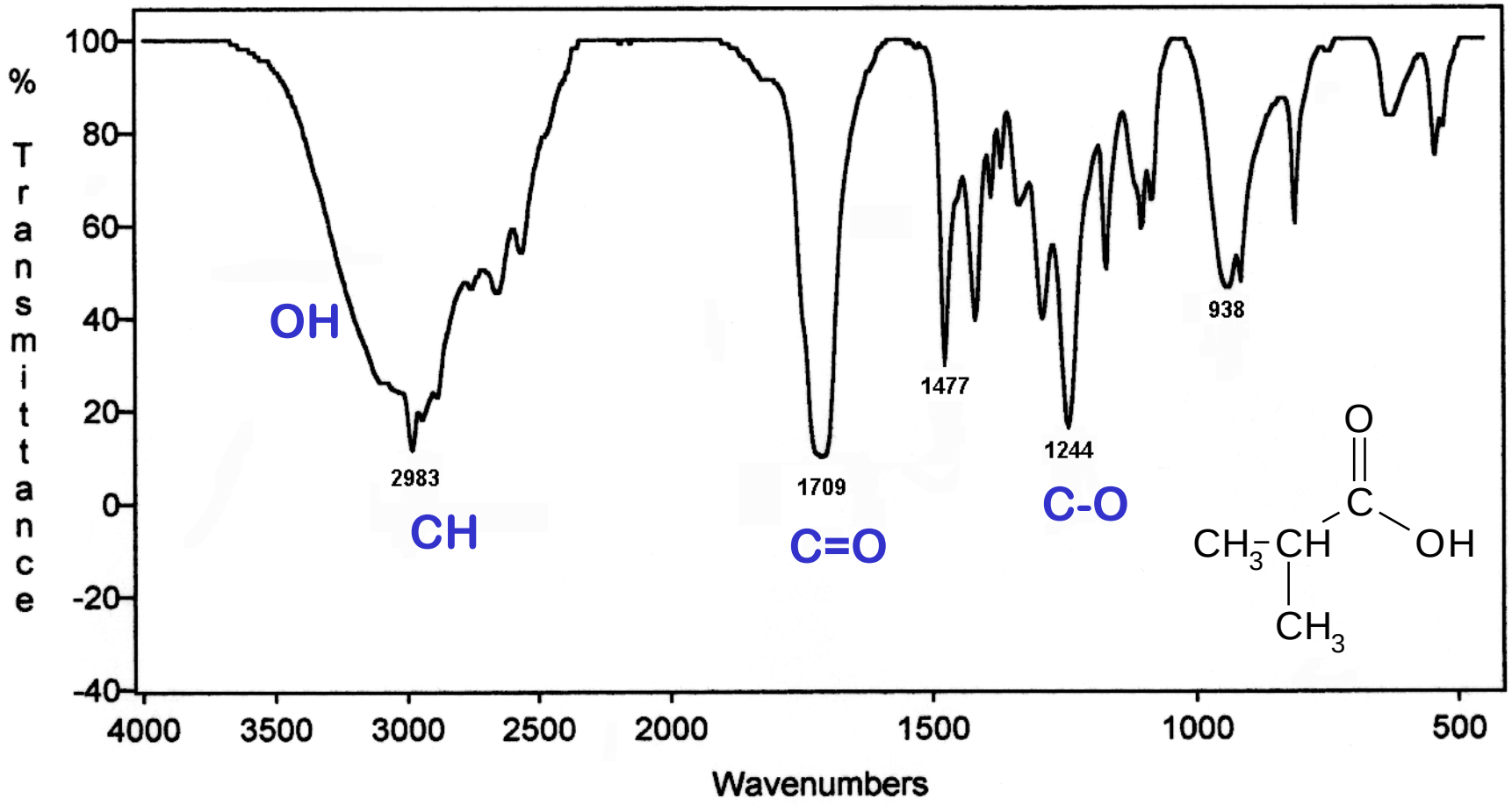
BASE = 3600
BASE = 1100

Cyclohexanol



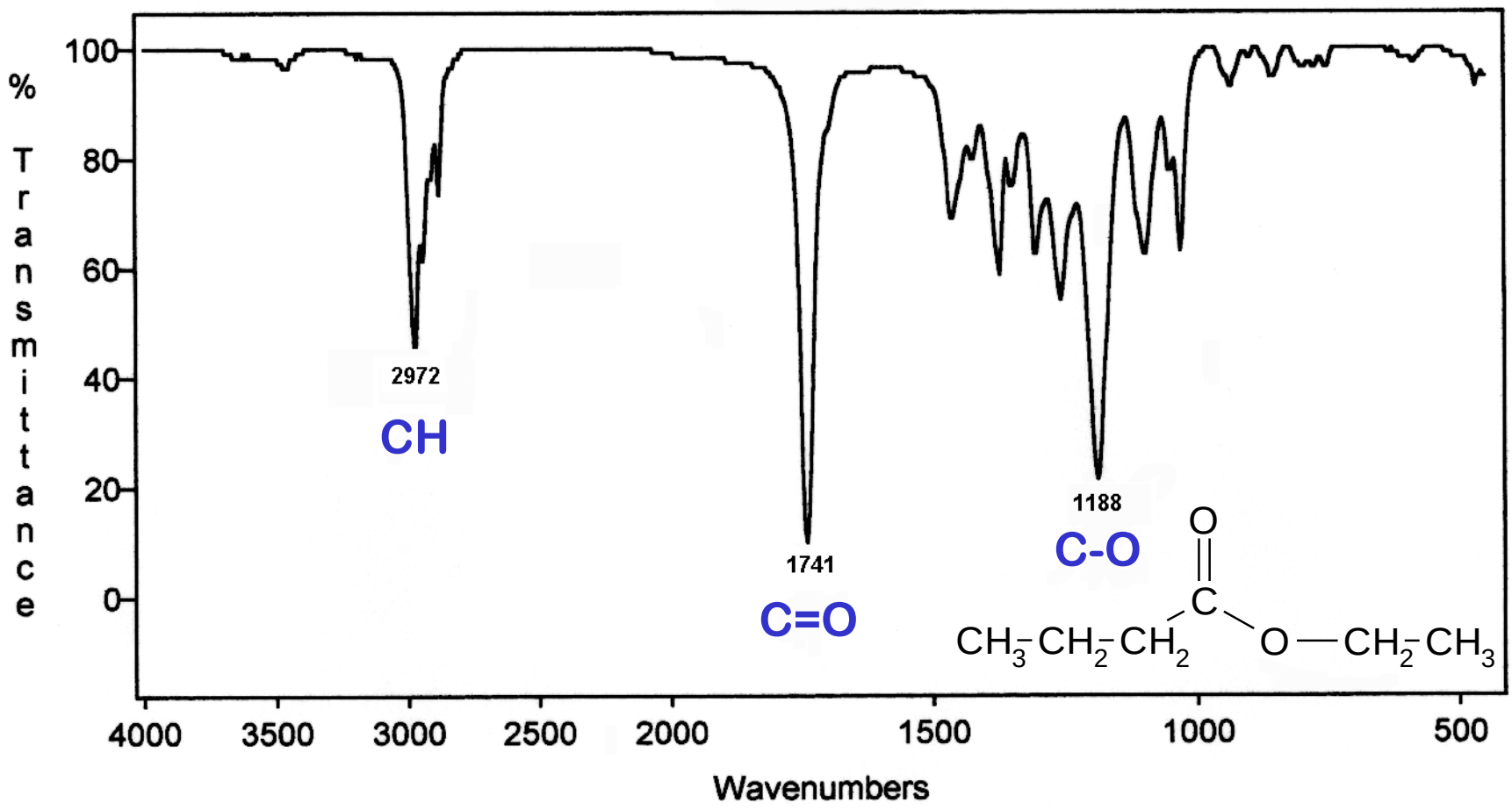
CARBOXYLIC ACID

2-Methylpropanoic Acid



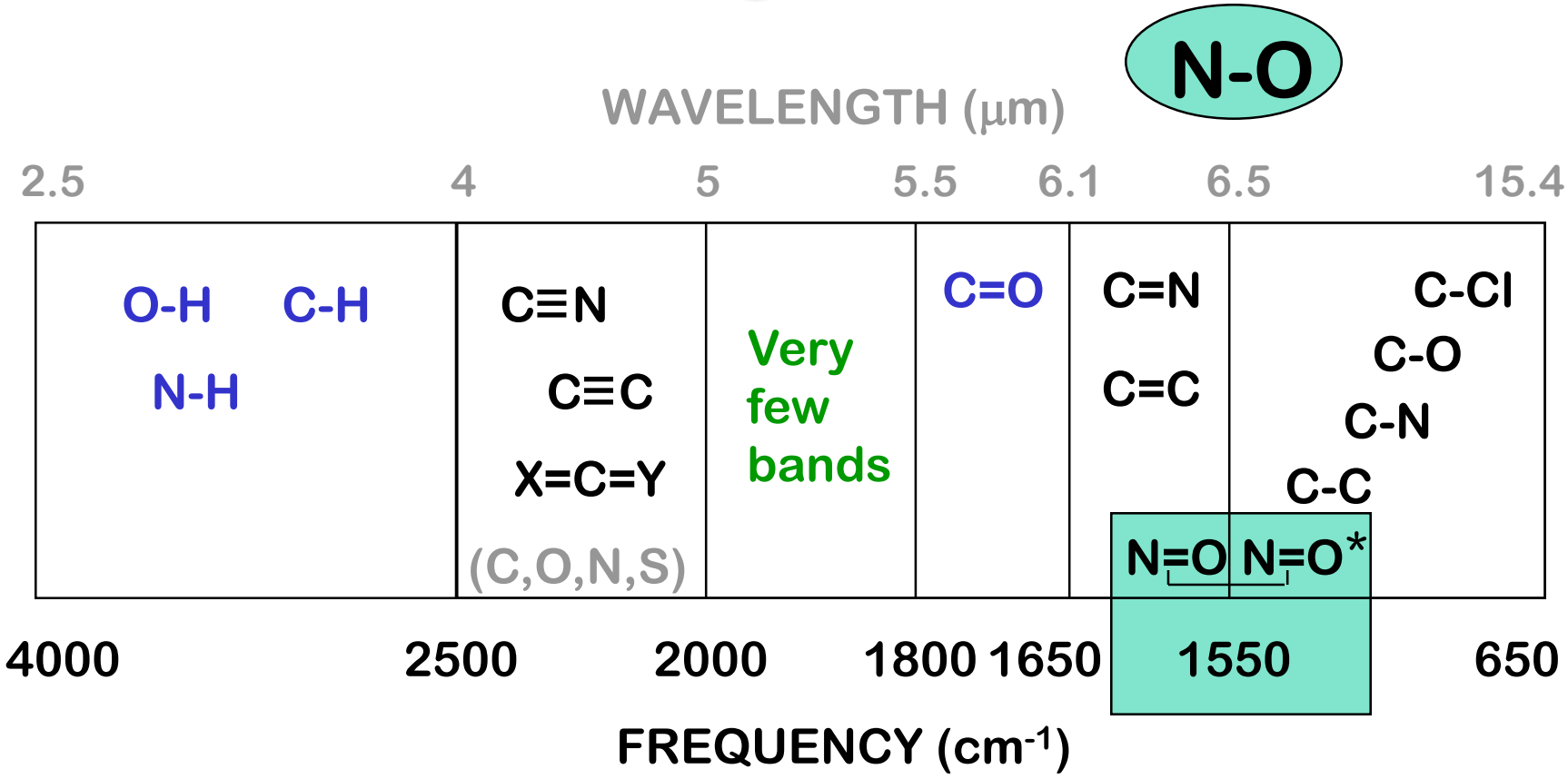
ESTER

Ethyl Butanoate



N=O STRETCHING

Typical Infrared Absorption Regions



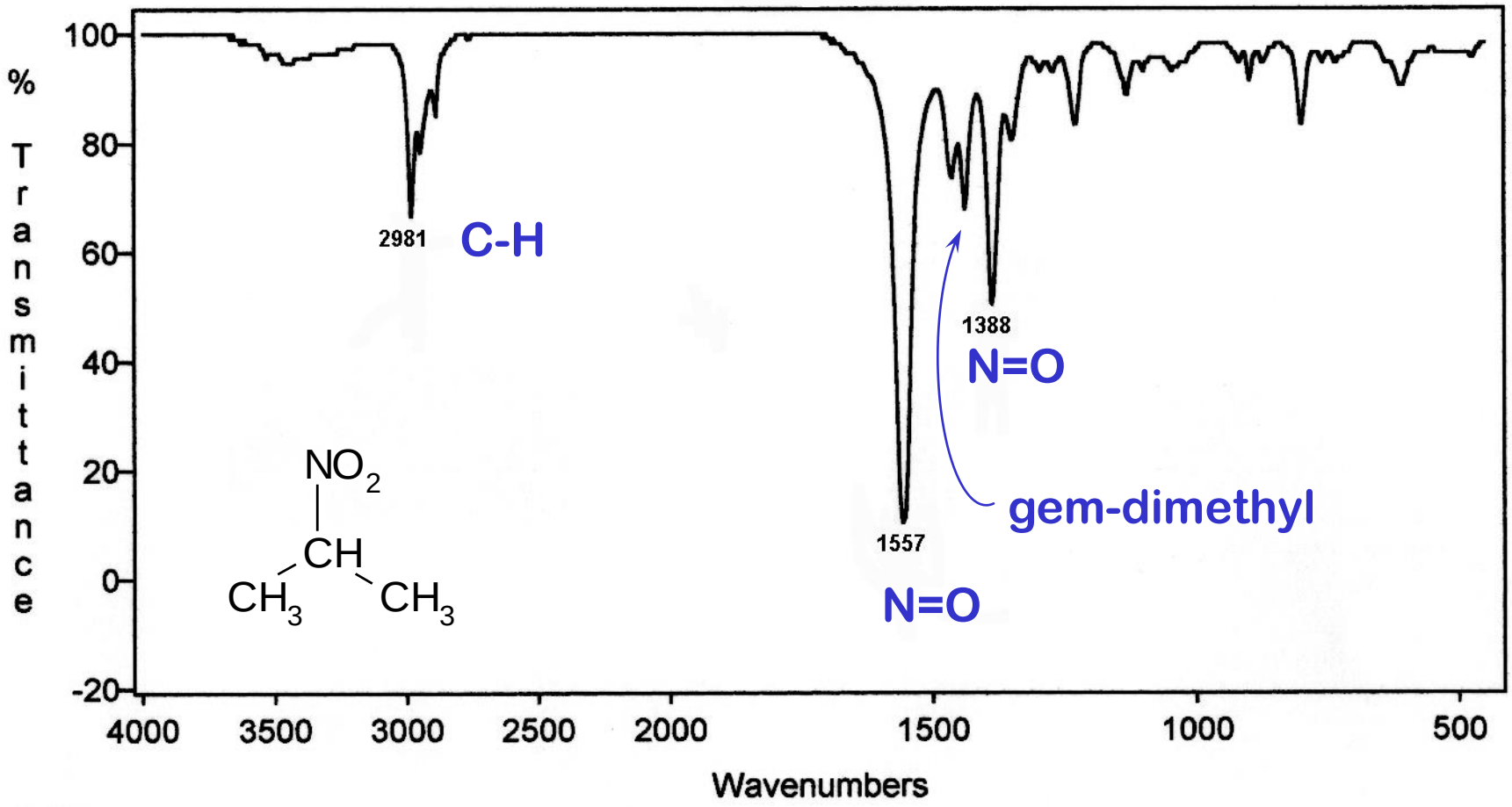
The N=O stretching region

- N=O stretching -- 1550 and 1350 cm^{-1} asymmetric and symmetric stretchings

- Often the 1550 cm^{-1} peak is stronger than the other one

NITROALKANE

2-Nitropropane



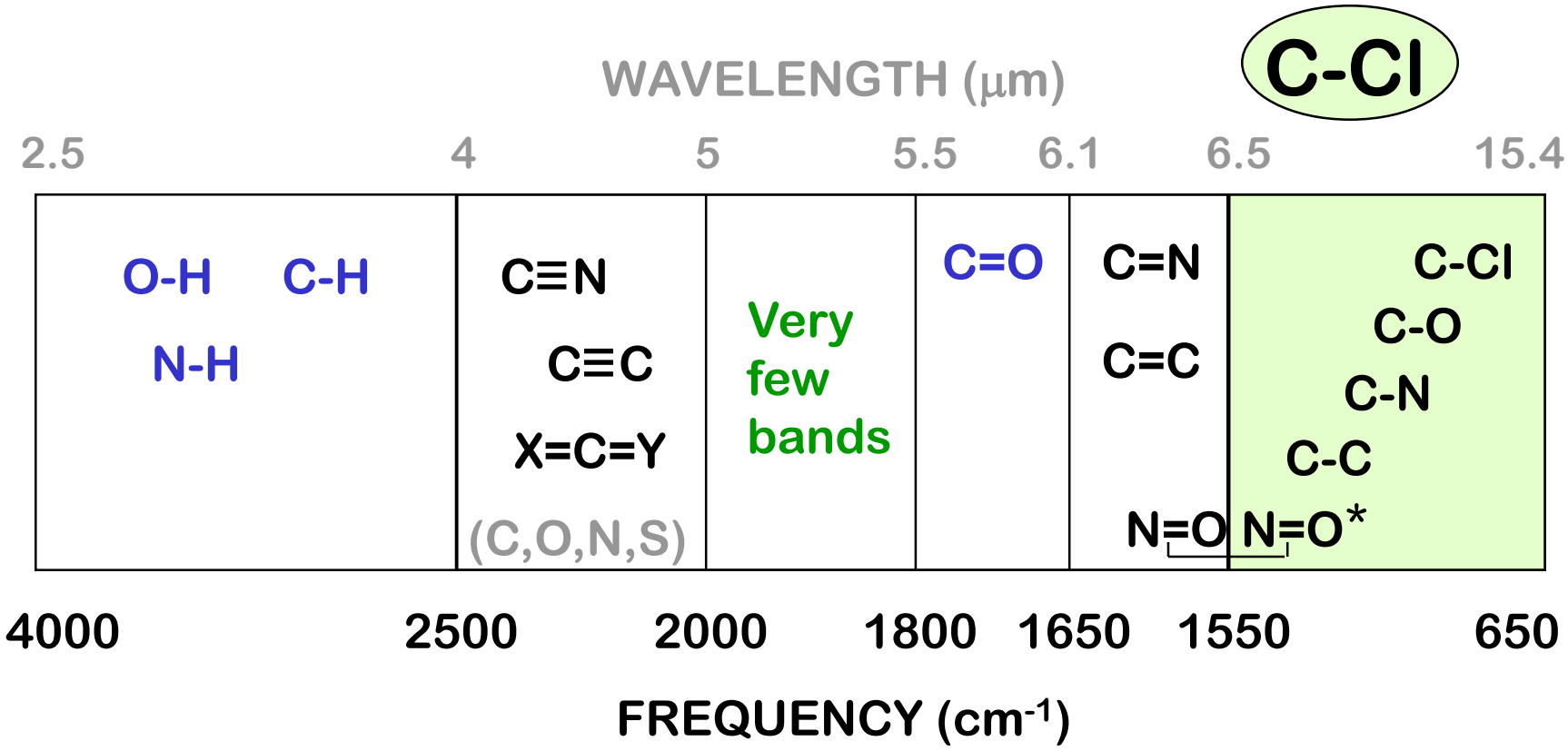
HALIDES

CH Out -of-Plane Bending

Making Decisions on a Functional Group
/ What you need to know

SURVEY OF SPECTRA

Typical Infrared Absorption Regions



The C-X stretching region

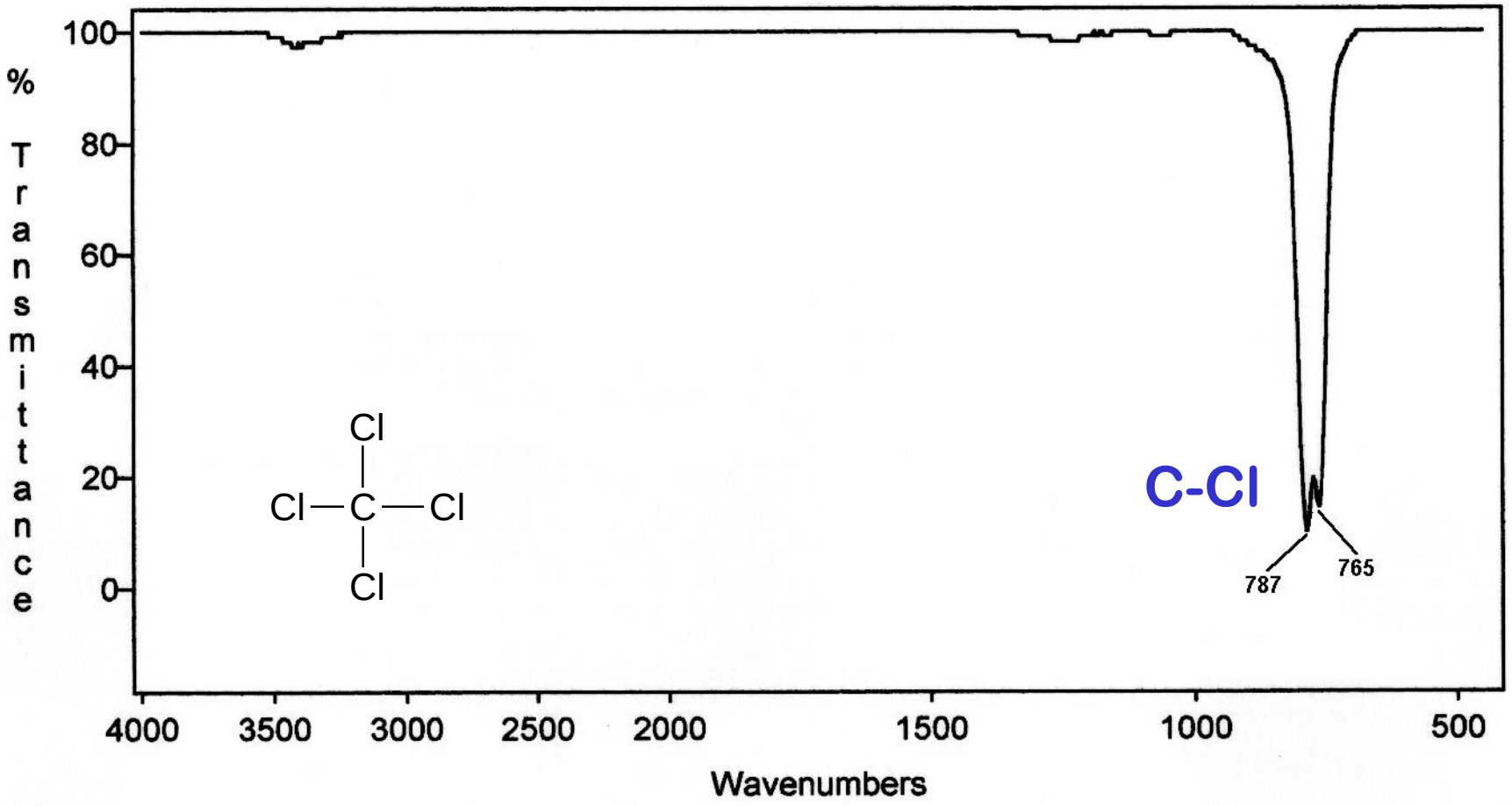
- C-Cl 785 to 540 cm^{-1},
  often hard to find amongst the
  fingerprint bands!!

- C-Br and C-I
  appear outside the useful range of
  infrared spectroscopy.

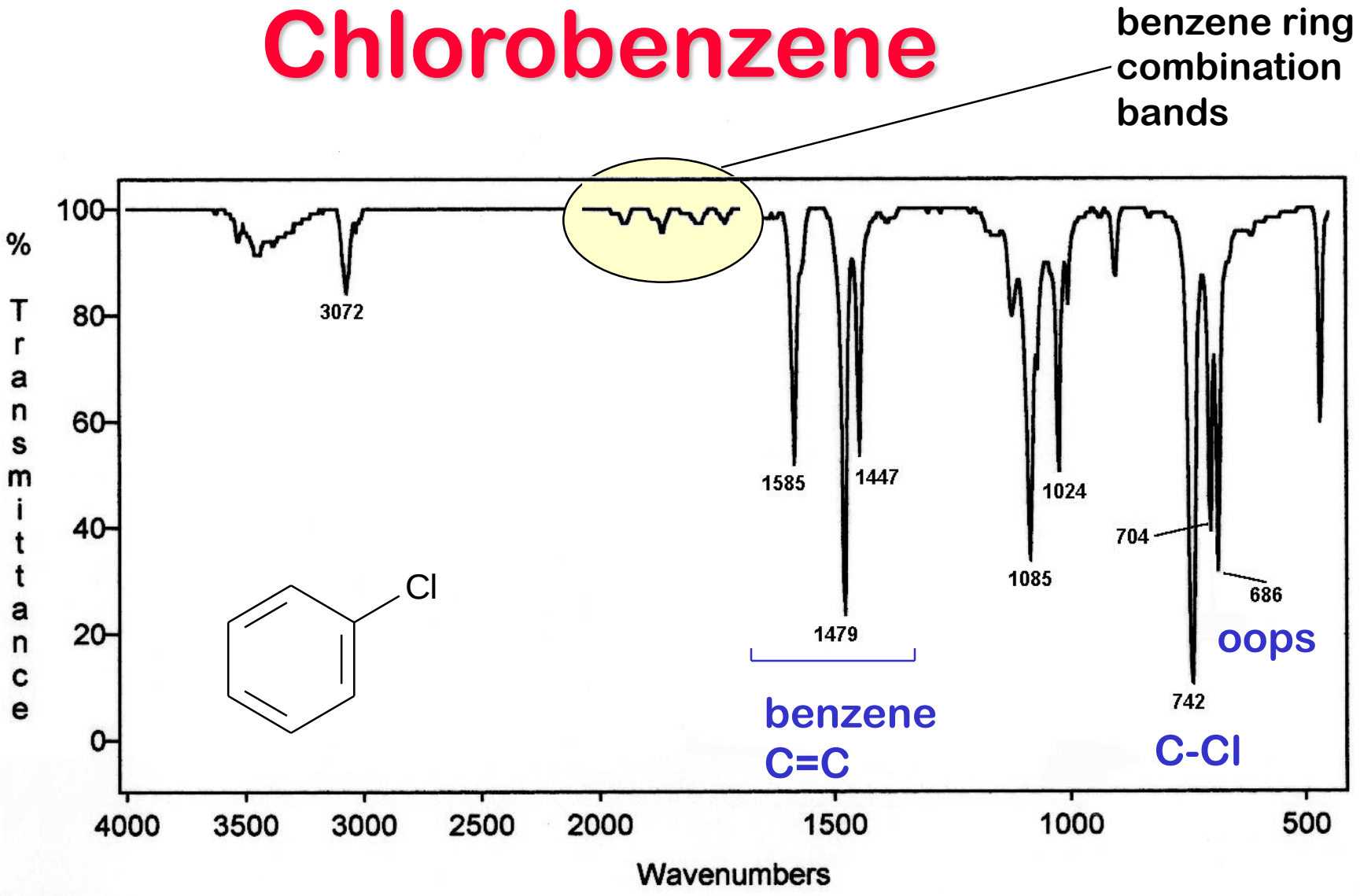
- C-F bonds can be found easily, but are not that common.

