CHEMISTRY 2600

Topic #1: Using Spectroscopy to Identify Molecules:

Infrared Spectroscopy (IR)

Spring 2021

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Thanks to Prof. Peter Dibble for many of the diagrams and spectra.

Spectroscopy and Organic Chemistry

- Spectroscopy has a variety of different applications in organic chemistry, but most of them boil down to the same two questions:
  - Did my reaction work?
  - What is this molecule I just found/made?

- Different kinds of spectroscopy give different types of information about organic samples:
  - Infrared spectroscopy (IR) can identify many functional groups.
  - Ultraviolet/visible spectroscopy (UV-VIS) measures concentrations of known substances. It may also suggest the presence of conjugated pi systems.
  - Mass spectrometry (MS, often coupled with gas chromatography as GCMS) indicates the molar mass of molecules in a sample and, depending on the type, may also indicate the exact molecular formula (high resolution MS) or what fragments the molecule can break down into (GCMS or similar).
    It's also very good at indicating which (if any) halogens are present.
  - Nuclear magnetic resonance spectroscopy (NMR) indicates how many types* of atoms of a particular element are in each molecule and what their environment is like (how many other atoms are nearby, how electronegative those atoms are, is the atom in or near a pi bond or extended pi system, etc.)
   *e.g. There are three types of H in pentane ($CH_3CH_2CH_2CH_2CH_3$).

Spectroscopy and Organic Chemistry

- In CHEM 2600, we'll focus on NMR (as it's by far the most useful kind of spectroscopy for most organic chemists) but first we'll look briefly at IR. You'll find that many of the spectroscopy problems we give you to solve will involve using information from multiple sources to solve a single problem. These will frequently include:
    - NMR (both carbon and hydrogen)
    - IR
    - Elemental analysis (% by mass of each element – from which you can calculate empirical formula)
    - Molar mass (obtained by MS)

- As you work through the problems, you'll want to develop a strategy of picking the most obvious information from each source first then going back and looking at each in more detail. Solving spectroscopy problems is a lot like solving jigsaw puzzles or crosswords. If the answer is right, **<u>EVERYTHING MUST FIT</u>**. If even one piece of information does not match your answer, there is probably a better answer.
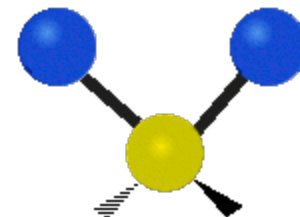
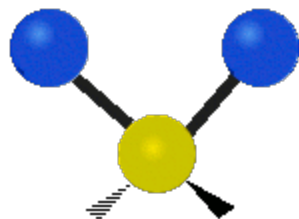# IR from a Physical Chemist's Perspective

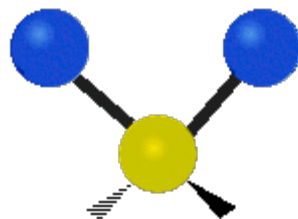- Molecules are always moving!
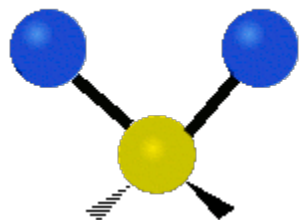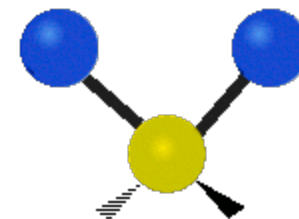
symmetric stretch
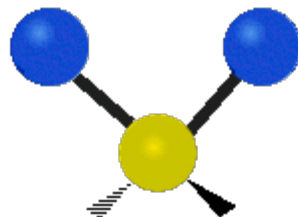
scissor

wag

asymmetric stretch

rock

twist

(For any vibration to appear on an IR spectrum, it must change the molecule's net dipole. Otherwise, it would appear on a Raman spectrum instead.)