Often used as a solvent for IR spectra.
When it is used, spectra show C-Cl absorptions.

Carbon Tetrachloride



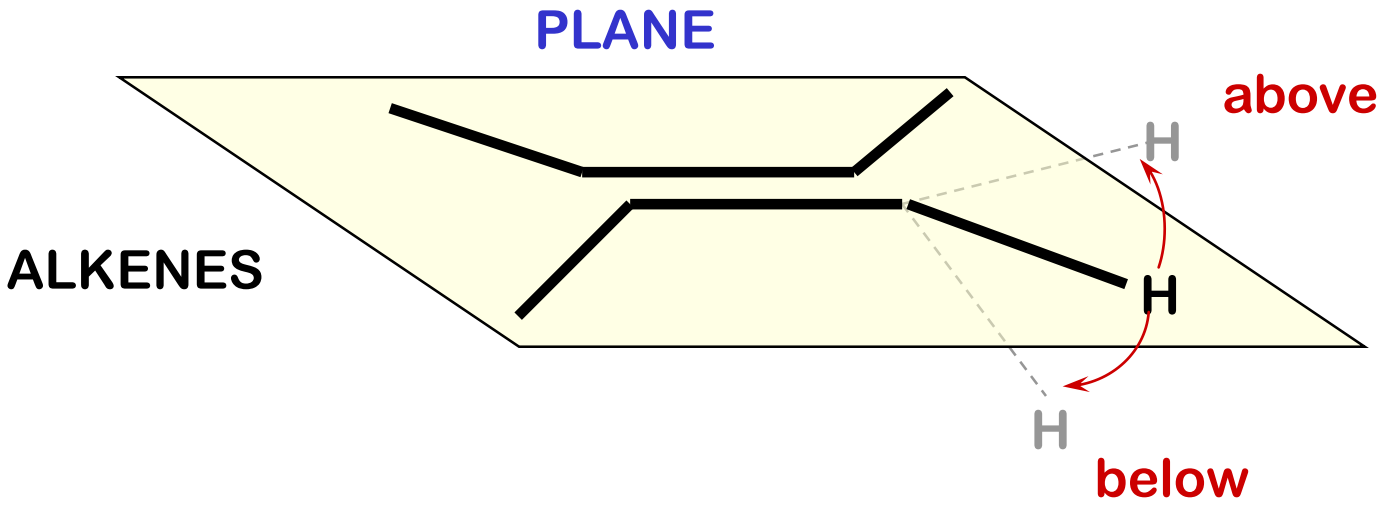
Chlorobenzene

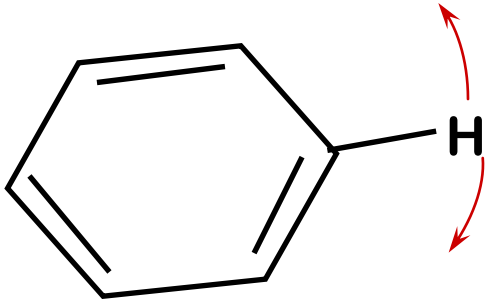


=C-H OUT OF PLANE BENDING

OUT-OF-PLANE BENDING

(OOPS)

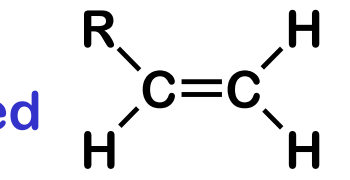




also with

BENZENES

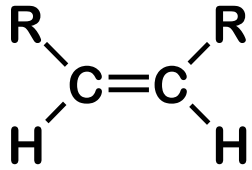
ALKENES



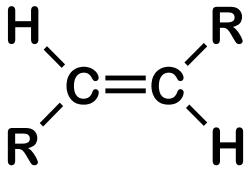
Monosubstituted

Disubstituted

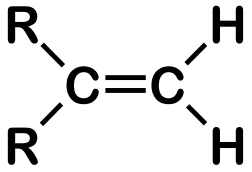
cis-1,2-



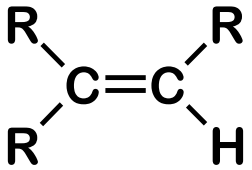
trans-1,2-



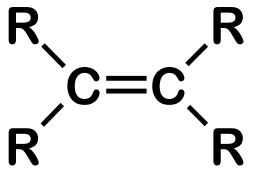
1,1-

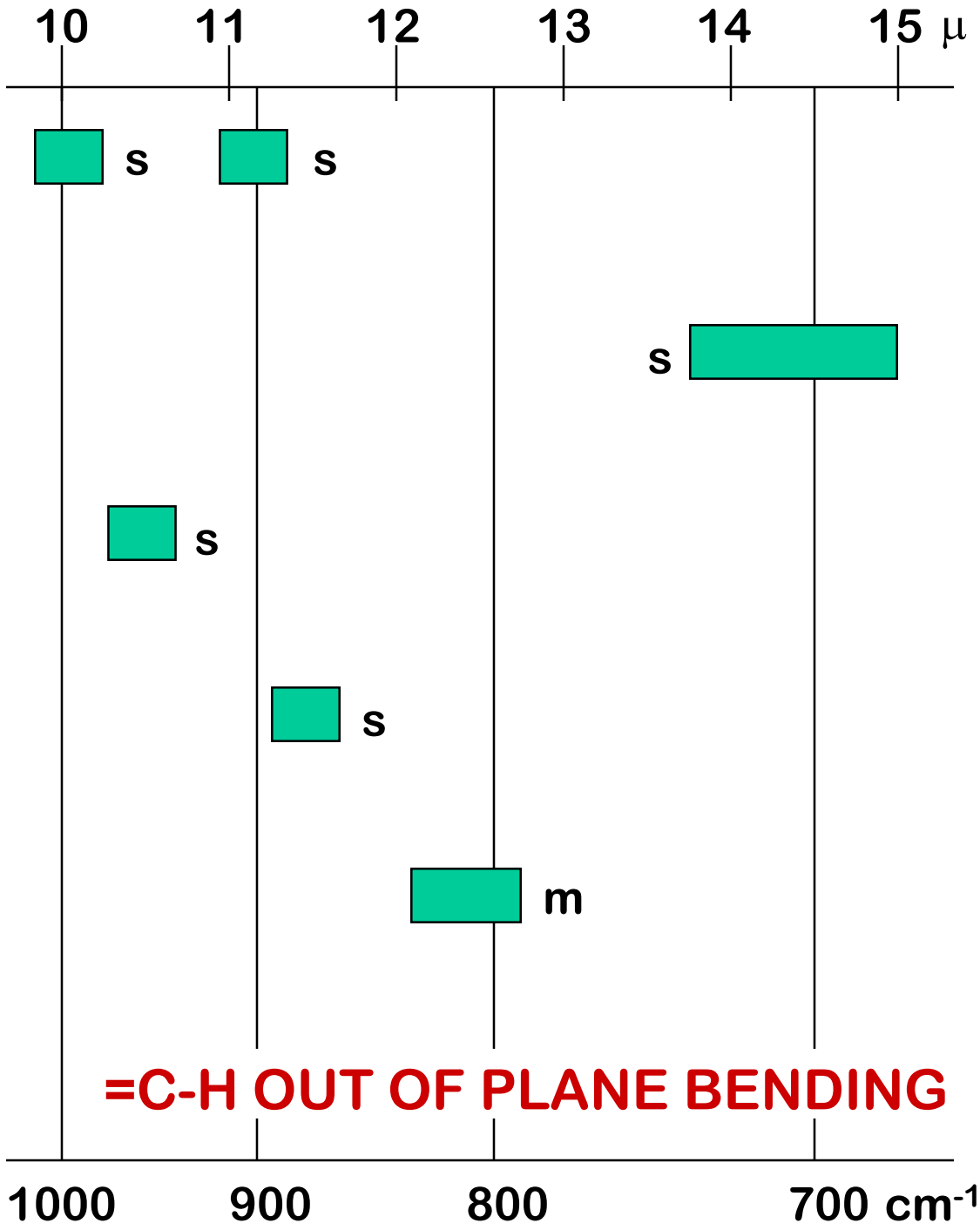


Trisubstituted

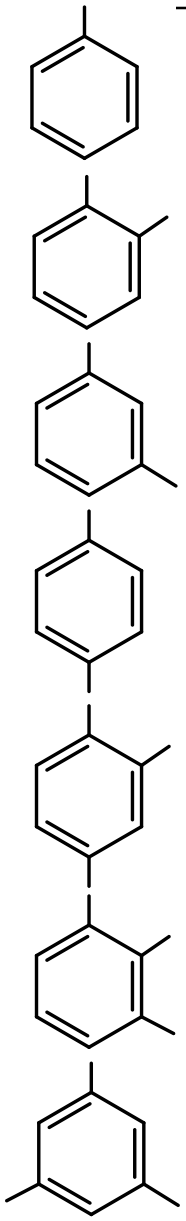


Tetrasubstituted





BENZENES



Monosubstituted

Disubstituted

ortho

meta

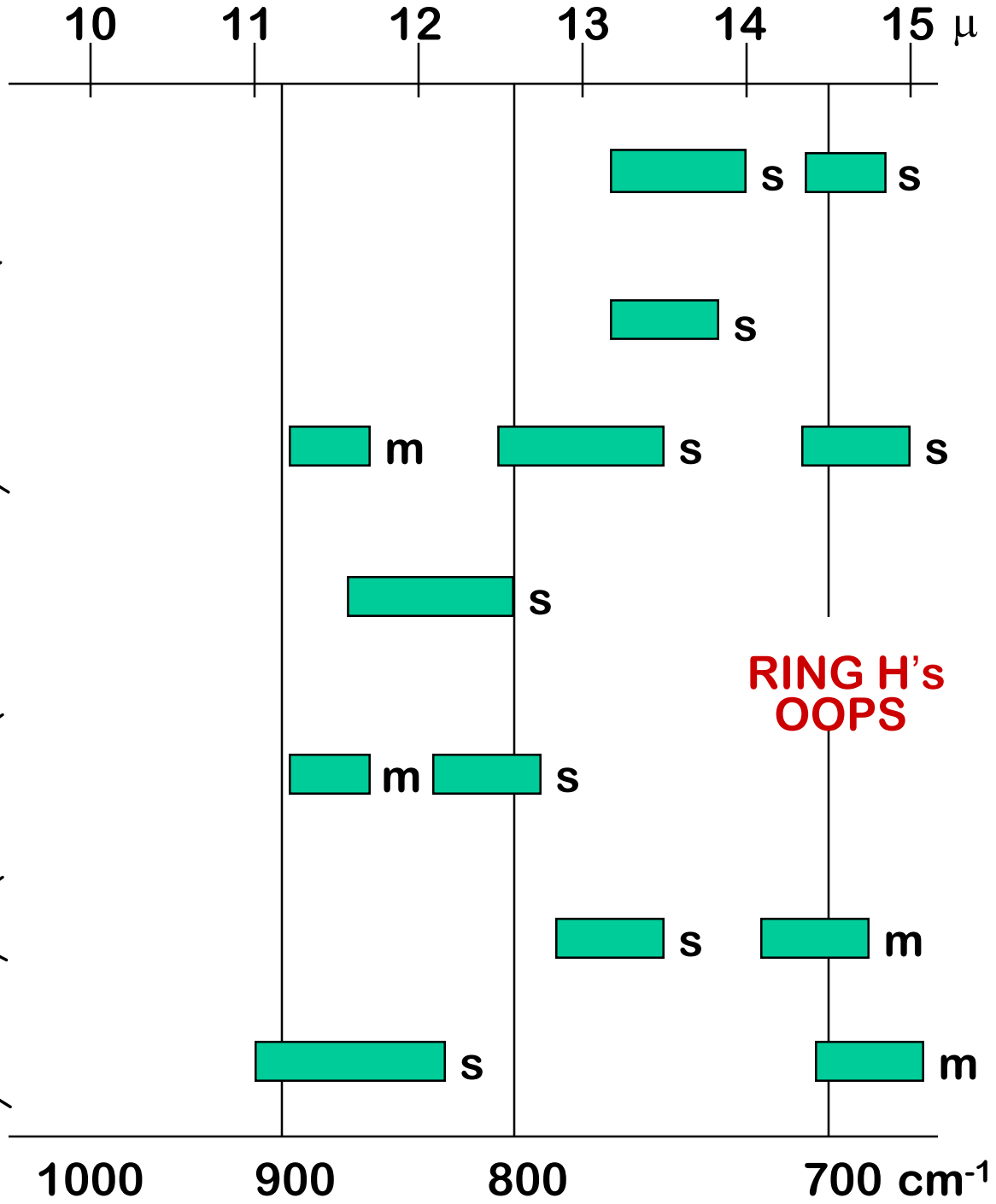
para

Trisubstituted

1,2,4

1,2,3

1,3,5



combination bands

YOU DO NOT NEED TO MEMORIZE THE ALKENE AND AROMATIC OOP ABSORPTION CHARTS !

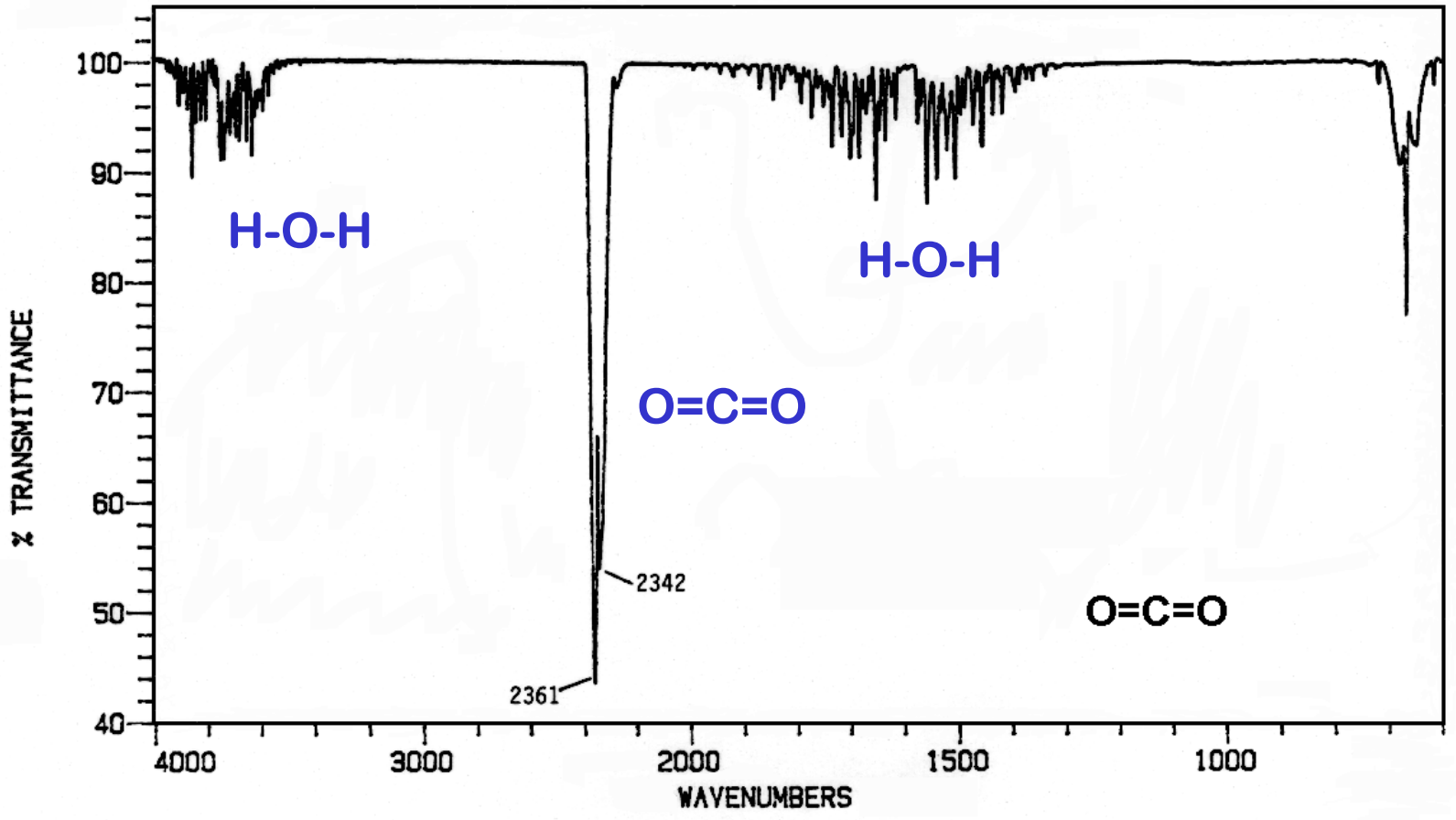
If they are needed to solve a problem on an exam, I will provide them.

BACKGROUND SPECTRUM

MODERN FT-IR INSTRUMENTS SUBTRACT THE "BACKGROUND"

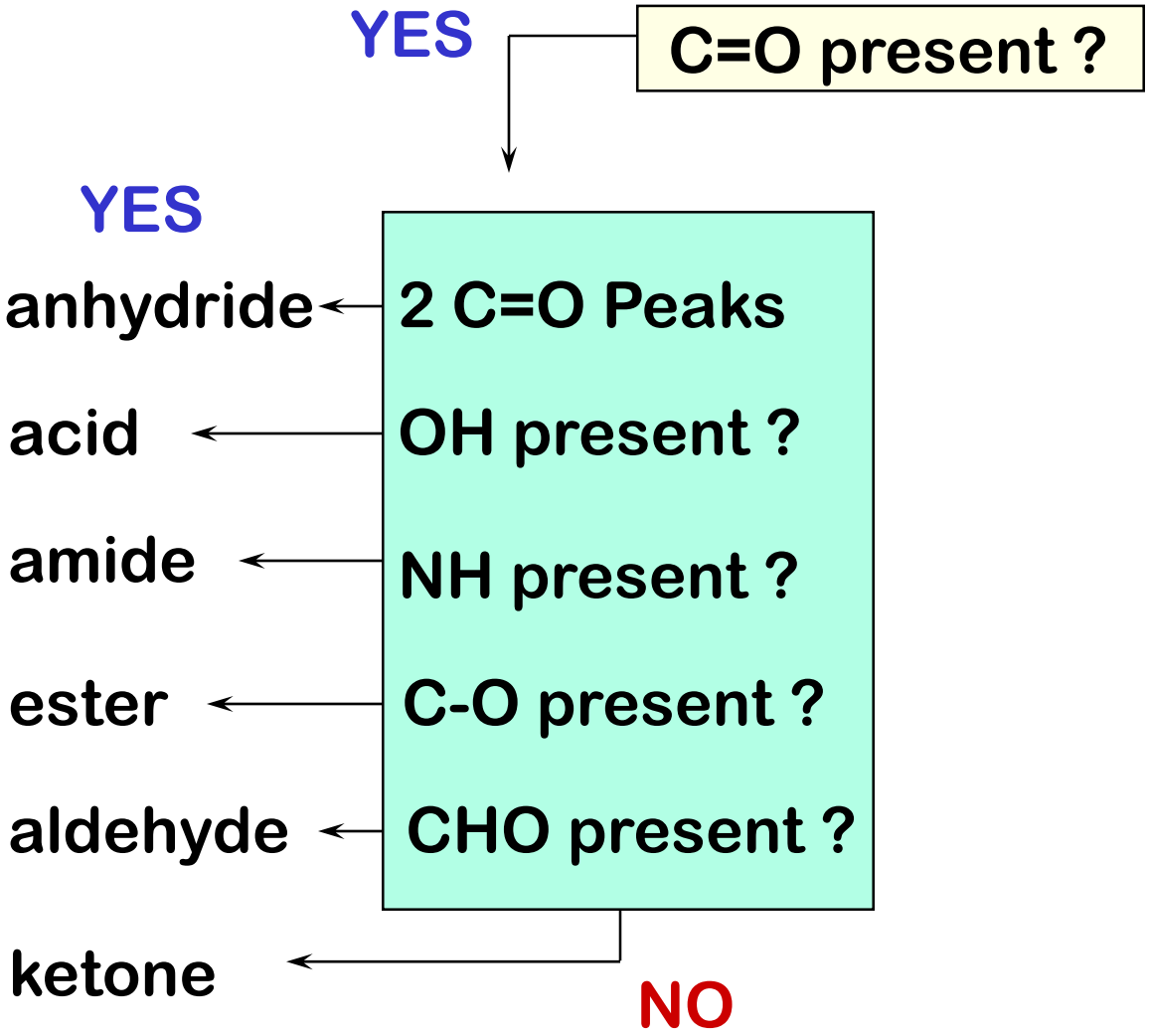
"BACKGROUND"