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IR from a Physical Chemist's Perspective

- In CHEM 2000, you saw that the potential energy curves for different bonds have the same general shape, but look a little different. Which of the two images below corresponds to a shorter, more rigid bond?
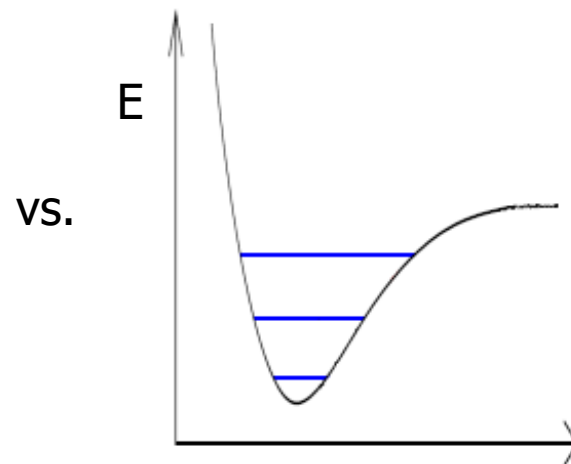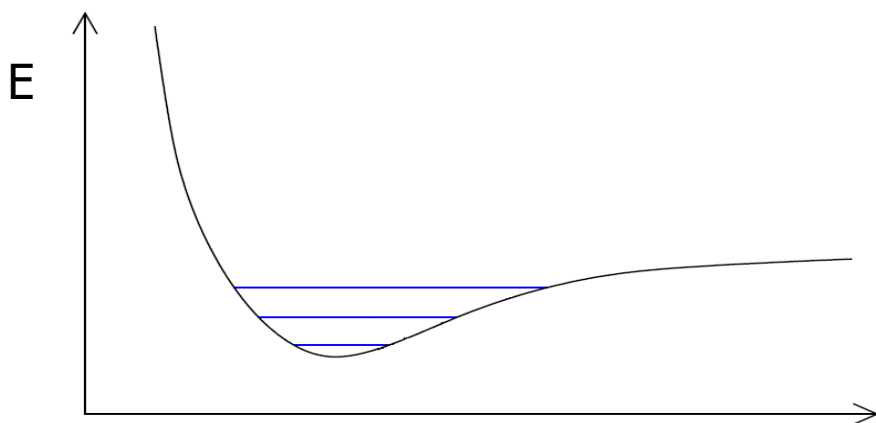
- The blue lines represent vibrational energy levels (or vibration states). To be excited from one vibrational state into a higher energy one, a molecule must absorb light in the infrared range.

- Shorter/stronger/more rigid bonds require higher energy light for this type of transition, so measuring the wavelengths absorbed by a molecule tells us about the bonds in it.

IR from an Organic Chemist's Perspective

- The convention for IR is not to report the ABSORBANCE but the TRANSMITTANCE. Transmittance is the light that passes through the sample unabsorbed. So, an IR spectrum looks something like this:
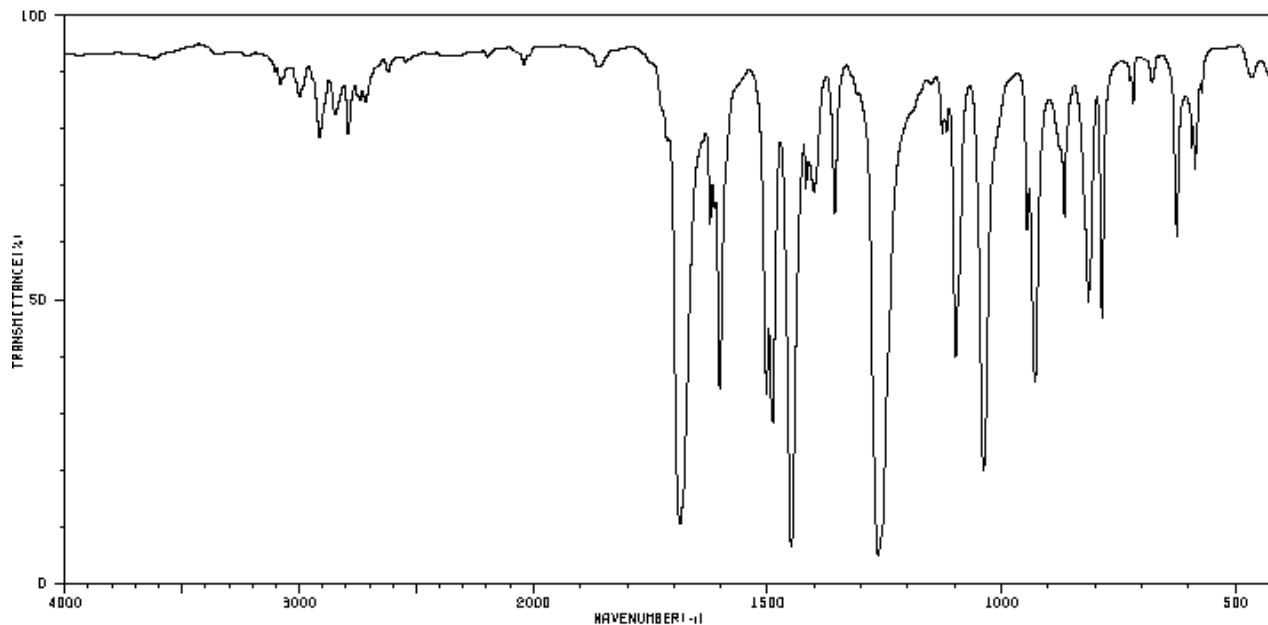
- The y-axis shows %transmittance (100% transmittance = no light absorbed) while the x-axis shows wavenumber ($\overline{\nu} = 1/\lambda$) which is usually reported in units of cm^{-1}.

IR from an Organic Chemist's Perspective

- Wavenumber is directly proportional to energy, so "peaks" with larger wavenumbers correspond to absorbance of higher energy light.

- The shortest and most rigid bonds in any organic molecule all involve the same element, hydrogen. Look for bonds involving hydrogen to appear on the left side of an IR spectrum – typically at wavenumbers higher than 2700 cm^{-1}.

- For bonds involving the other elements, bond order tells us where to look on an IR spectrum. Triple bonds ($\sim$2000-2500 cm^{-1}) tend to be shorter/stronger/more rigid than double bonds ($\sim$1500-2000 cm^{-1}) which are, in turn, shorter/stronger/more rigid than single bonds (usually <1500 cm^{-1} but buried in the "fingerprint region").

IR from an Organic Chemist's Perspective

- When we compare C≡C to C=C to C-C, we get the order we'd expect:

- As you might expect, bonds with fractional bond order will behave accordingly.

  e.g. benzene

IR from an Organic Chemist's Perspective

- Lastly, it's worth noting that size (or at least mass) does matter in IR:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

The masses of the atoms.
K is the force constant.

- The influence of mass is most obvious when comparing H to larger atoms, but can be seen in other cases to a lesser degree:

C-H	C-D	C-C
just below 3000 cm^{-1}	~2200 cm^{-1}	~1200 cm^{-1}

see also http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-ir-2.html
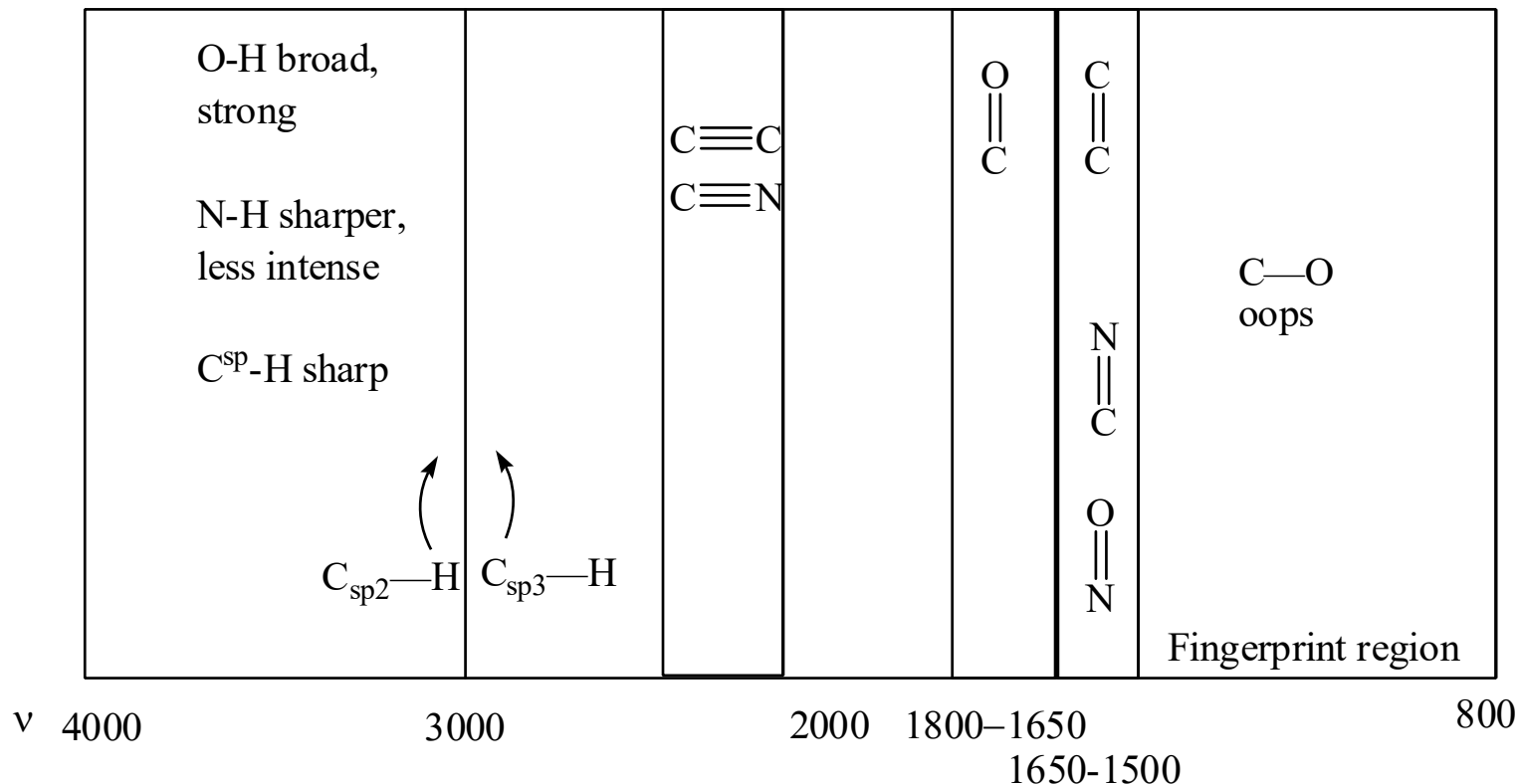
IR from an Organic Chemist's Perspective