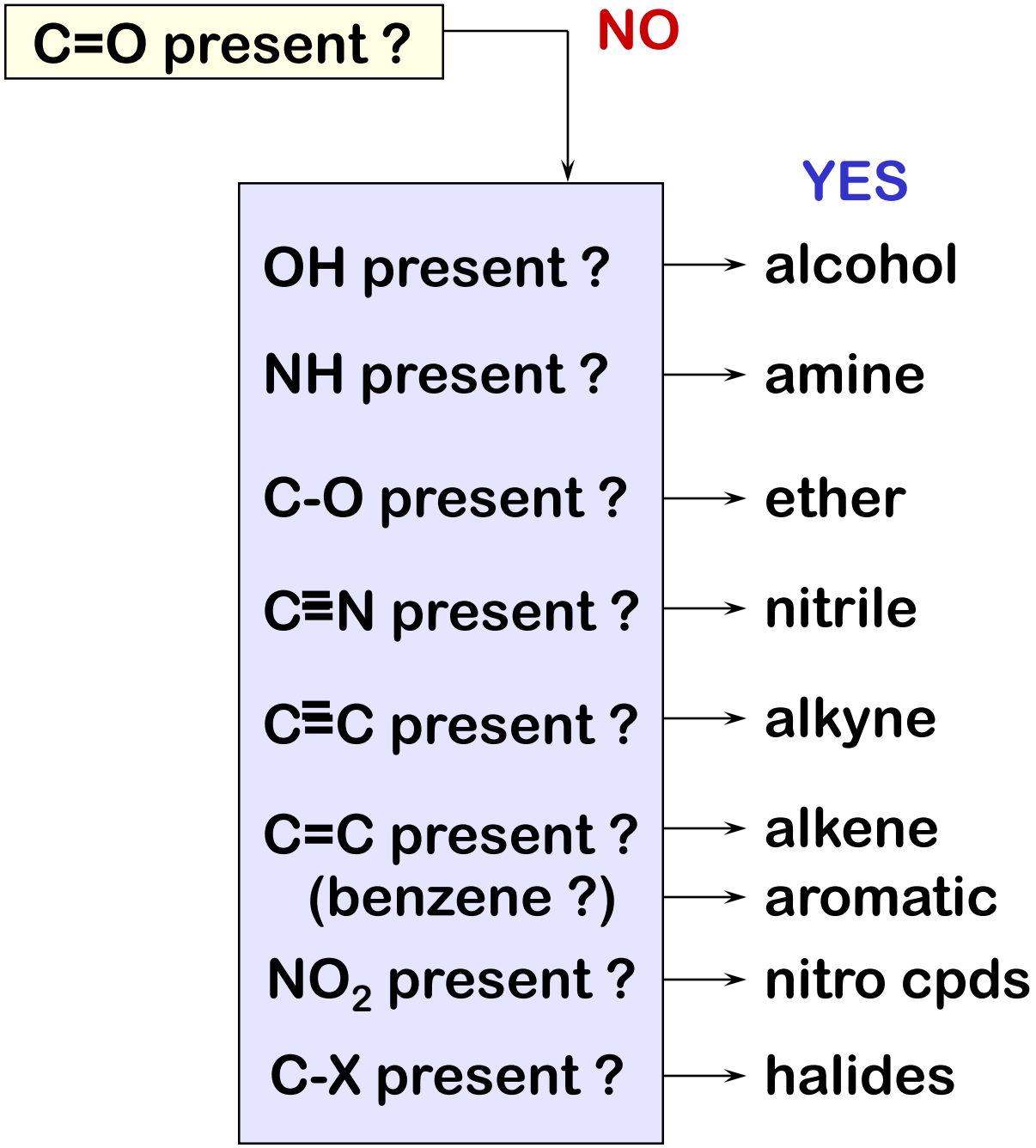
Carbon Dioxide and Water

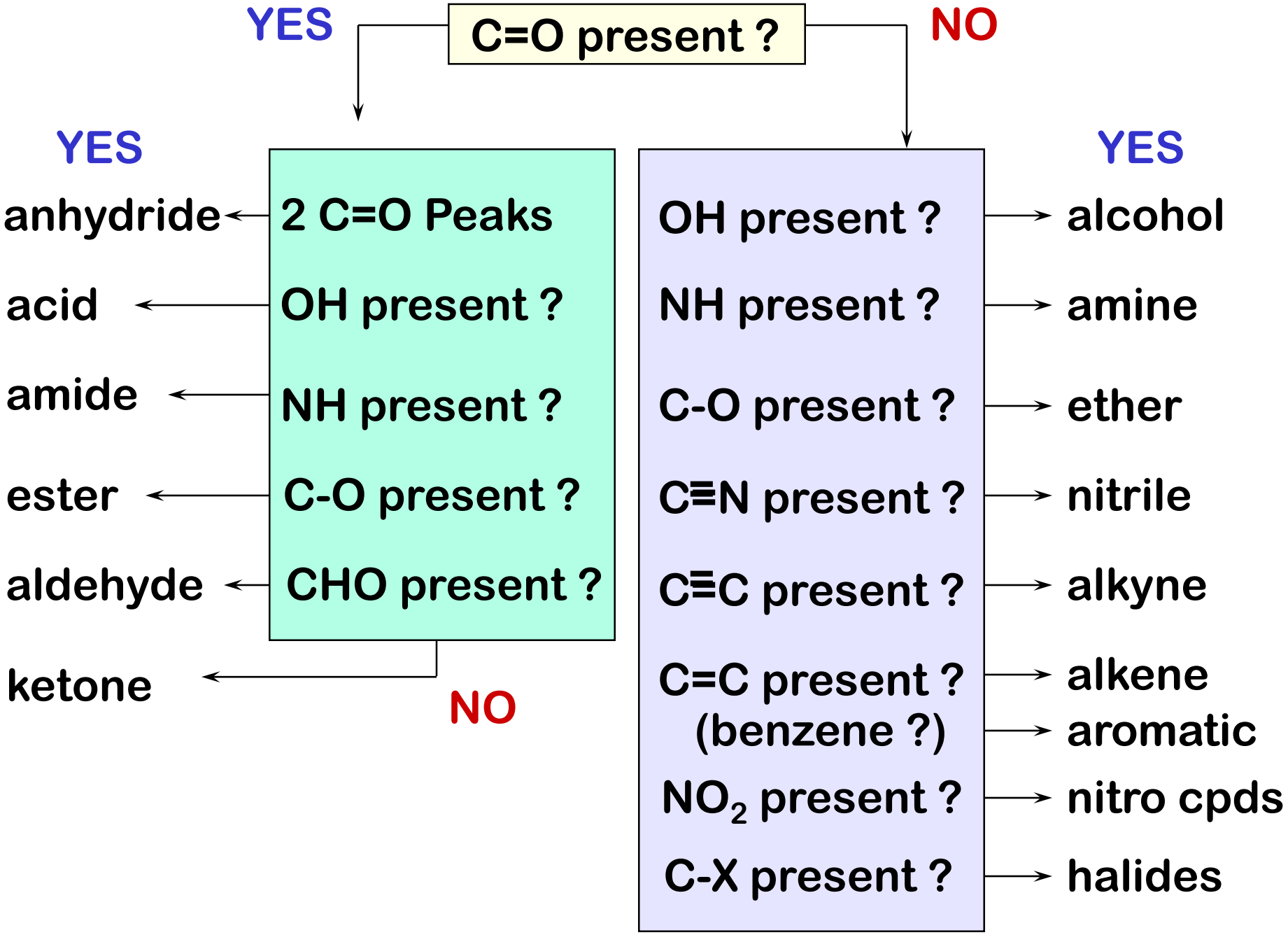


MAKING DECISIONS

DECISION FLOW CHART
Tables 11-8 and 11-9


YES
C=O present ?
YES
anhydride
2 C=O Peaks
acid
OH present ?
amide
NH present ?
ester
C-O present ?
aldehyde
CHO present ?
ketone
NO


C=O present ?
NO
YES
OH present ?
alcohol
NH present ?
amine
C-O present ?
ether
C≡N present ?
nitrile
C≡C present ?
alkyne
C=C present ?
alkene
(benzene ?)
aromatic
NO2 present ?
nitro cpds
C-X present ?
halides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YES
2 C=O Peaks
anhydride
OH present ?
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alkene
(benzene ?)
aromatic
NO2 present ?
nitro cpds
C-X present ?
halides

GUIDELINES

DECISION FLOW CHART
Tables 11-8 and 11-9

How to Use an Infrared Spectrum

1) **Molecular formula:**
calculate index of hydrogen deficiency

2) **Check for carbonyl:**
note any shift from 1715 cm^{-1}

3) **Check for O-H, N-H**

4) **Check for triple bonds**

5) **Check for C=C, benzene rings**

How to Use an Infrared Spectrum

CONTINUED

6) Look below 1550 cm^{-1}; check for C-O and nitro

7) Go back over spectrum for refinements; check the C-H region for aldehydes and for peaks above 3000 cm^{-1}

(alkenes and terminal alkynes)

FINAL SUMMARY

WHERE YOU SHOULD HAVE A SECURE GRASP WHEN READING INFRARED SPECTRA

THE MINIMUM YOU NEED TO KNOW

BASE VALUES

OH	3600
NH	3400
CH	3000
C≡N	2250
C≡C	2150
C=O	1715
C=C	1650
C-O	1100

EXPANDED CH

3000

3300	3100	2900	2850
≡C-H	=C-H	-C-H	2750 -CHO

CH_2 and CH_3 bend : 1465 and 1365

1800 1735 1725 **1715** 1710 1690

aldehyde acid

acid chloride ester ketone amide

anhydride : 1810 and 1760

EXPANDED C=O

benzene C=C : between 1400 and 1600

Know also the effects of H-bonding, conjugation and ring size.

WHERE CAN I GET MORE SPECTRA FOR PRACTICE?

ADDITIONAL SOURCES OF INFRARED SPECTRA

1) In the back of your laboratory book is an index of all the infrared spectra in the book.

Pavia, Lampman, Kriz and Engel, Introduction to Organic Laboratory Techniques, Saunders College Publishing

2) In the Chemistry Department computer lab in the ChemApps/Spectroscopy folder are two programs called "Spectrabook I" and "Spectrabook II".

These programs can display the IR spectra of many compounds and the selection lists can be grouped by functional group. When you click on a peak with the mouse the group of atoms resposible for the absorption is shown.

3) There are several web sites that have spectra, including:

http://www.dq.fct.unl.pt/qoa/jas/ir.html

http://www.aist.go.jp/RIODB/SDBS/menu-e.html

http://webbook.nist.gov/chemistry/

http://www.chem.ucla.edu/~webnmr/index.html

http://www.nd.edu/~smithgrp/structure/workbook.html

4) Books on the subject of spectroscopy, such as:

D.L.Pavia, G.M.Lampman, and G.S.Kriz,
Introduction to Spectroscopy, 3rd ed., Harcourt.

You will probably be able to find some local WWU students who have this book (it is used in Chem 454 and 455)
- but it is more advanced than you probably need.

5) **The program "IR Tutor" can be found in the ChemApps folder in the Chemistry Department computer lab.**

This program contains a number of sample spectra and the vibrations responsible for each peak can be viewed as an animation.

Infrared Spectroscopy Problems

(sample exam problems)

For Problems 1-5 :

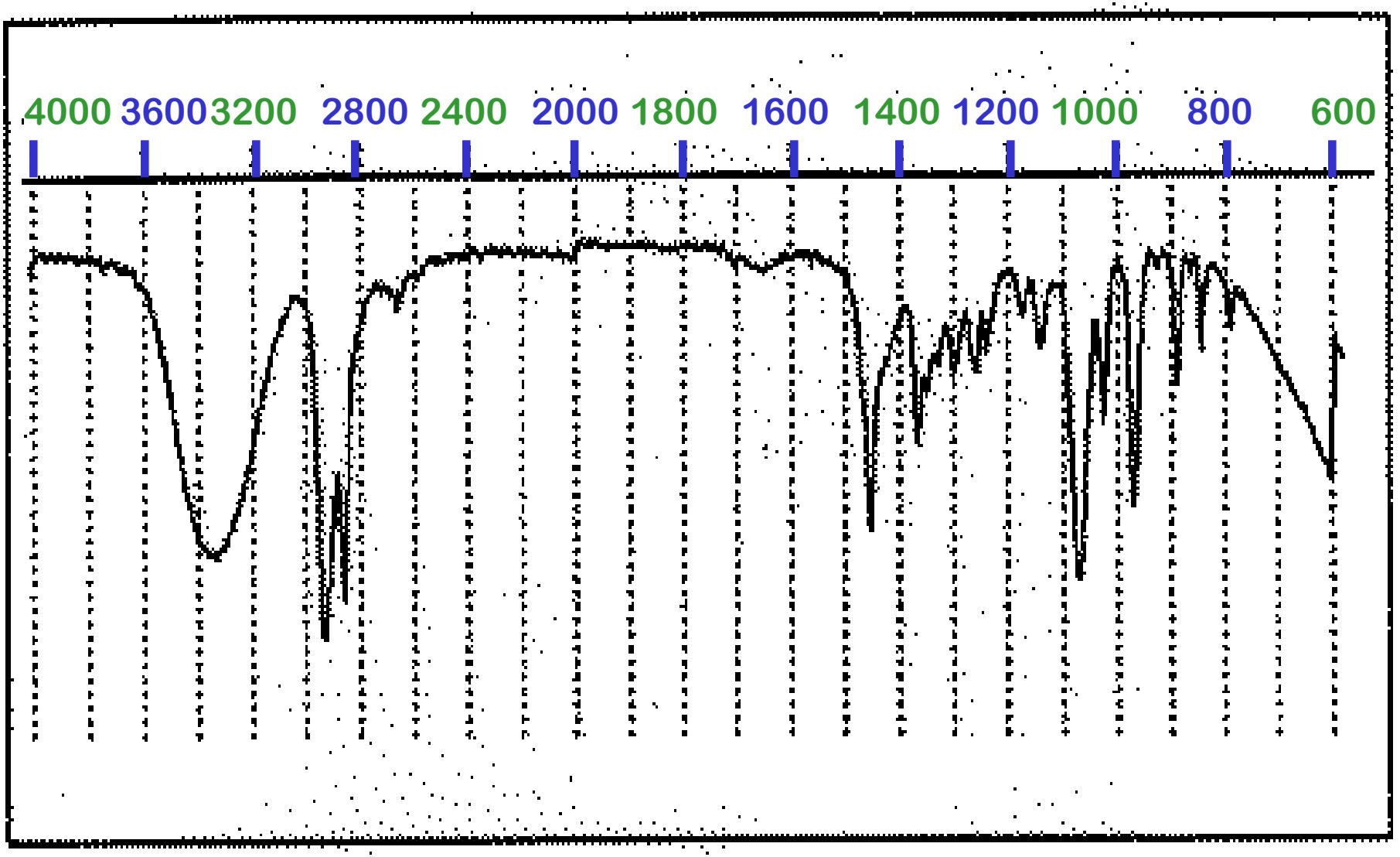
1. Calculate the index of hydrogen deficiency

2. Label the major peaks right on the spectrum, using arrows to indicate the desired peak.

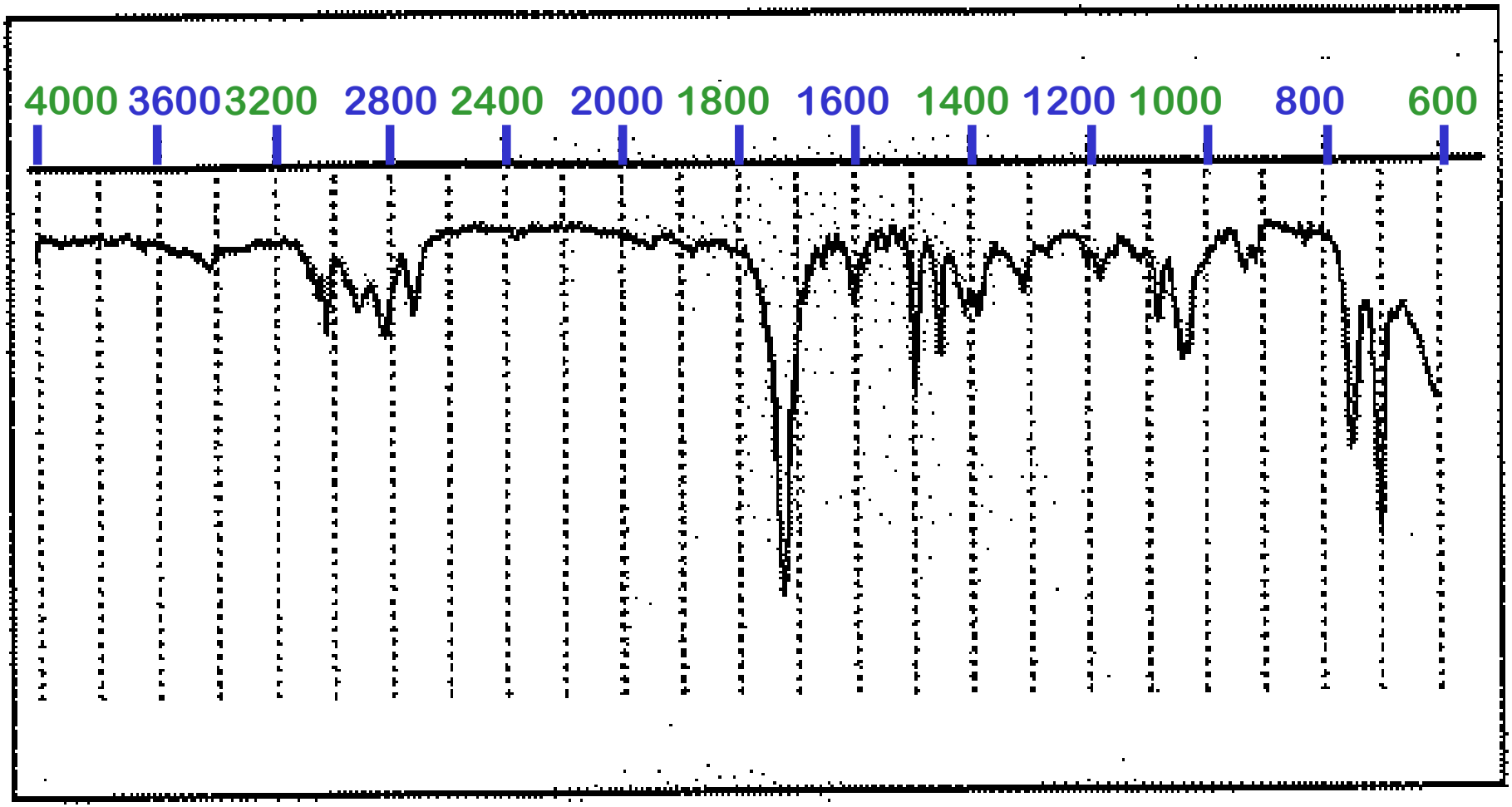
3. Specify the major class to which the compound belongs (ester, ketone, alcohol, etc.).