- That said, except for bonds to H, the effect of mass rarely trumps the effect of bond strength. C=O absorbs higher energy light than C=C. Why?

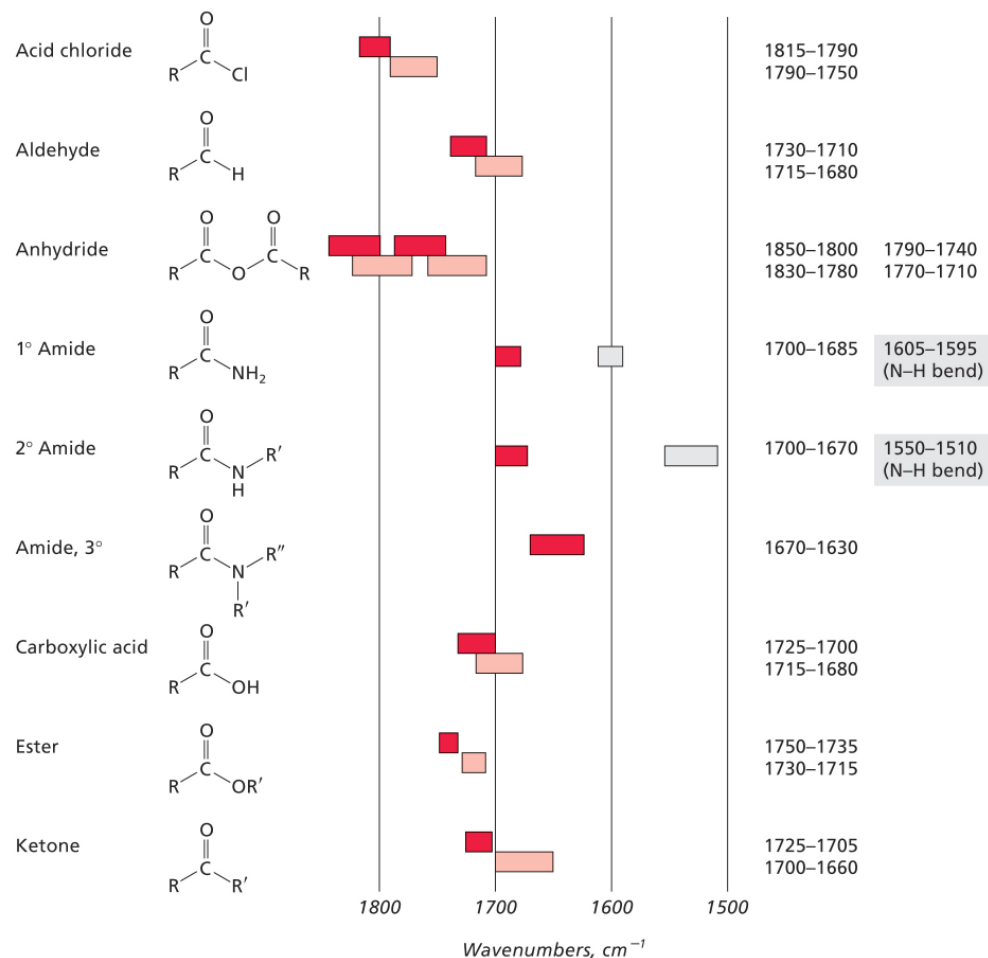# IR from an Organic Chemist's Perspective

Getting the most out of an IR in 30 seconds.