4. Suggest a complete structure which would fit the spectrum and the formula.

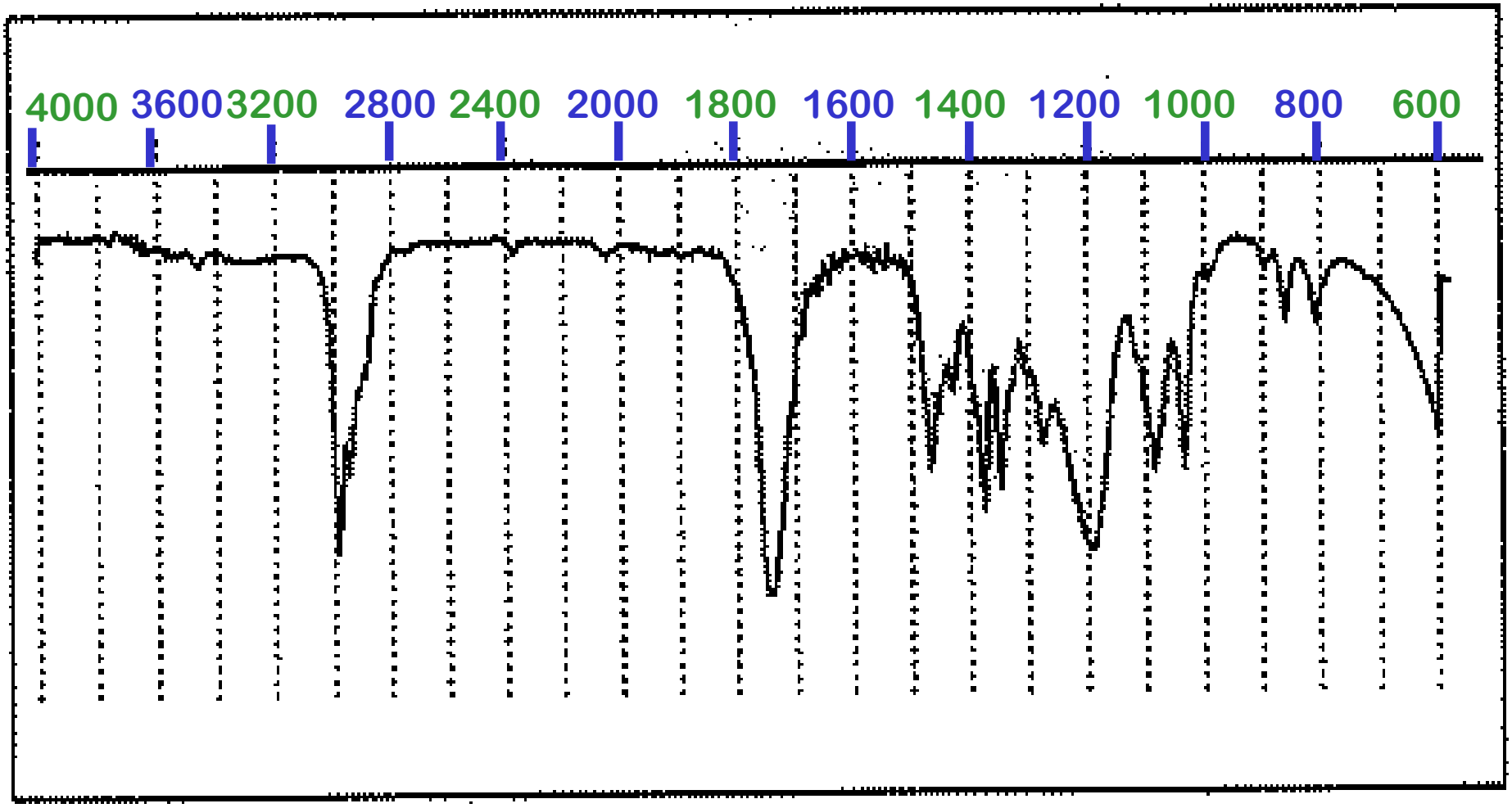
Problem 1 $C_6H_{12}O$



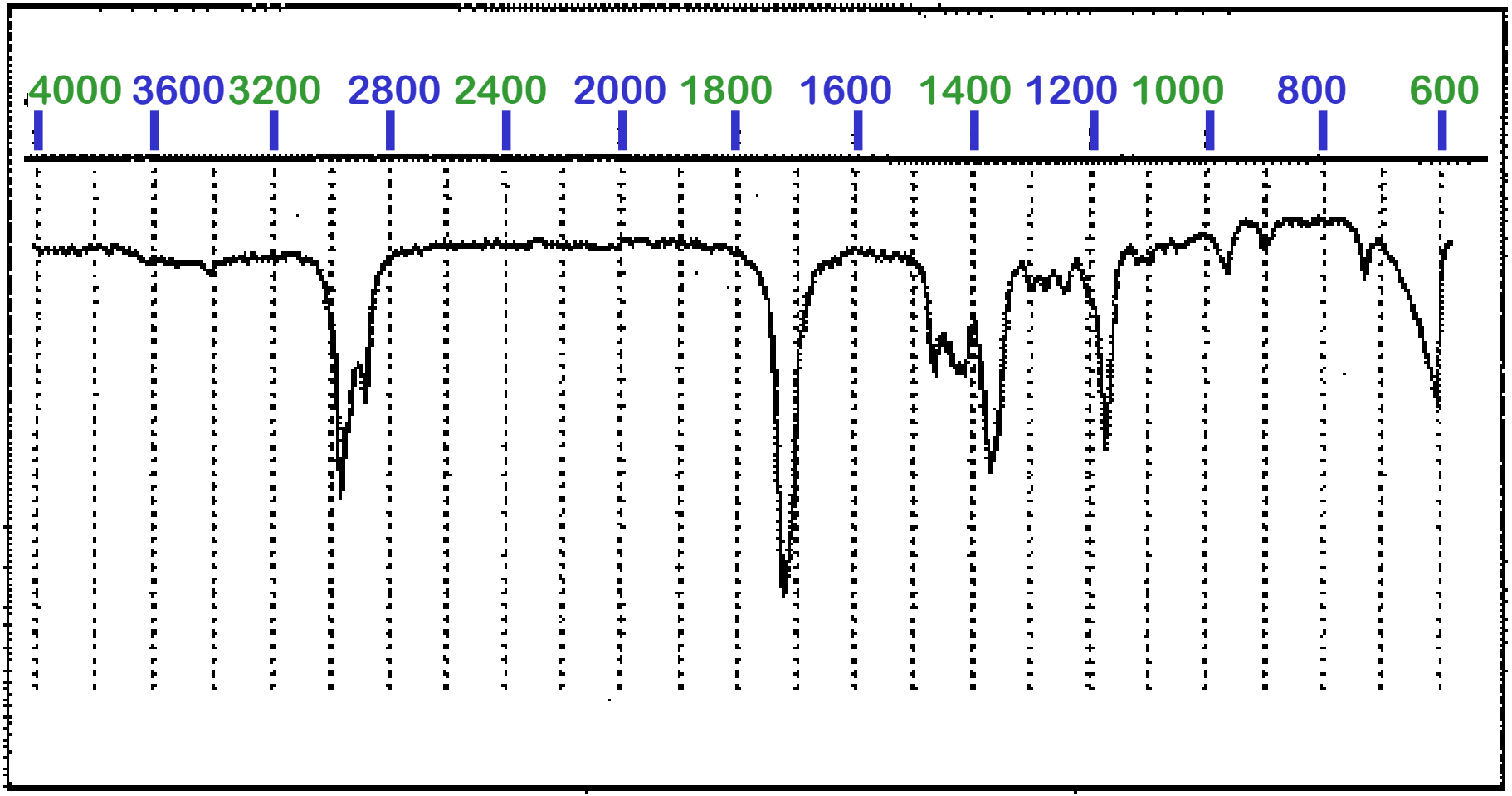
Problem 2 C_8H_8O



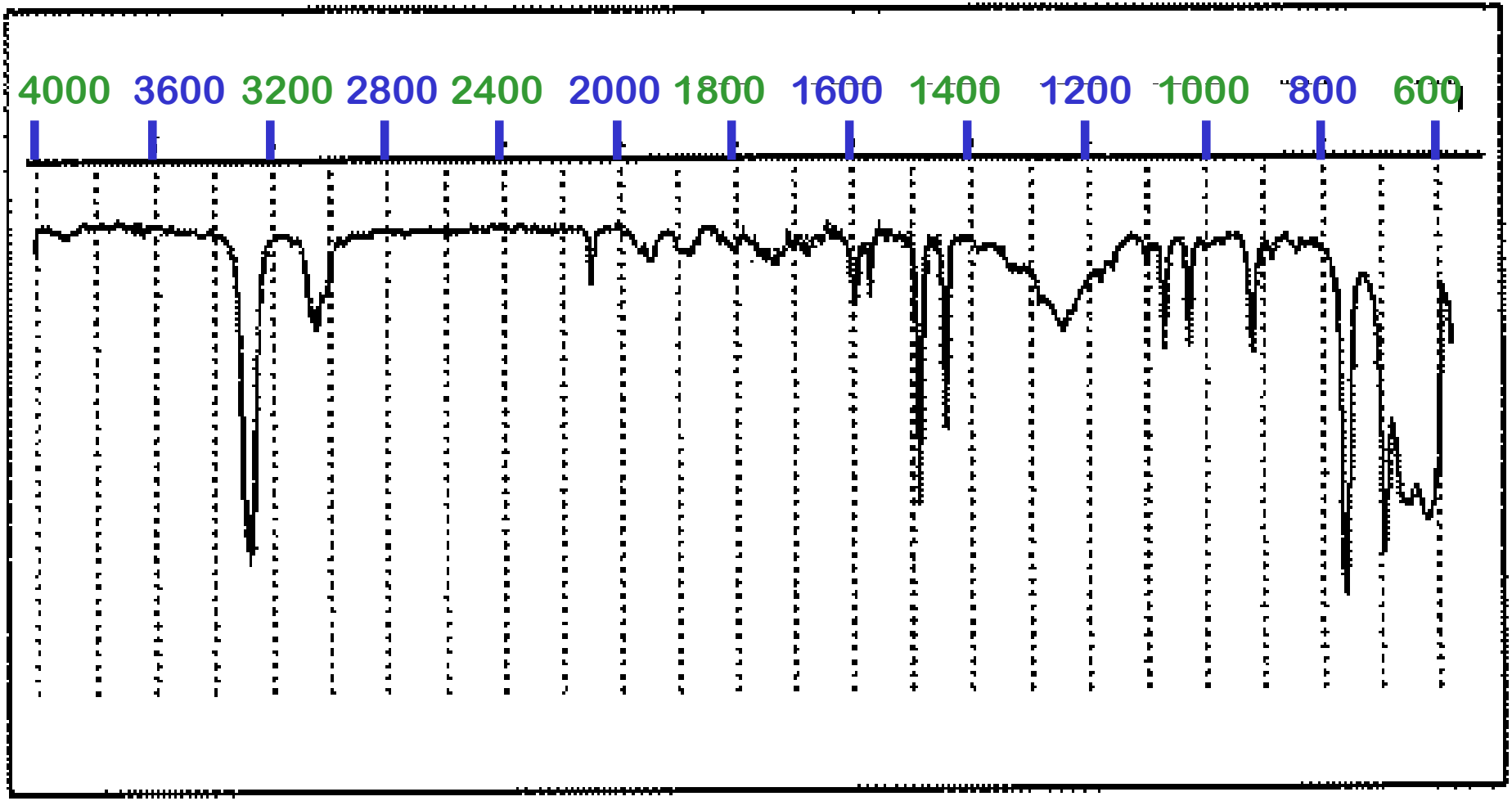
Problem 3 $C_5H_{10}O_2$



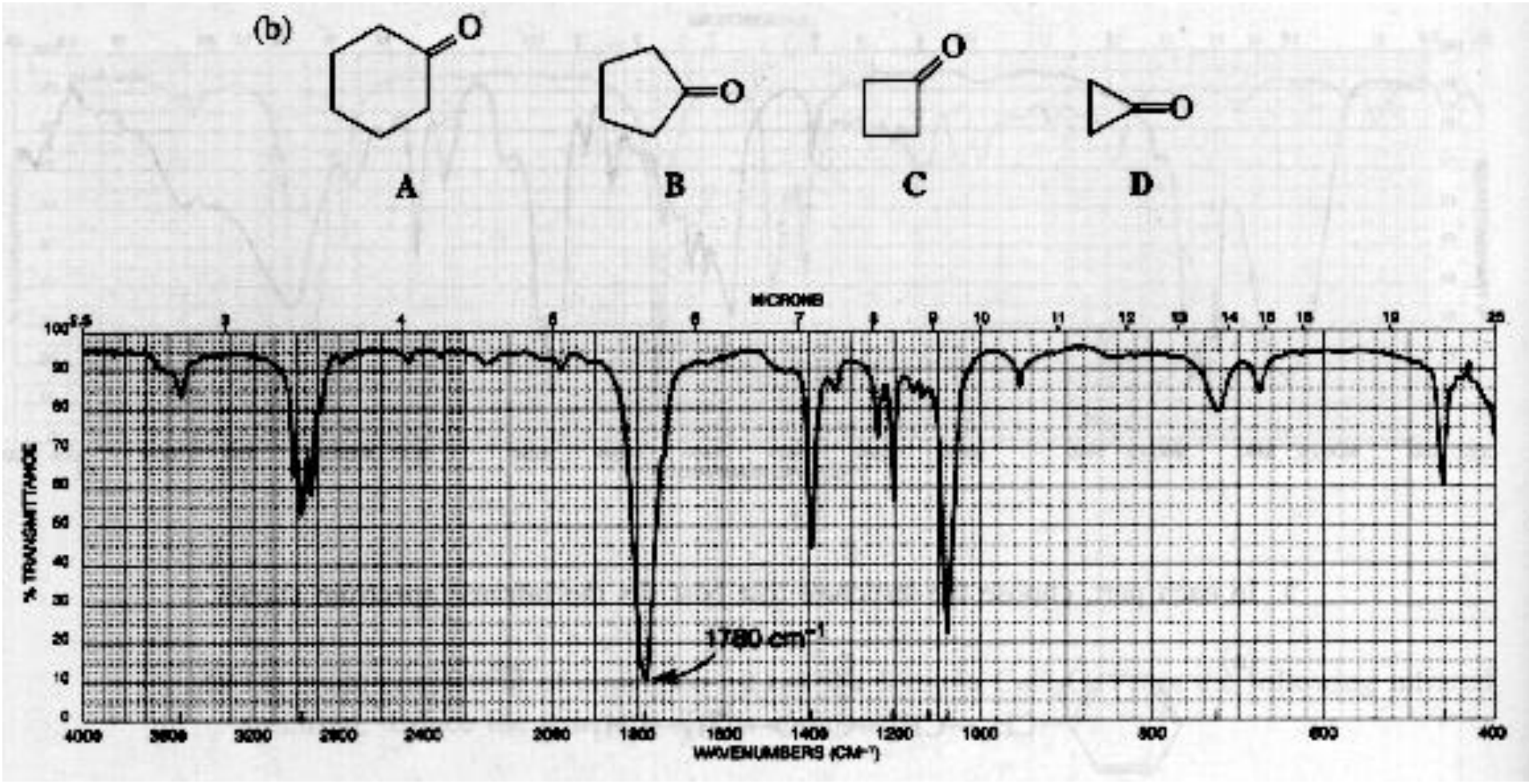
Problem 4 $C_5H_{10}O$



Problem 5 C_8H_6



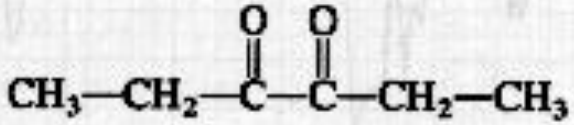
6. Which structure is the correct one?



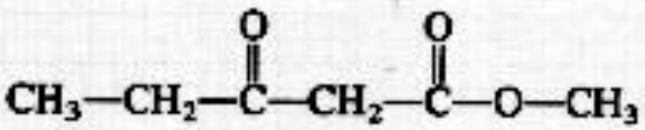
1780

7. Which structure is the correct one?

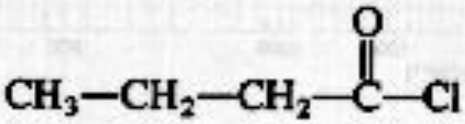
(e)



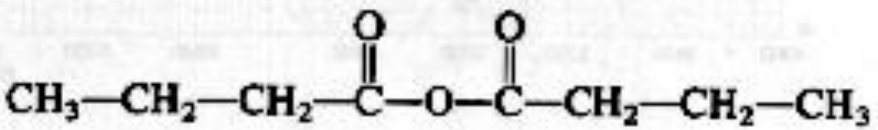
A



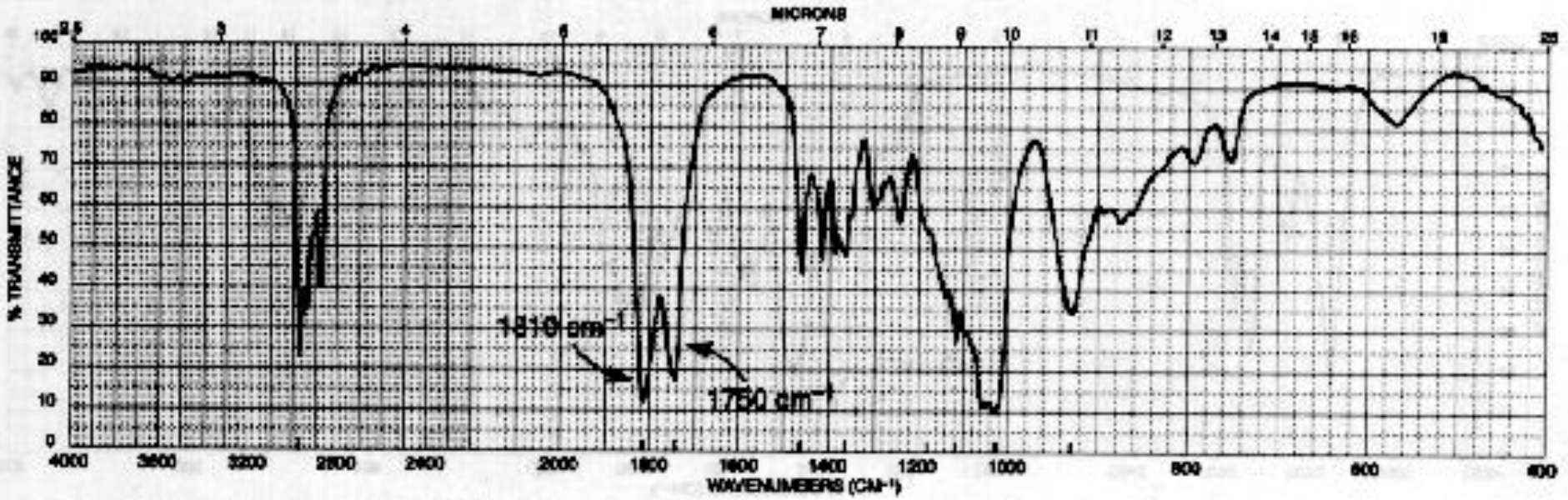
B



C



D



1819 1750

8. The C-H stretch vibrations of most organic compounds come at about 3000 cm-1. How can you predict where the C-D stretch vibration will appear?

These can be solved using infrared and an index of hydrogen deficiency.

SOME SIMPLE IR PROBLEMS

Assign all the peaks that you can (that is, label them right on the spectrum) with the type of bond responsible for the absorption: C=O, C-H, -CH_2- or -CH_3 bending, N-H, O-H, C-O, -C=N, C≡C, benzene, oops, etc.).

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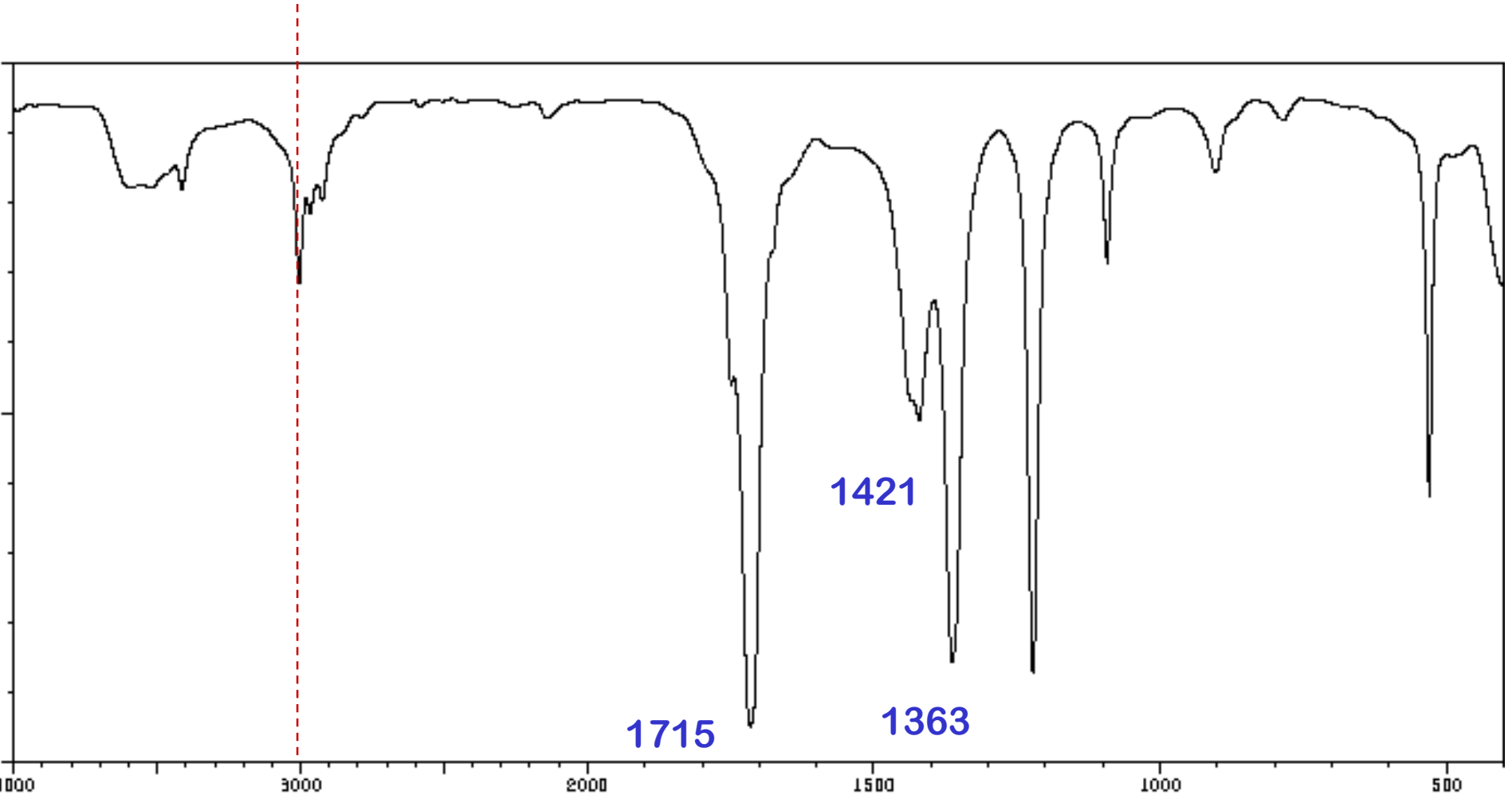
C_3H_6O

HINT: Can be made from propyne when treated with aqueous H_2SO_4 and $HgSO_4$.



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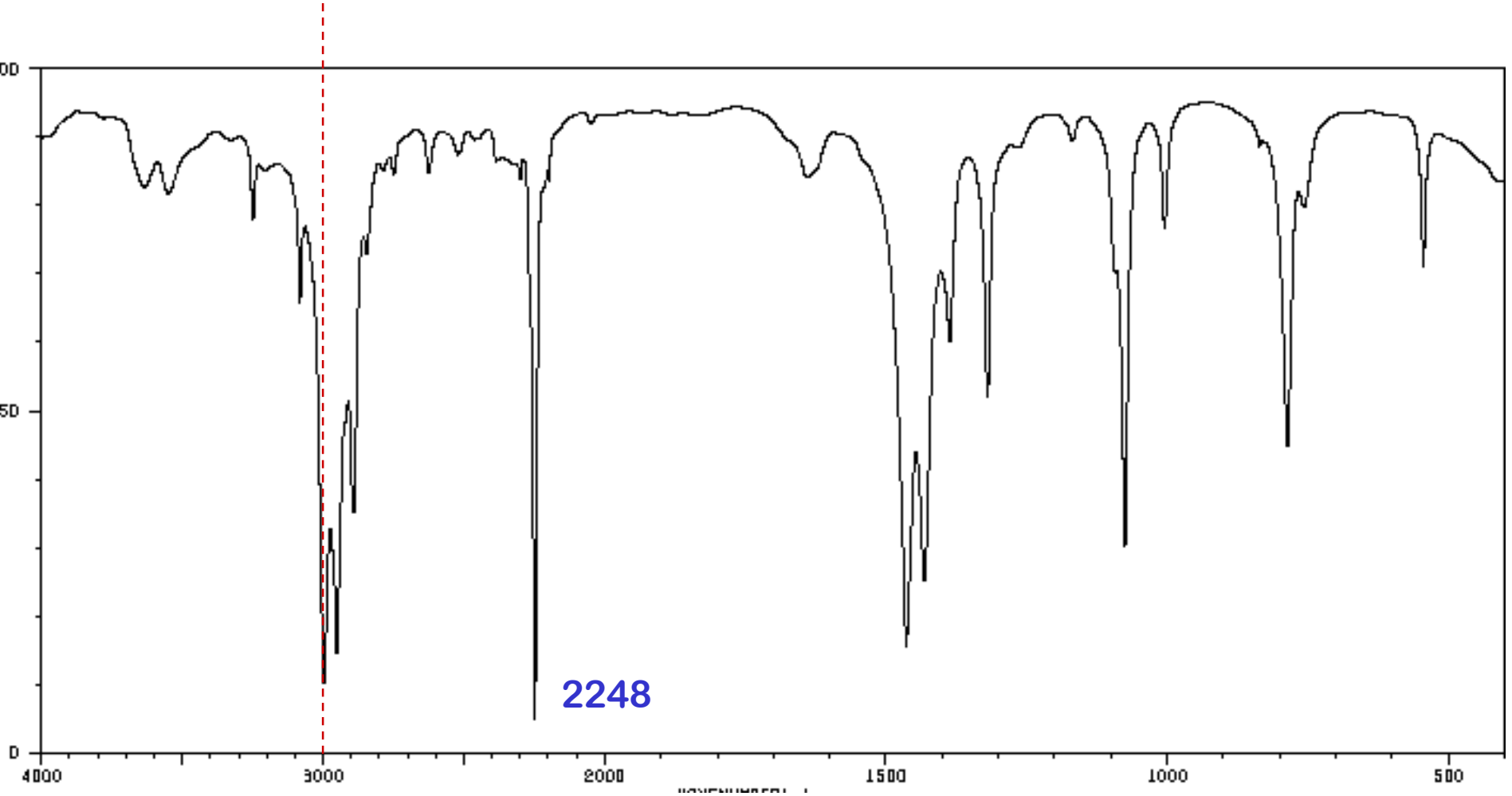

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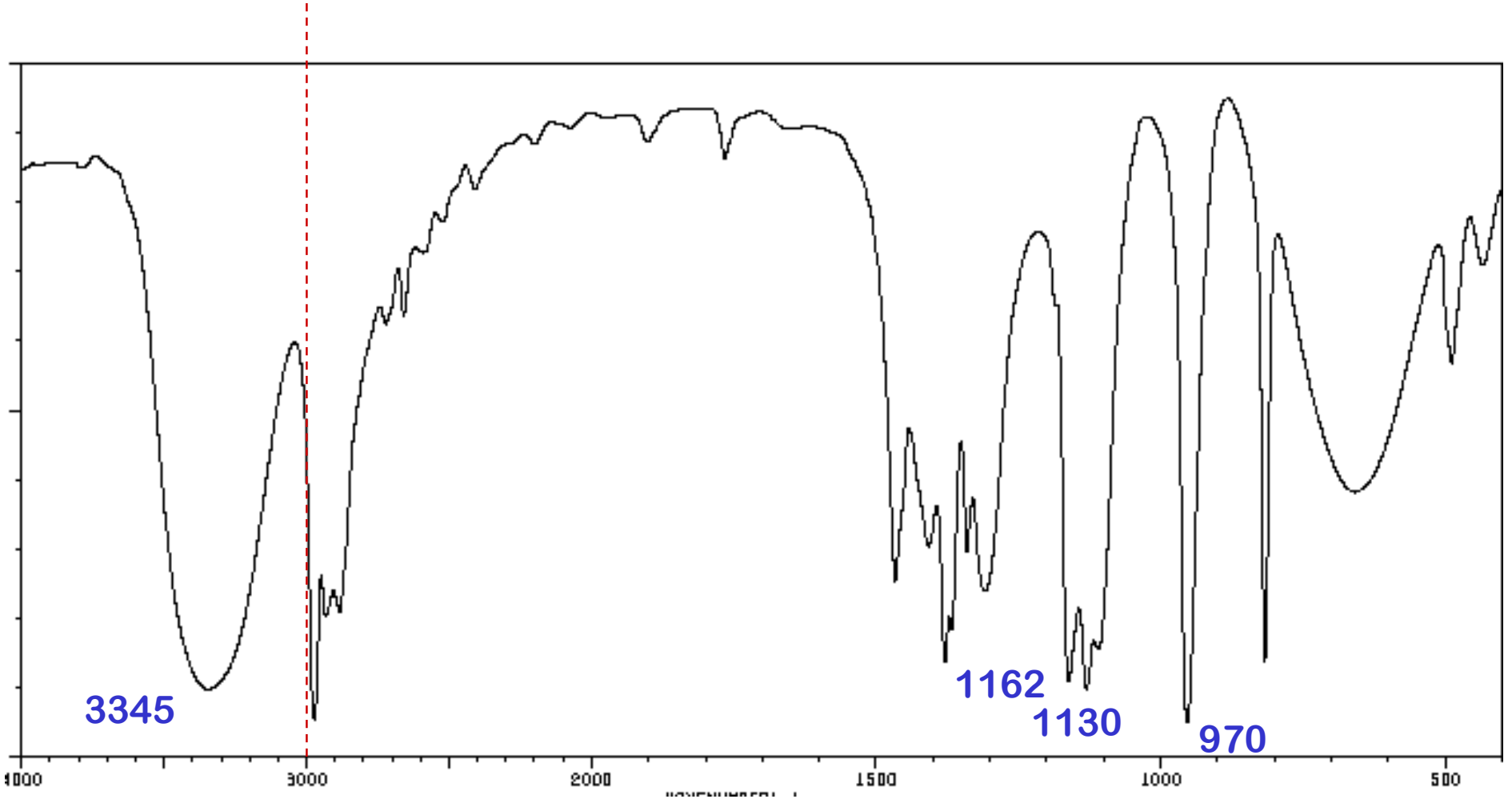
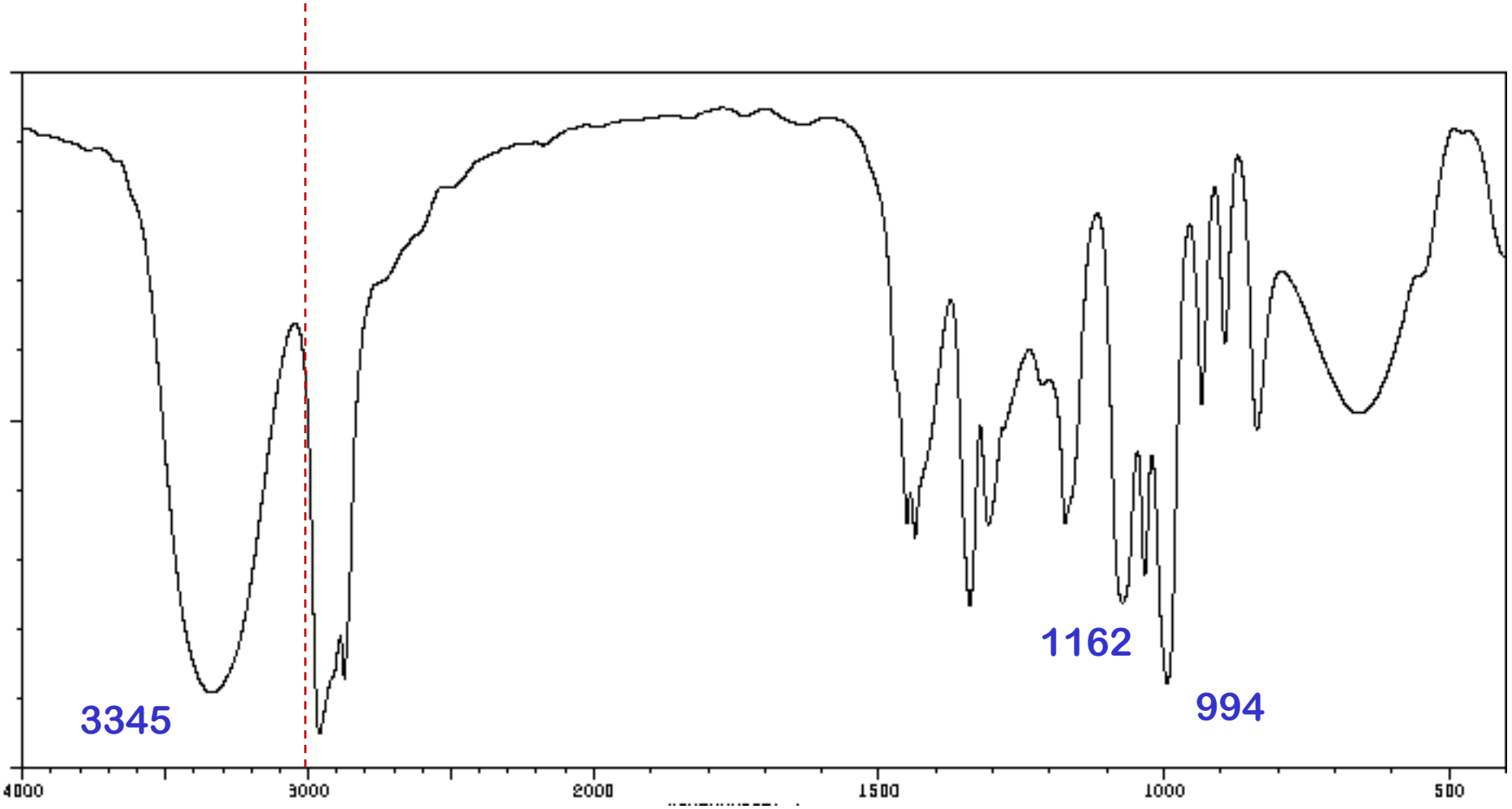


Problem 4

$C_5H_{10}O$

HINT: The solution to this one is in the hydrogen deficiency index.



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C_7H_5N

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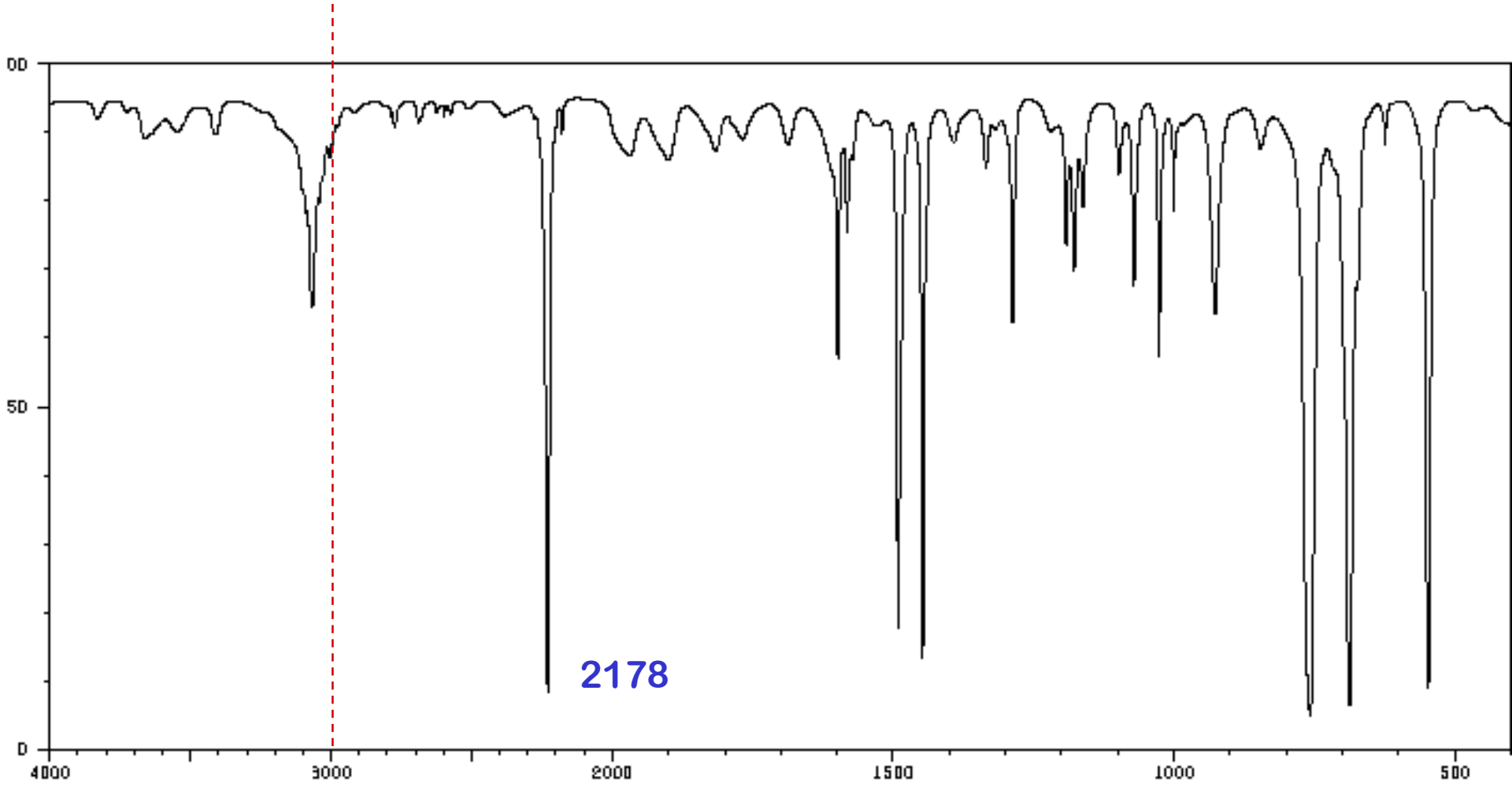

Problem 6

C_8H_8O

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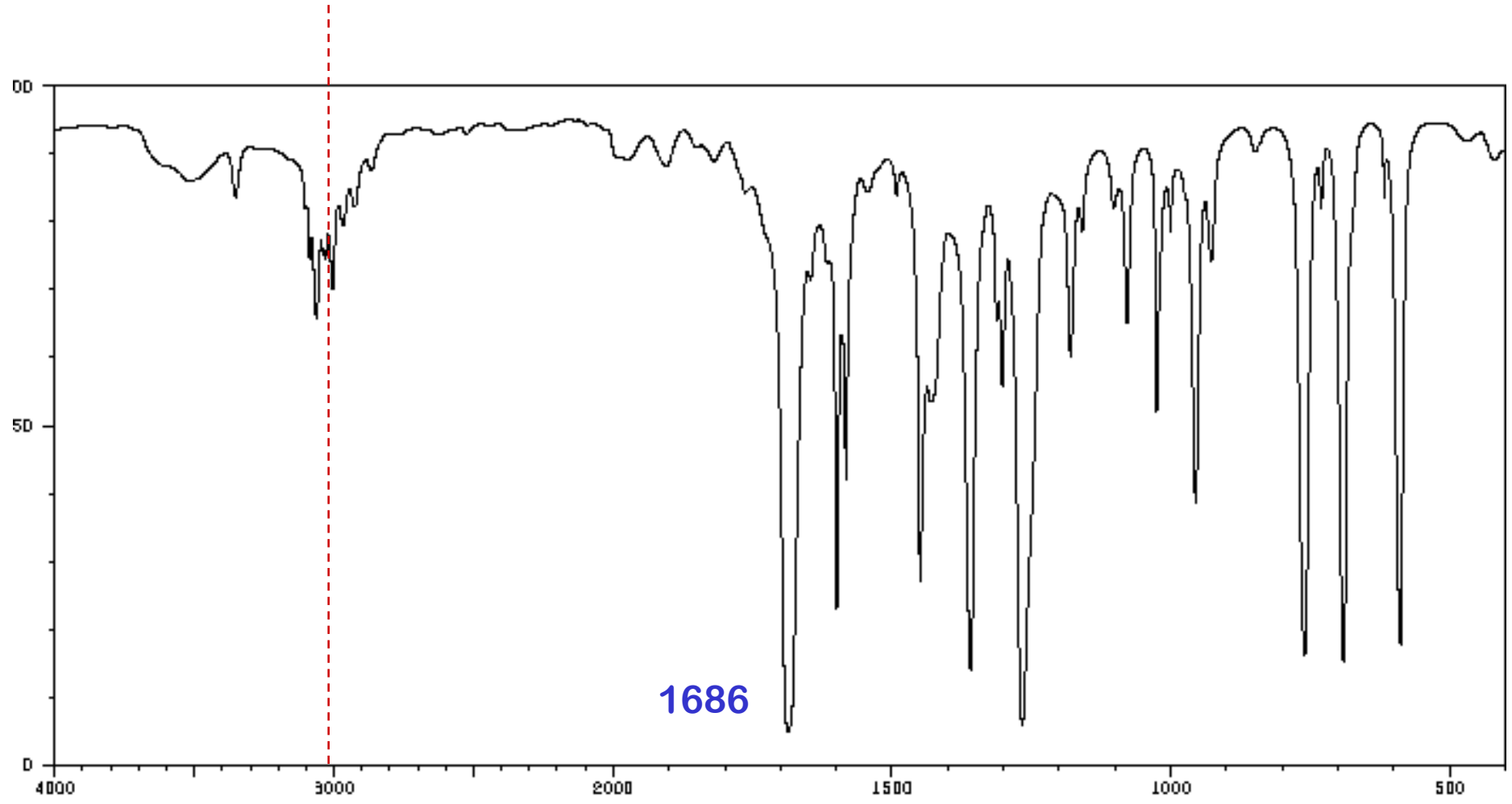
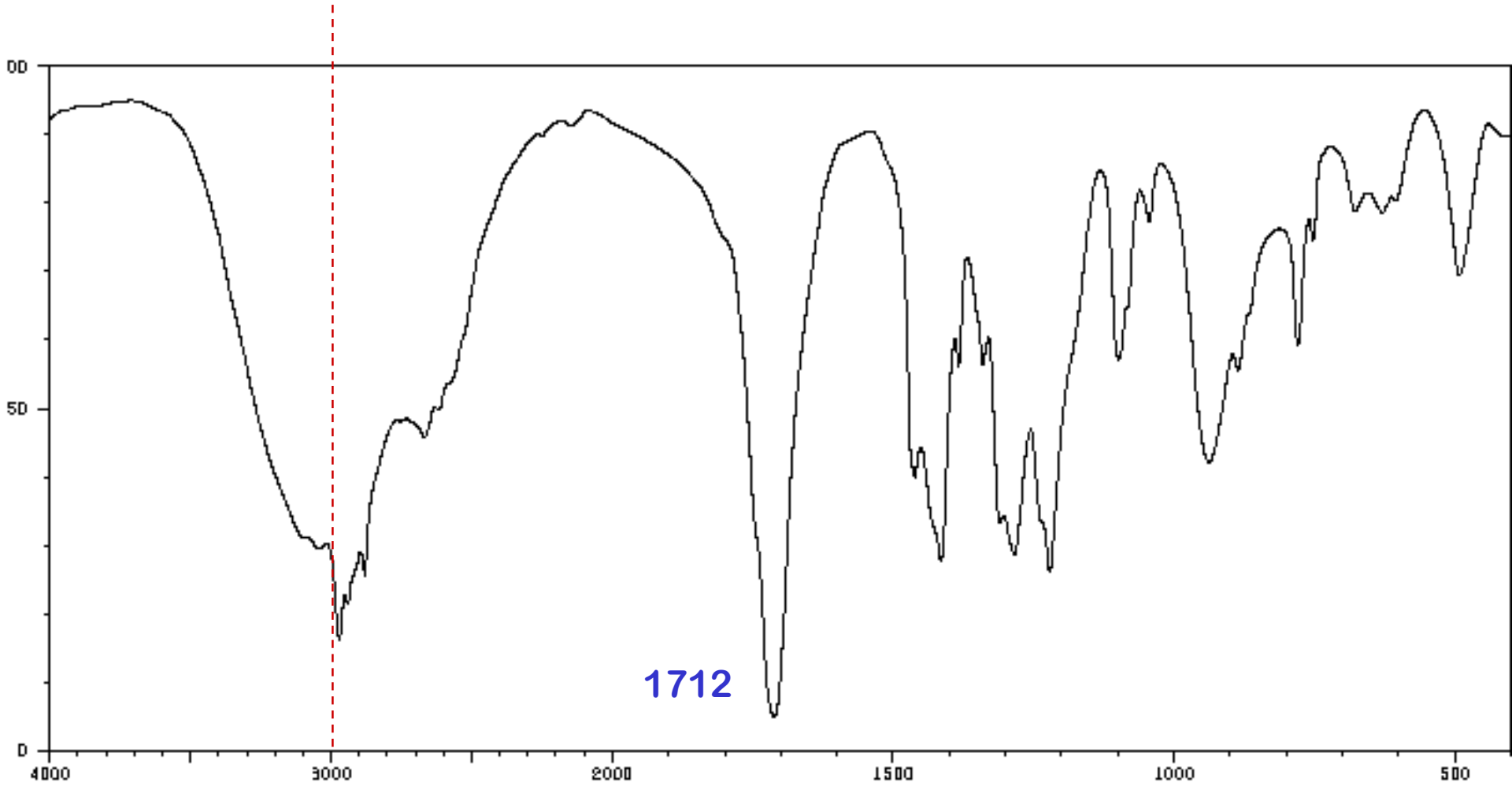


Problem 7

$C_4H_8O_2$

HINT: This one stinks like rancid butter.



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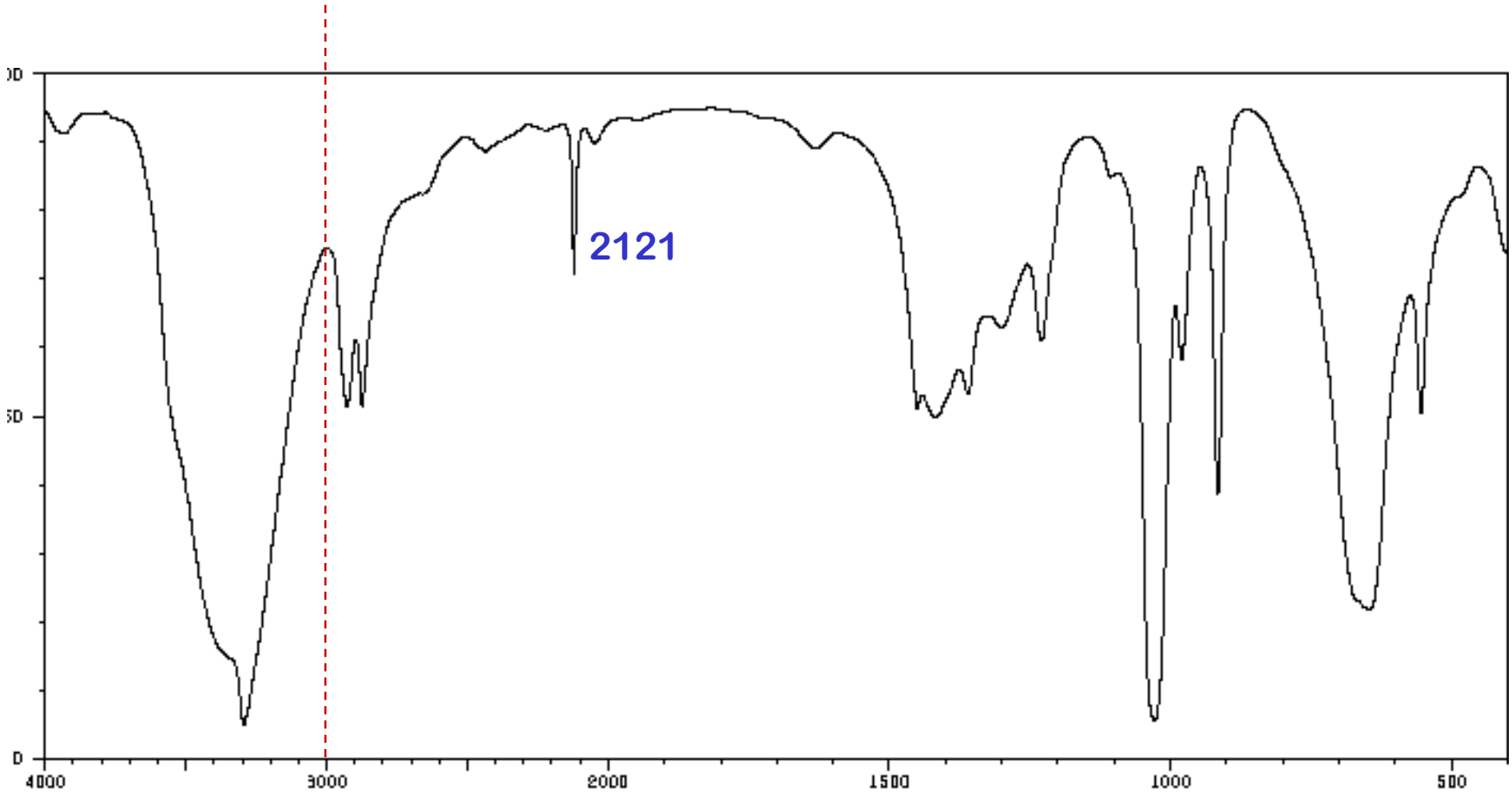
HINT: There are two functional groups.



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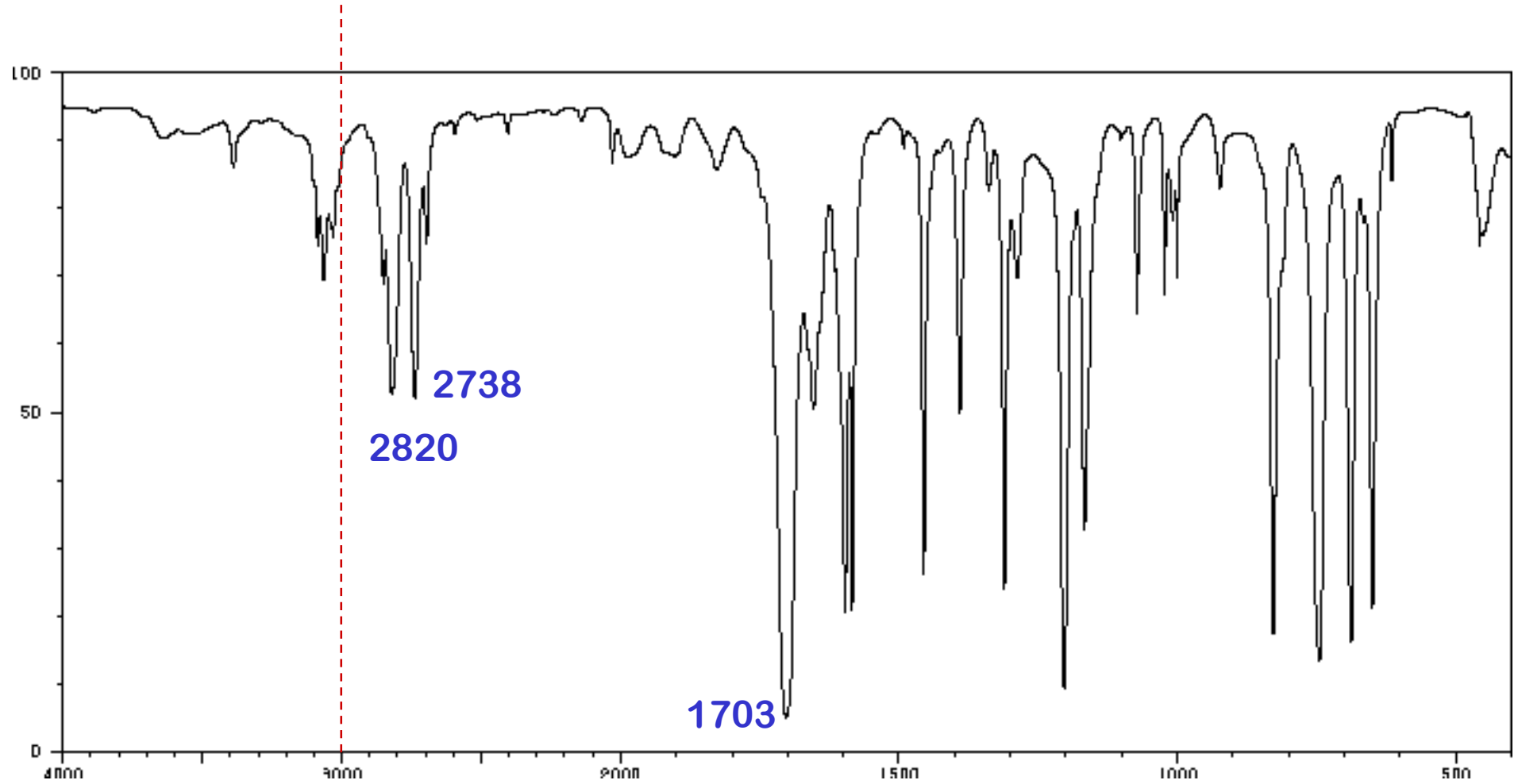
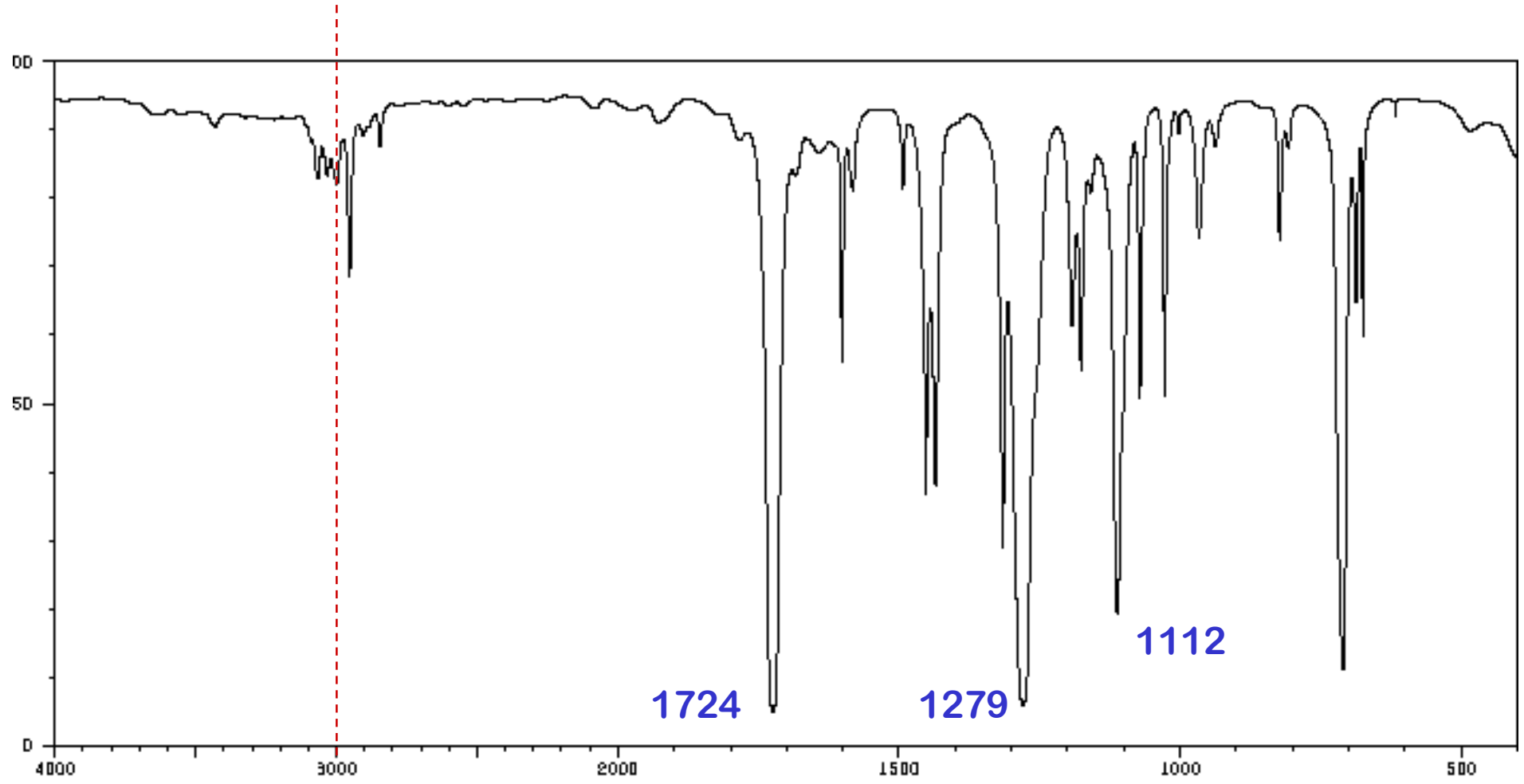


Problem 10

$C_8H_8O_2$

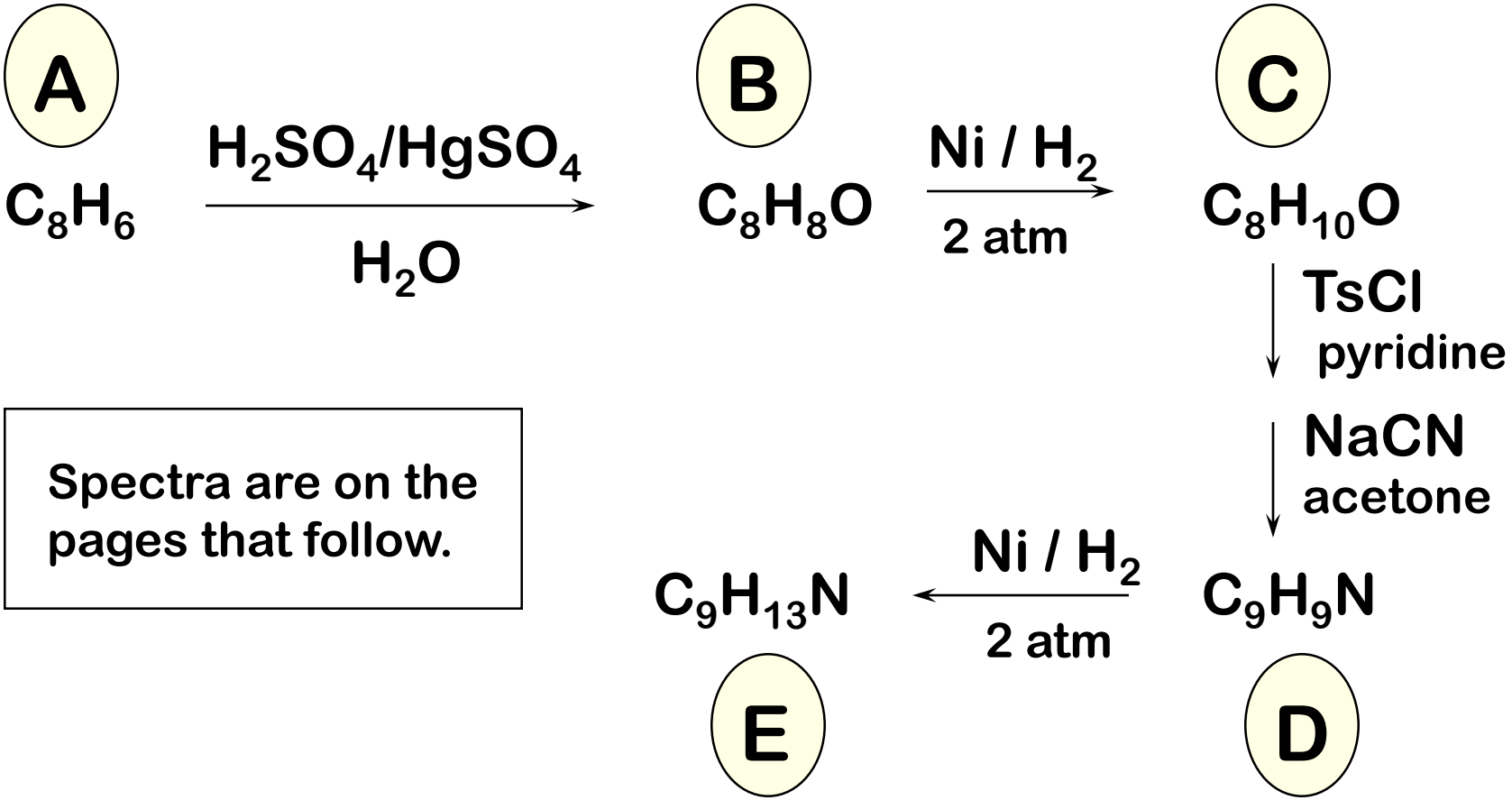


PRACTICAL APPLICATION

This next problem is a little more difficult, requiring both infrared and a knowledge of reactions.