Try to avoid making negative conclusions about alkenes or alkynes based on an IR. Sometimes, the peak is just too small to see (or missing due to symmetry). It's usually better to just say "*probably* no C≡C" until/unless something else backs up your suspicion.

IR from an Organic Chemist's Perspective

- If you find any C=O stretches, try to find the exact wavenumber:

|		
Acid chloride		1815–1790 / 1790–1750
Aldehyde		1730–1710 / 1715–1680
Anhydride		1850–1800 1790–1740 / 1830–1780 1770–1710
1° Amide		1700–1685 1605–1595 (N–H bend)
2° Amide		1700–1670 1550–1510 (N–H bend)
Amide, 3°		1670–1630
Carboxylic acid		1725–1700 / 1715–1680
Ester		1750–1735 / 1730–1715
Ketone		1725–1705 / 1700–1660

Wavenumbers, cm⁻¹

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…and that's pretty much it for IR.

IR from an Organic Chemist's Perspective

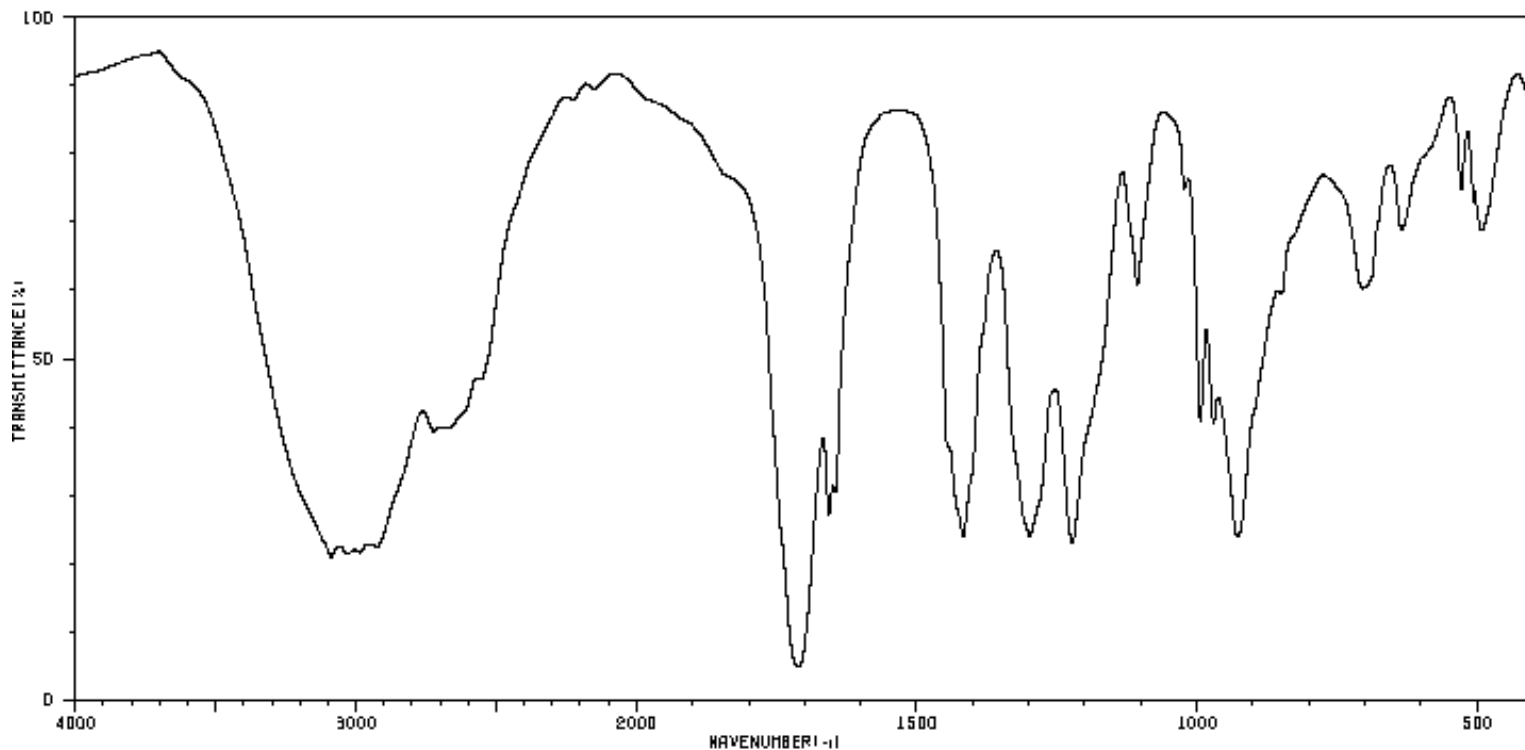- What can we infer from the IR below?
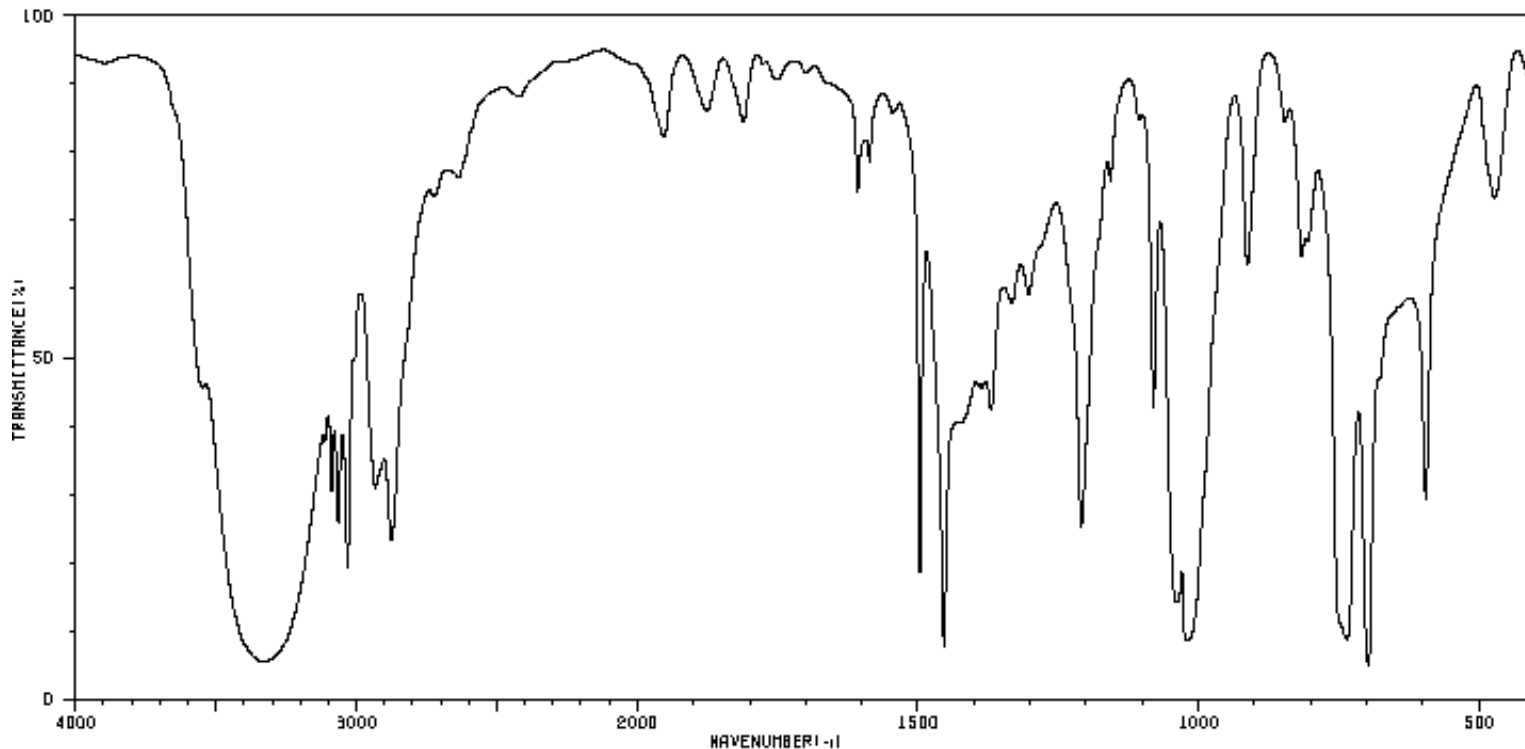
3325	5	1962	79	1497	18	1080	41	606	64
3088	29	1876	84	1454	7	1039	13	736	8
3065	24	1811	81	1370	41	1018	8	698	4
3031	18	1607	72	1332	66	913	60	595	27
2932	29	1593	79	1303	57	846	81	473	70
2875	22	1587	77	1209	23	817	62		
2419	84	1644	81	1157	72	812	64		

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IR from an Organic Chemist's Perspective

- What can we infer from the IR below?