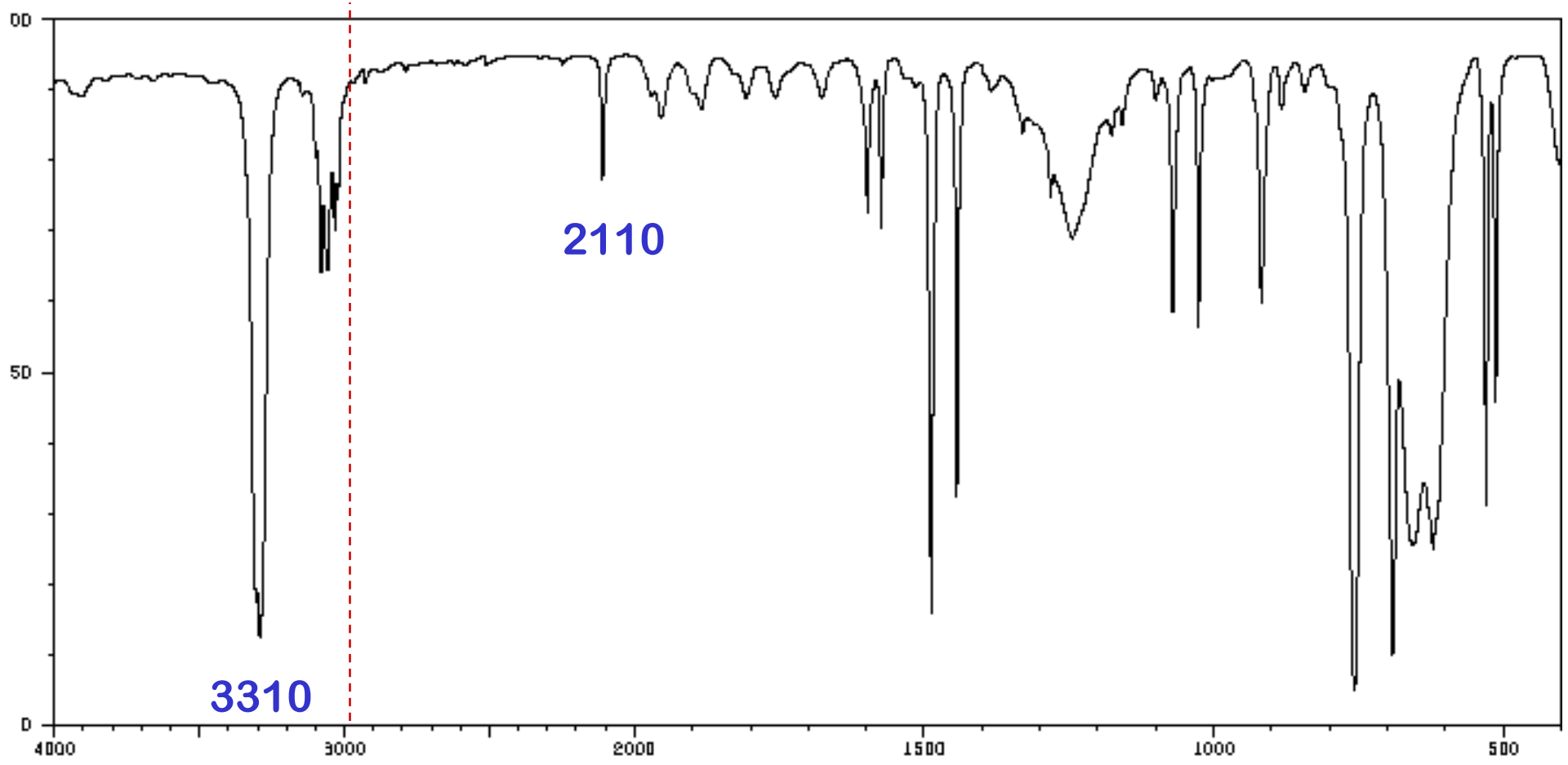
Problem 11

As a project, Mary was given an unknown compound A, and told to perform the reactions listed below. At the end of each reaction step she was told to submit the major product for microanalysis, in order to obtain the molecular formula, and to also determine its infrared spectrum. The structure of each compound was to be identified. Can you help her solve the structures and pass this class?

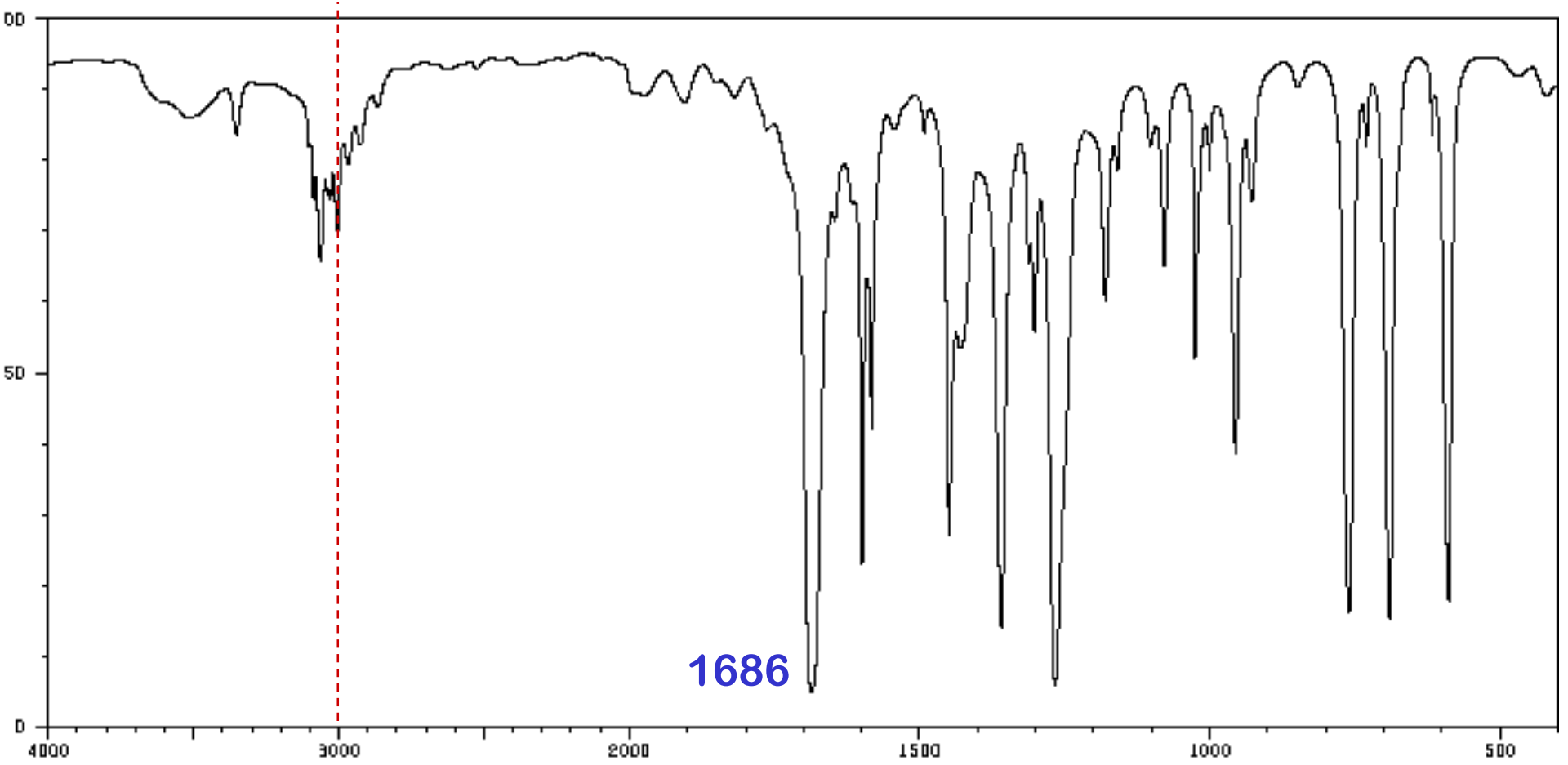


Spectra are on the pages that follow.

A C_8H_6



B C_8H_8O



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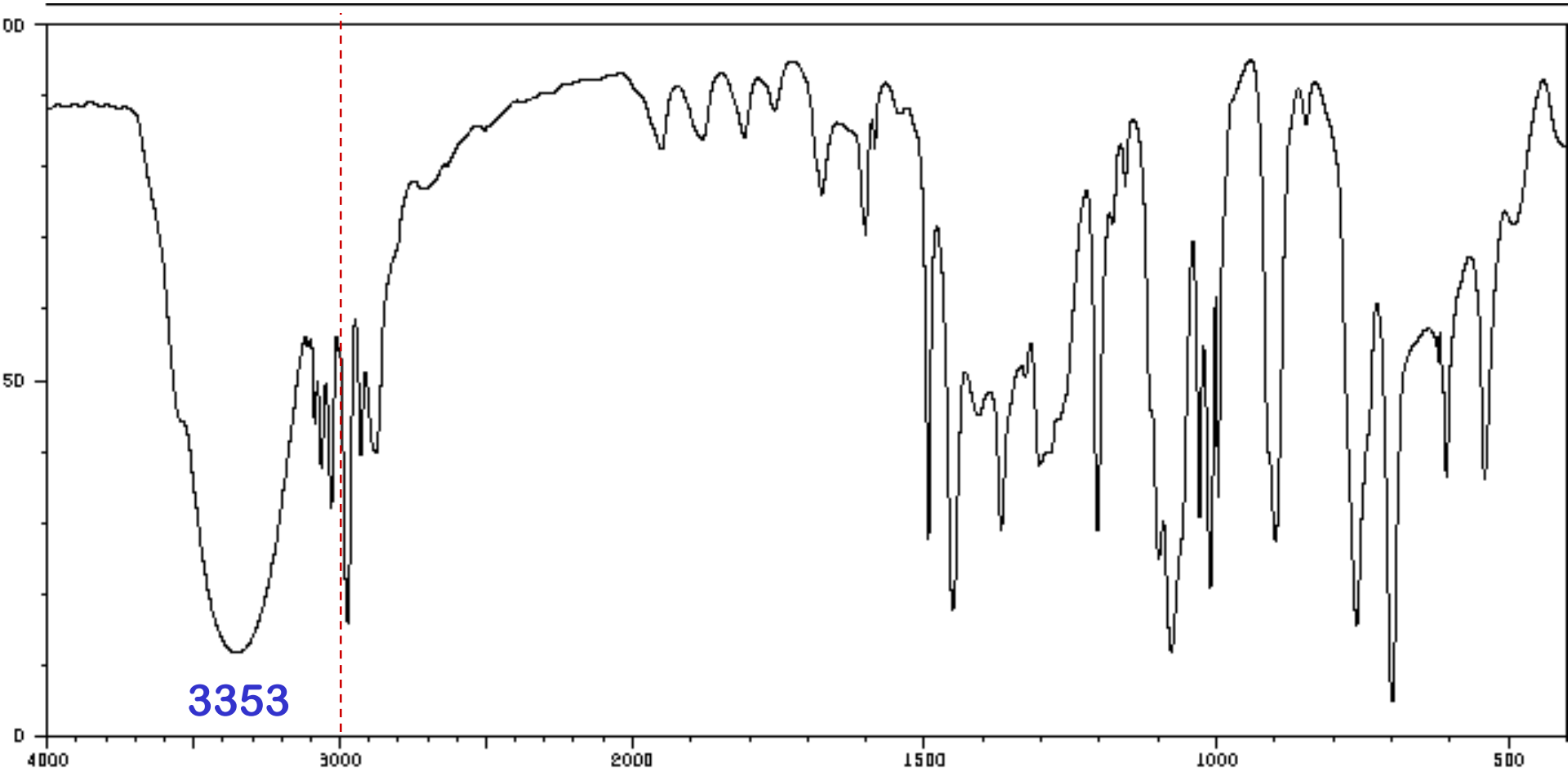
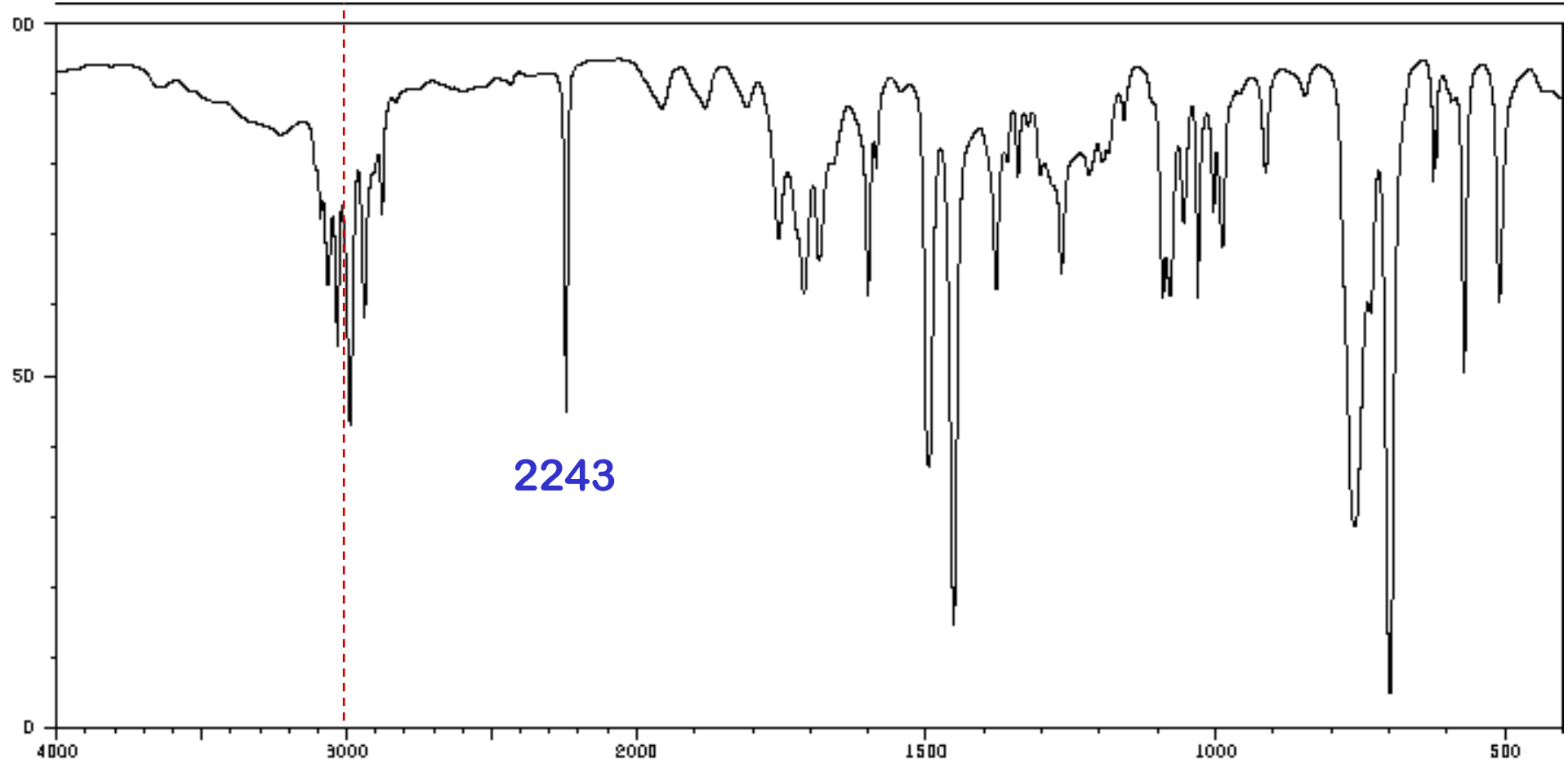
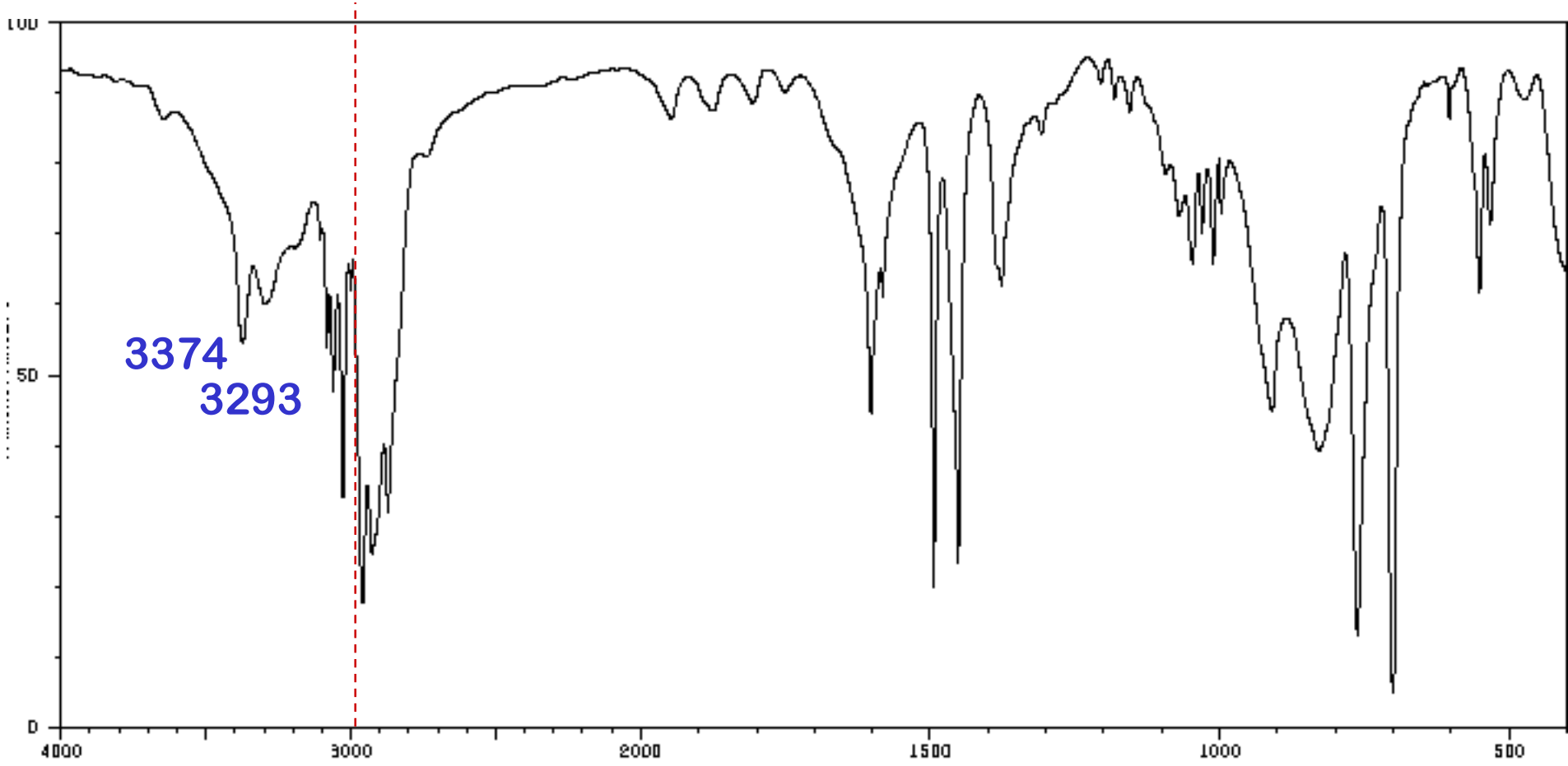


D C_9H_9N



E $C_9H_{13}N$



Also check out Problems 74 and 75 at the end of Chapter 12.

You should able to solve these now that we have finished Chapter 11.

These can be solved using infrared and an index of hydrogen deficiency.

SOME SIMPLE IR PROBLEMS

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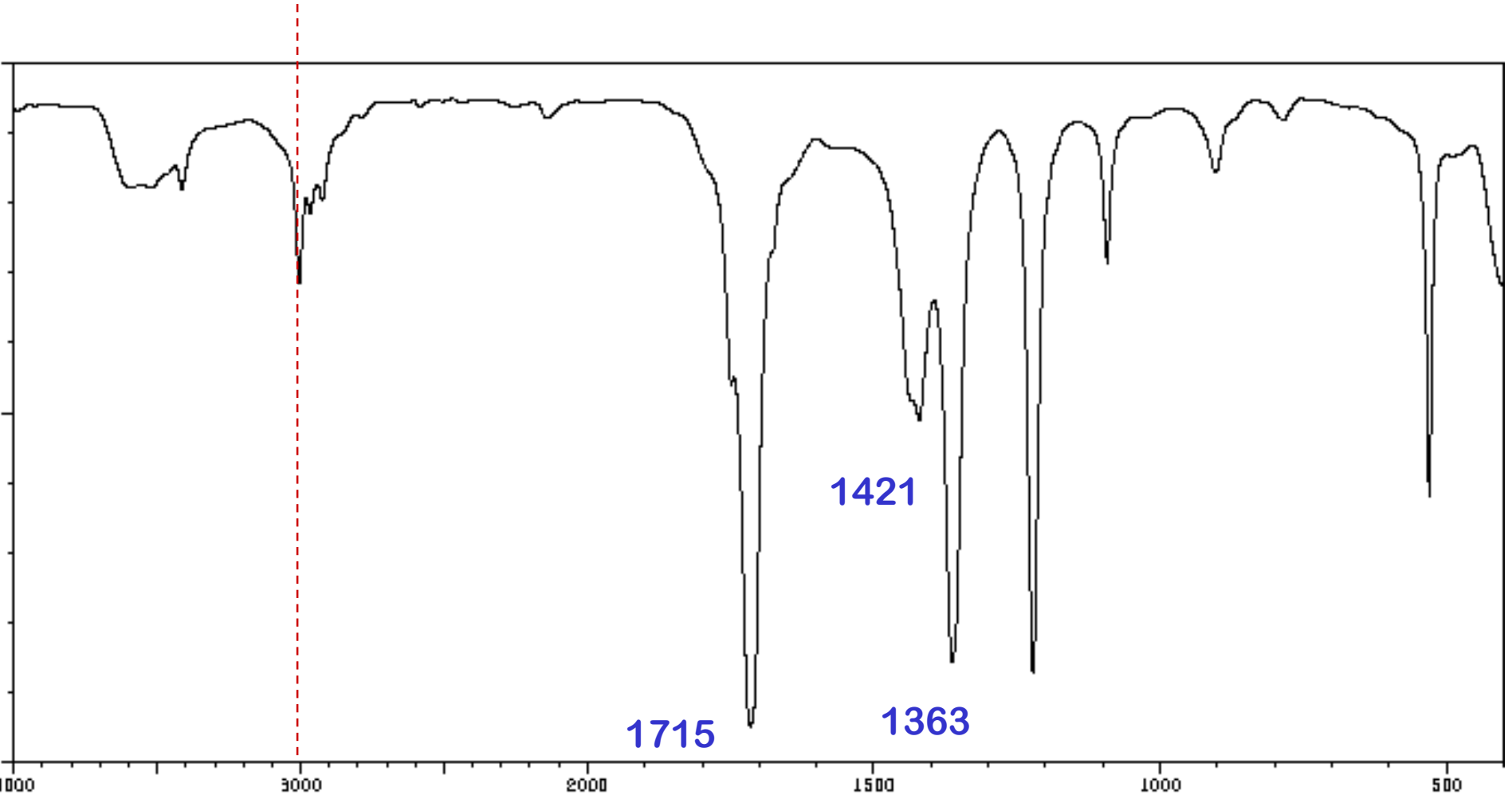

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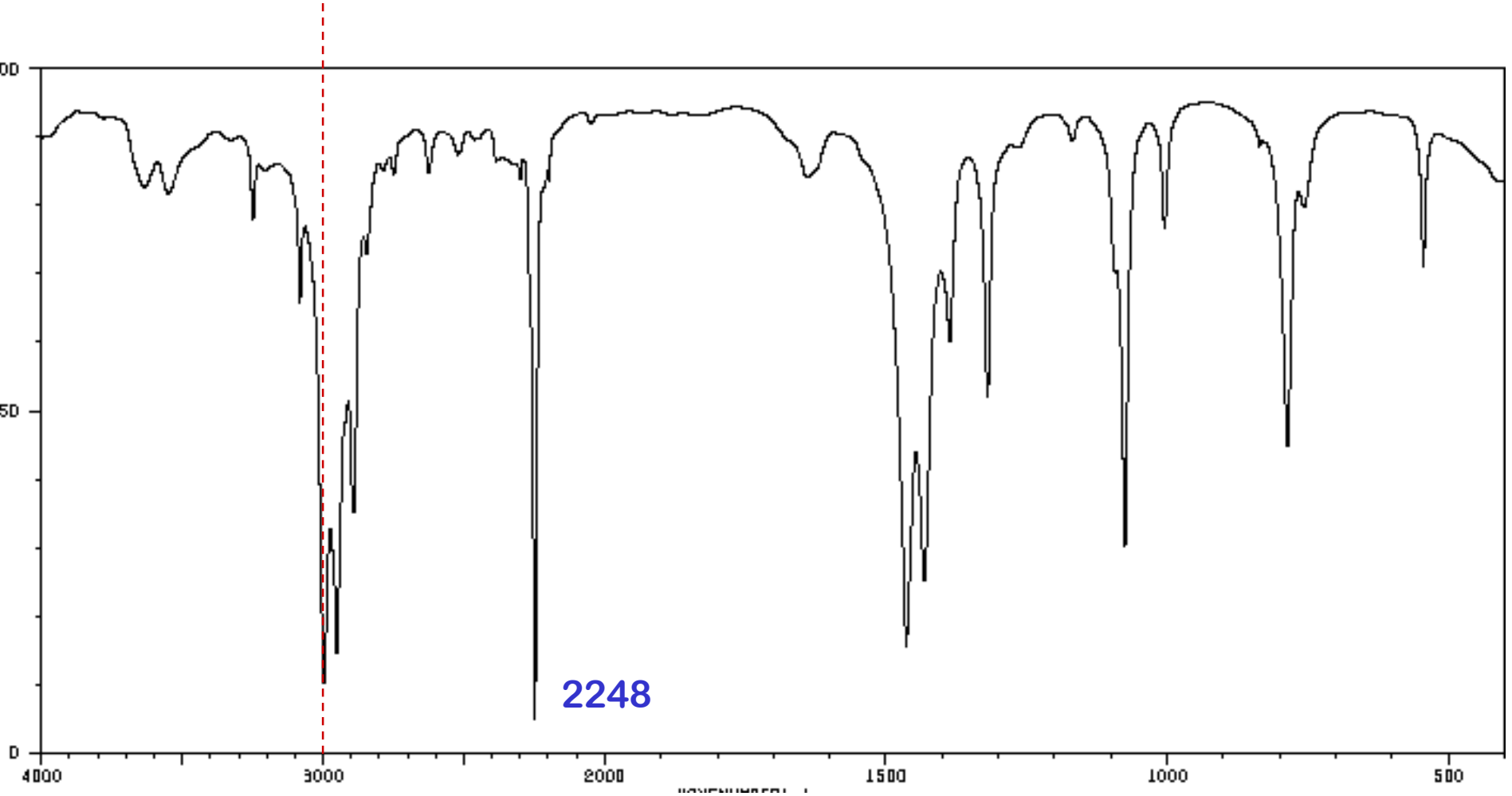

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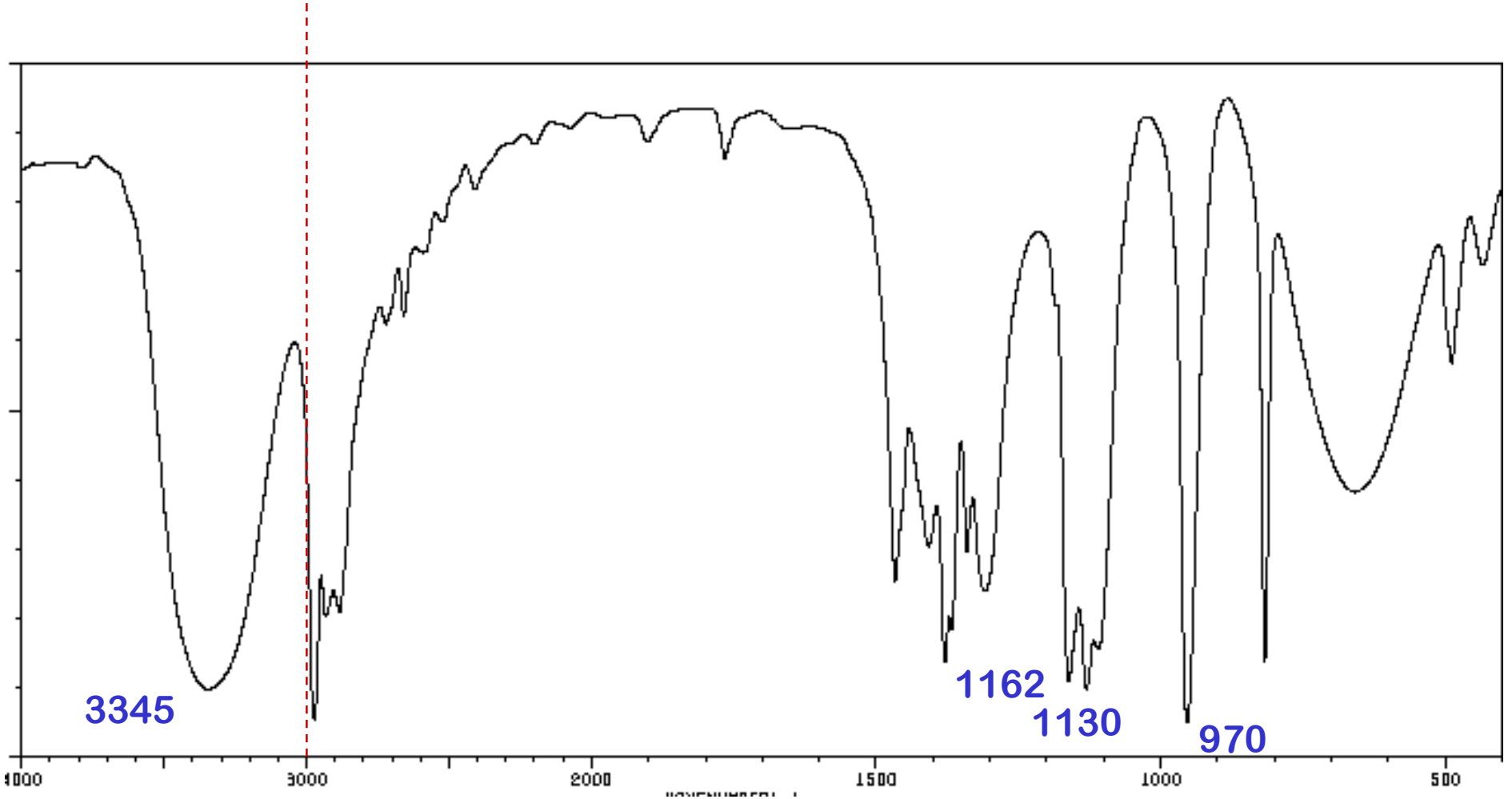

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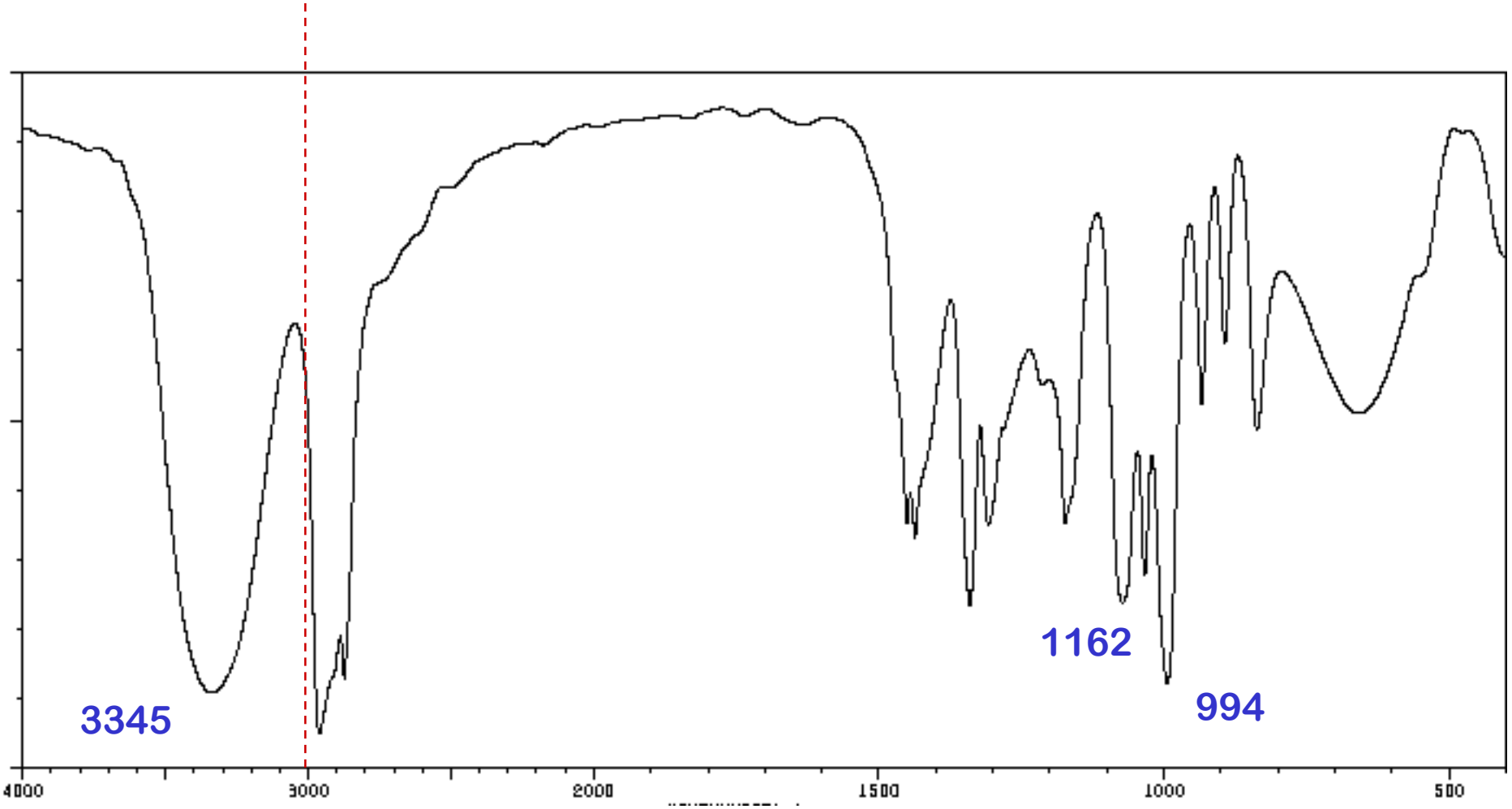

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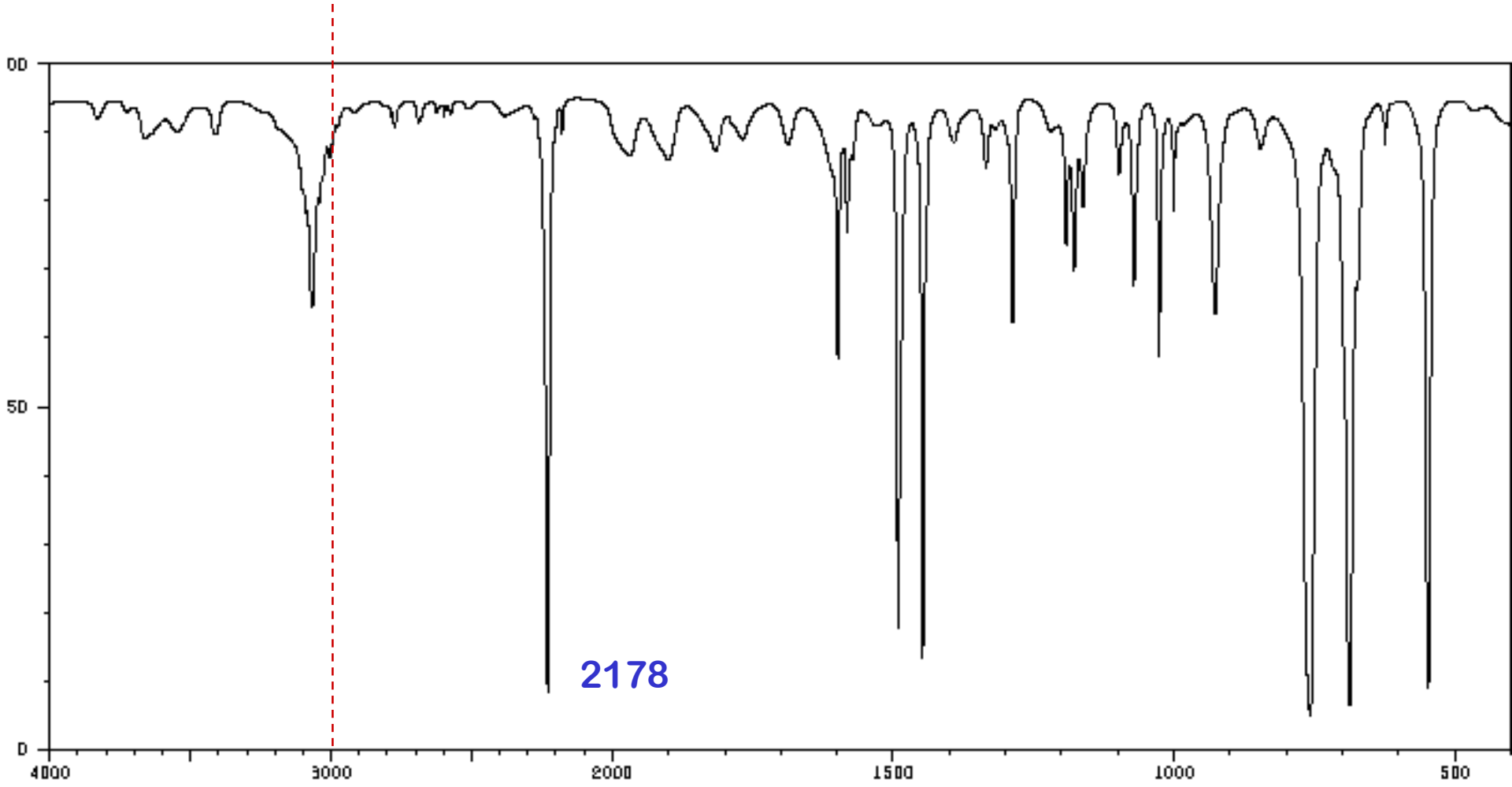

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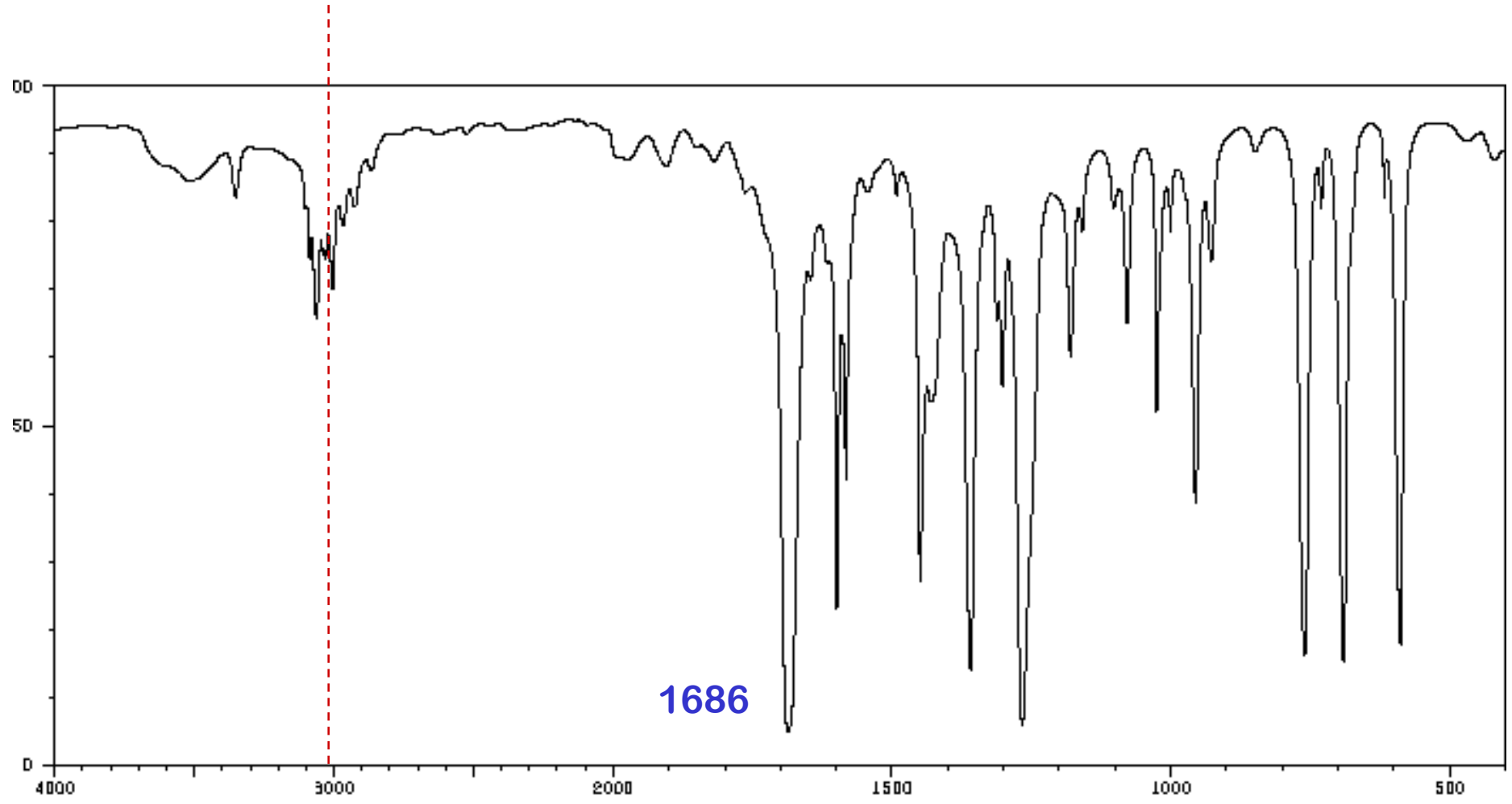

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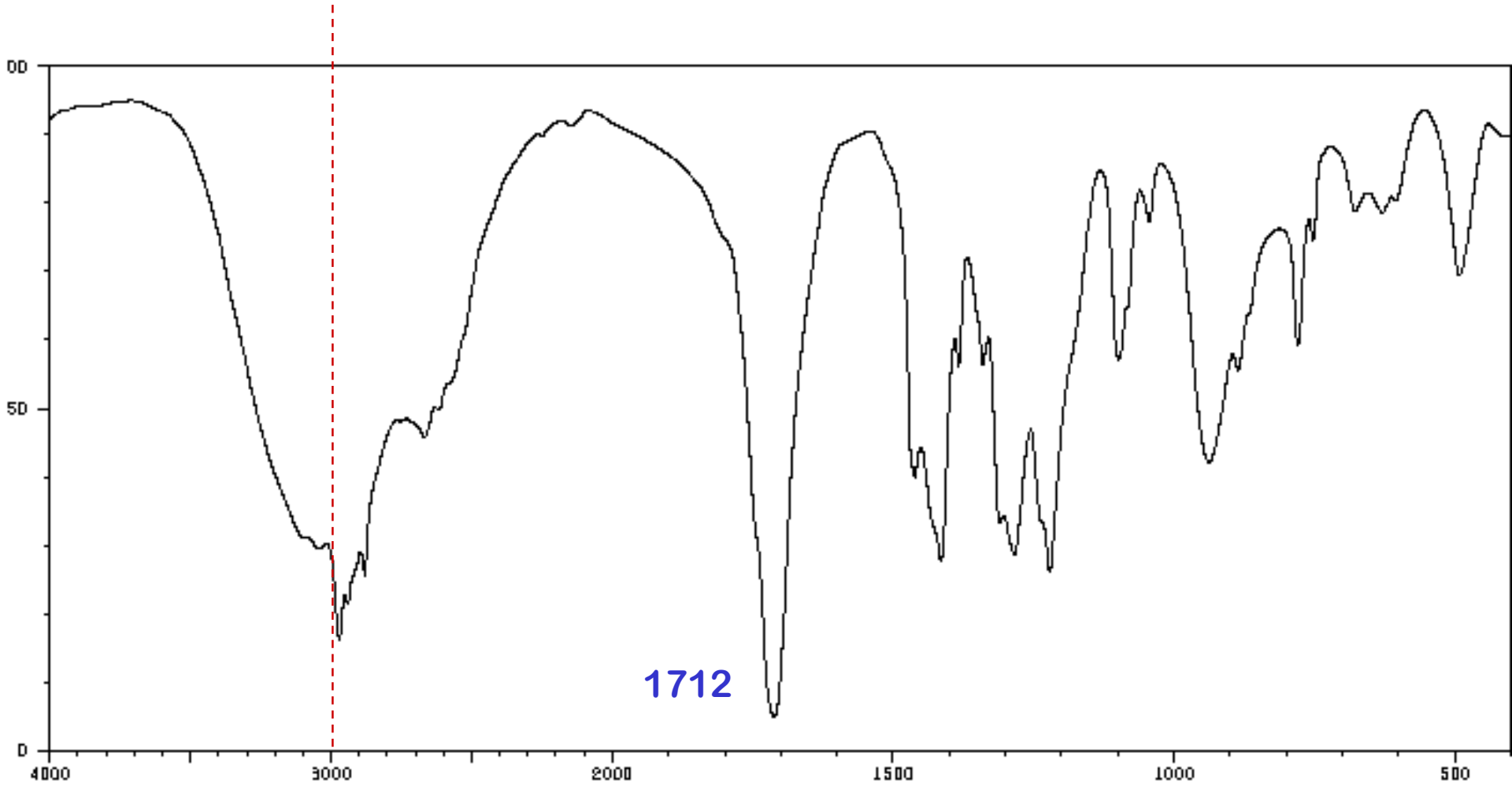

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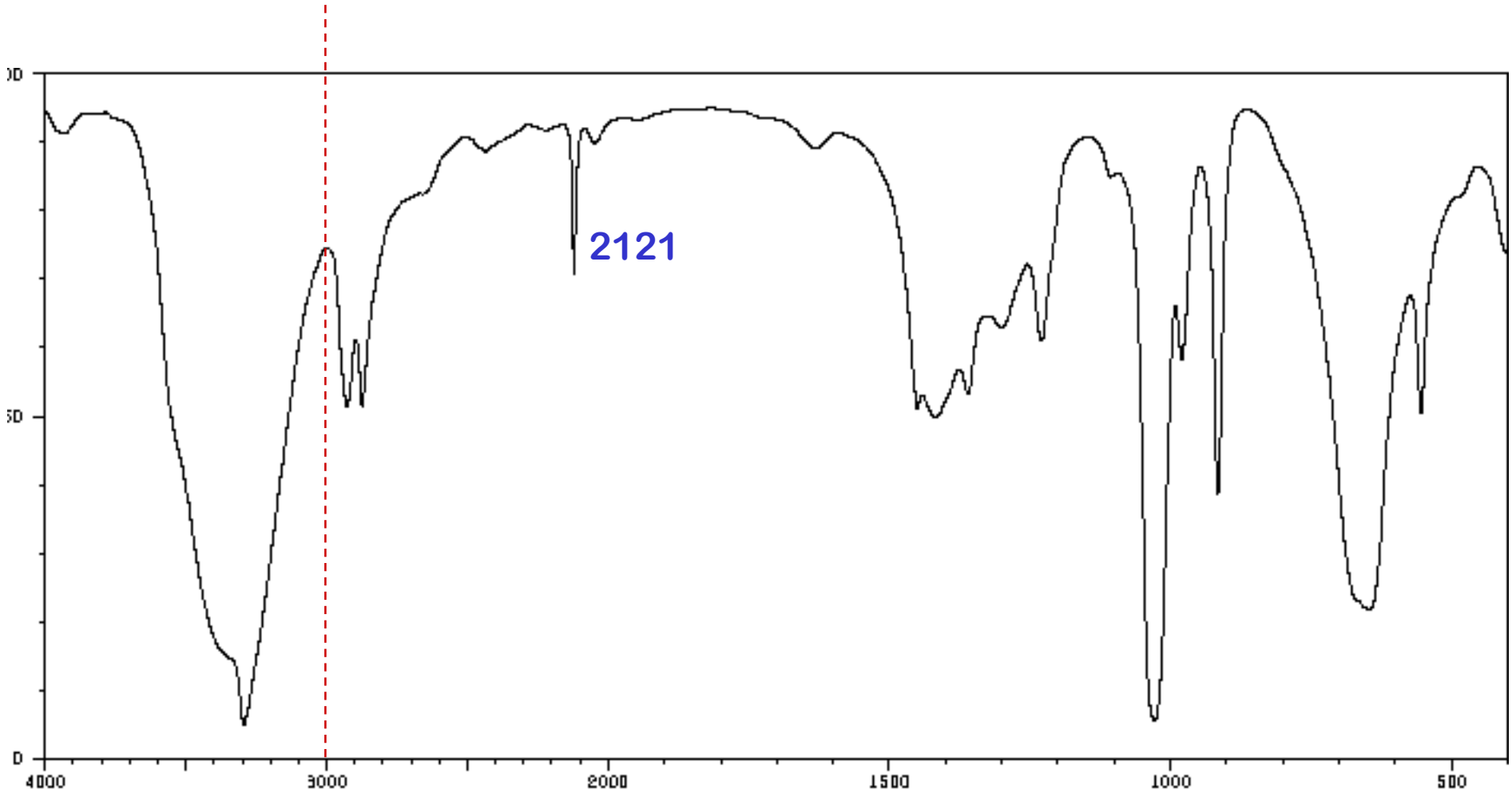