3087	20	1107	58	629	72
1712	4	1022	72	493	66
1657	26	994	39		
1646	29	971	39		
1417	23	927	23		
1299	23	704	58		
1223	22	634	66		

IR from an Organic Chemist's Perspective

- What can we infer from the IR below?
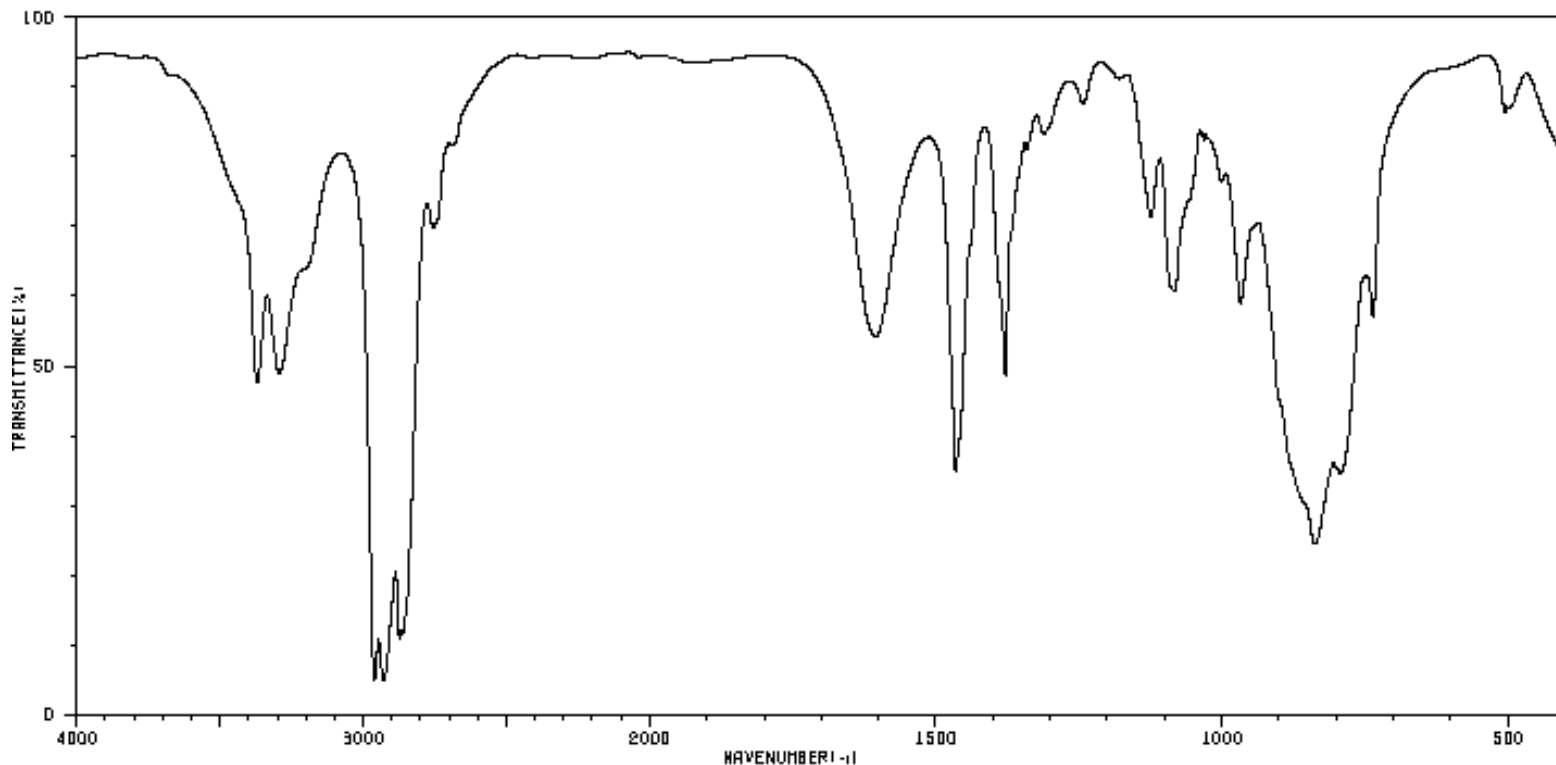
3369	46	1606	52	1083	68	498	84
3293	47	1465	33	1001	74		
2960	4	1379	46	967	57		
2928	4	1340	77	837	23		
2874	10	1312	79	792	33		
2862	10	1243	84	736	55		
2757	66	1124	68	606	84		