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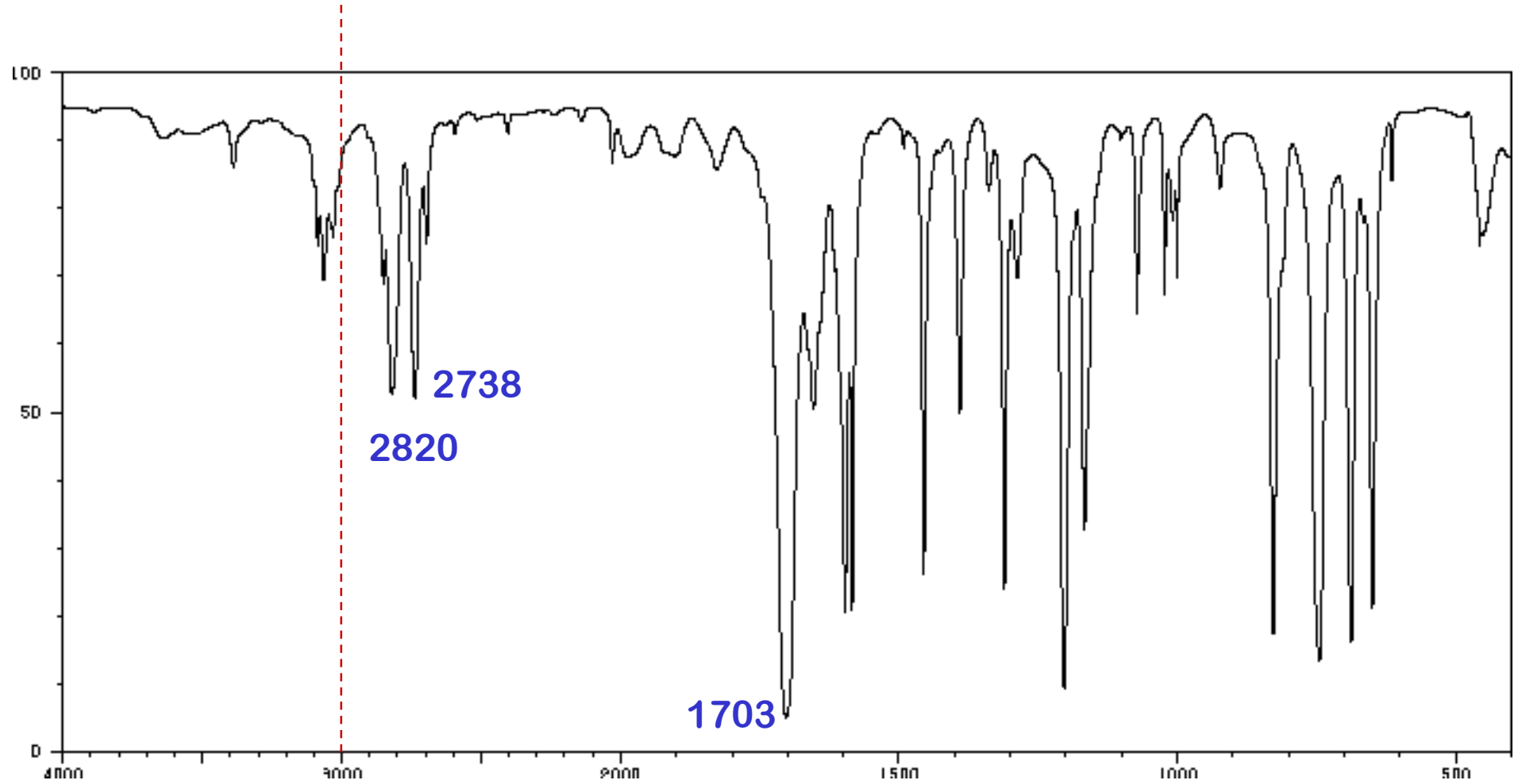

Problem 10

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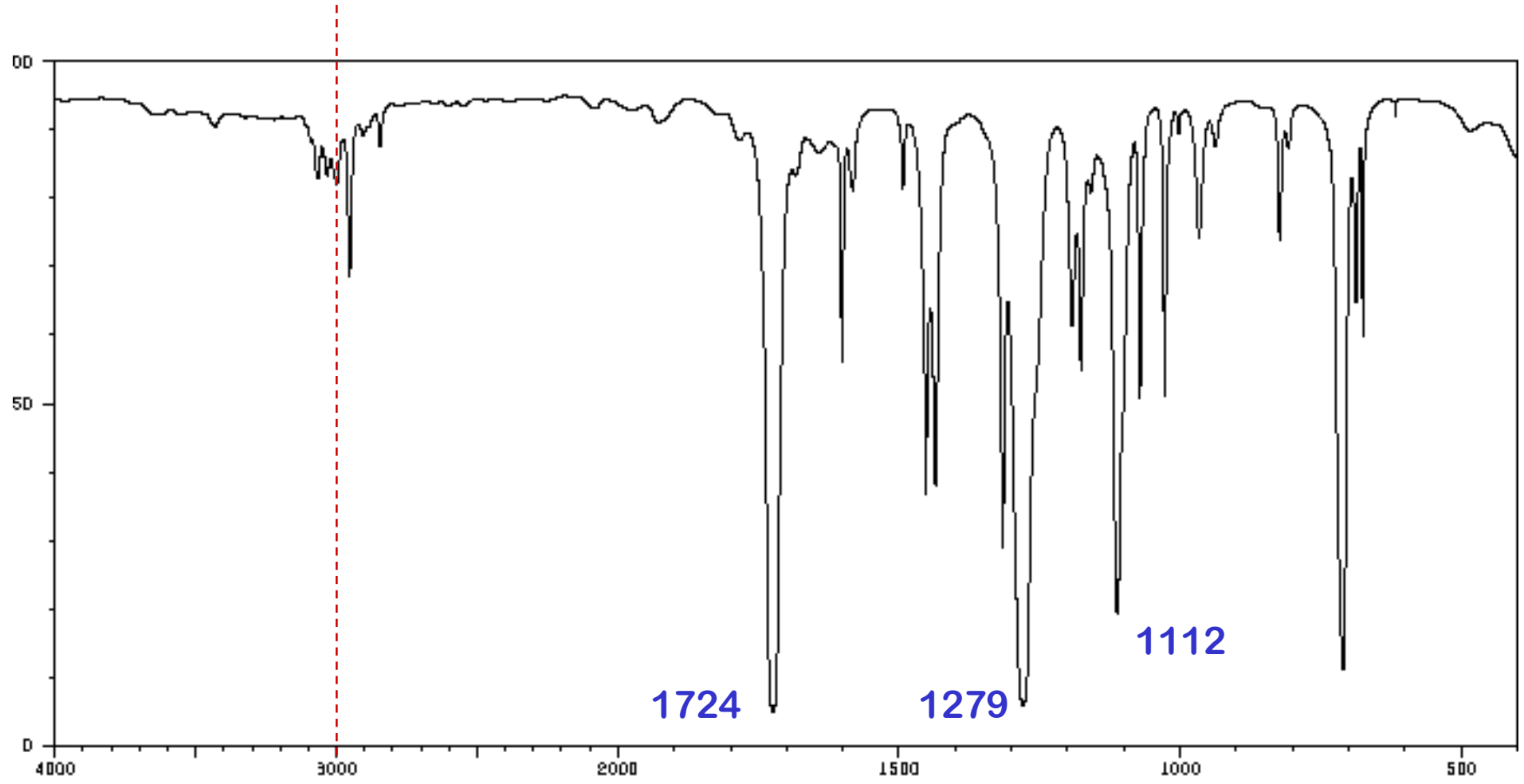

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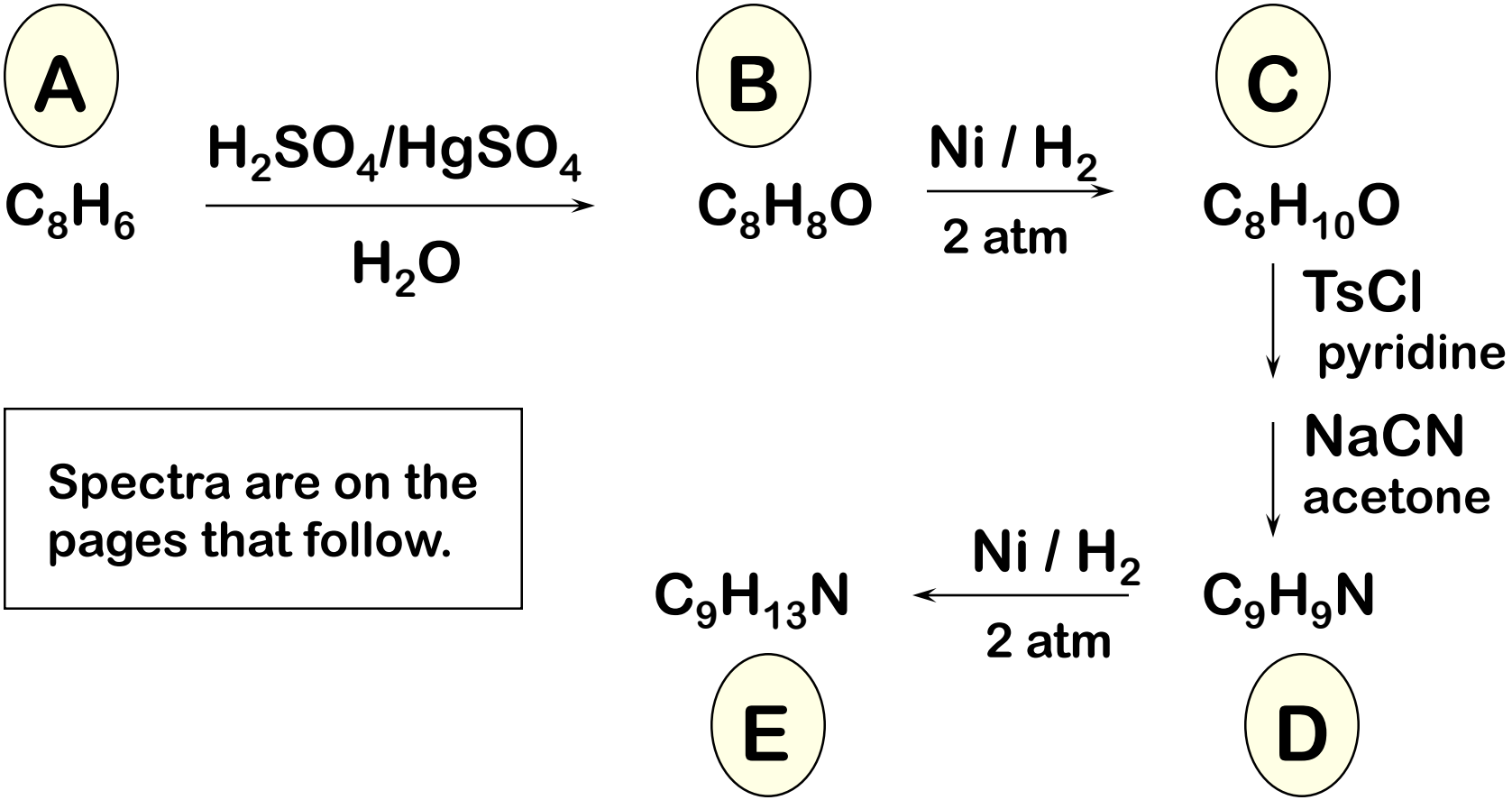
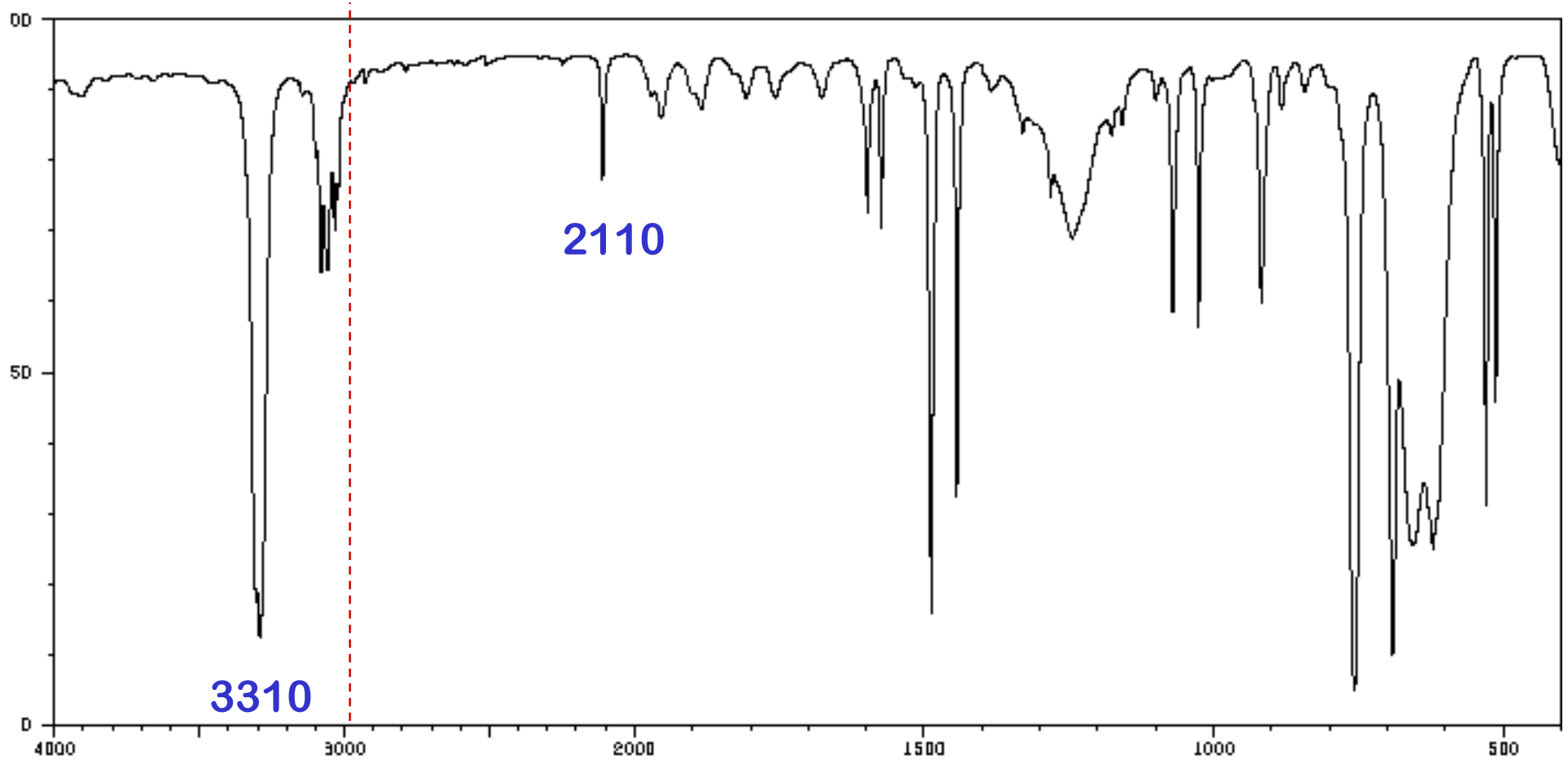
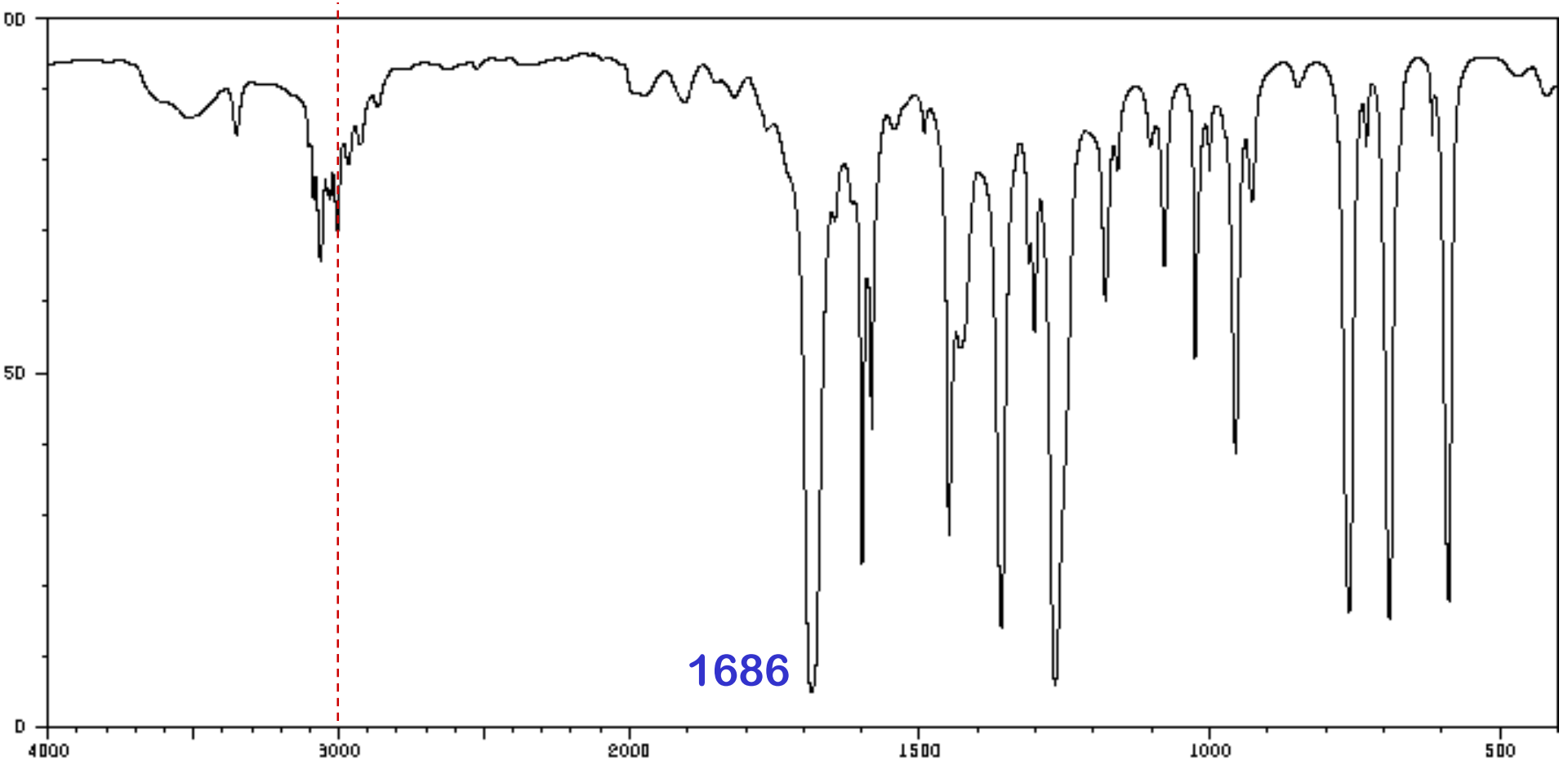


Spectra are on the pages that follow.

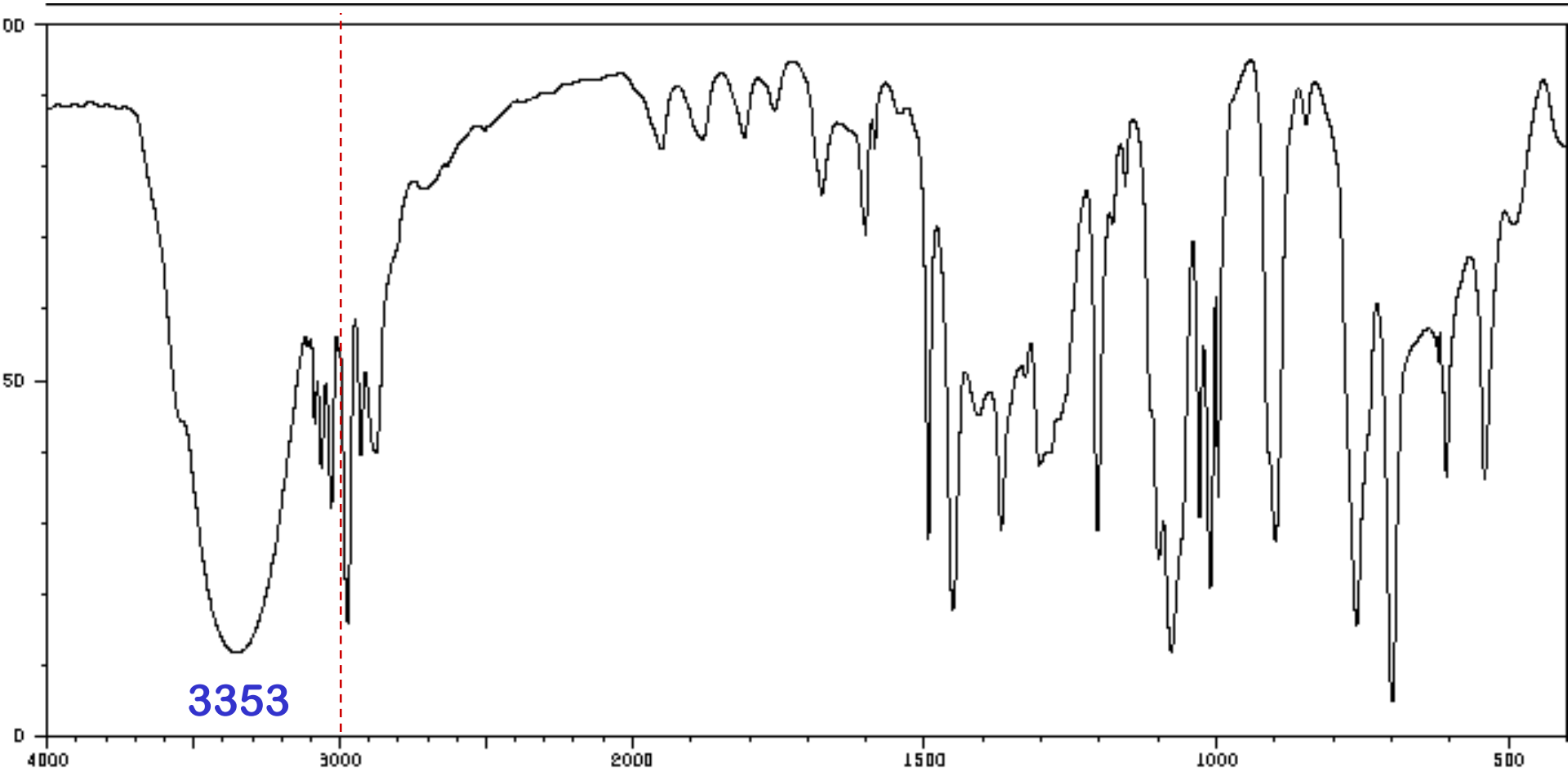
A C_8H_6



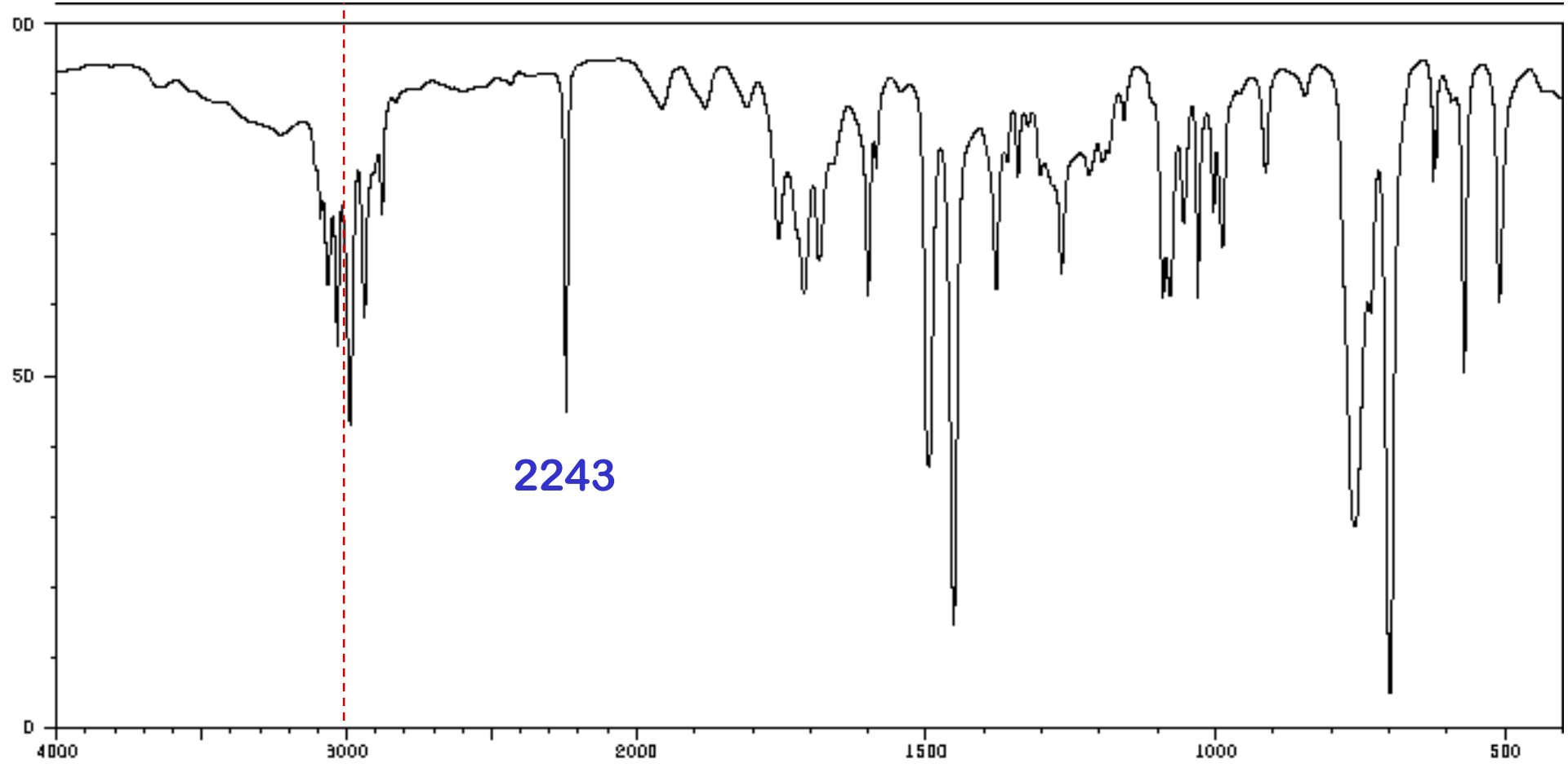
B C_8H_8O



C $C_8H_{10}O$



D C_9H_9N



E $C_9H_{13}N$