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IR from an Organic Chemist's Perspective

- What can we infer from the IR below?
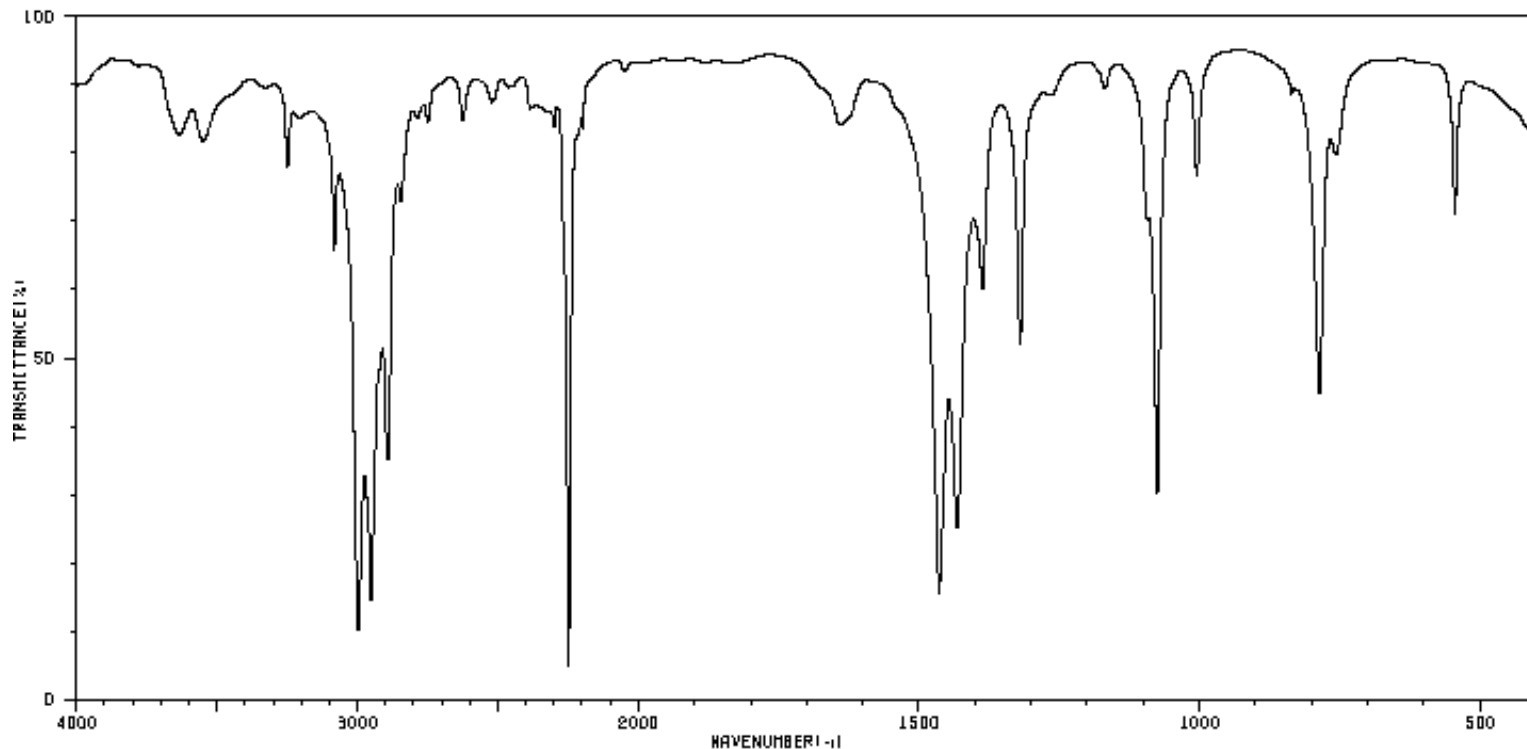
3632	79	2844	70	2299	81	1320	60	646	68	
3548	79	2787	81	2248	4	1170	86			
3249	74	2749	81	2198	81	1075	29			
3082	64	2624	81	1639	81	1006	74			
2997	10	2521	84	1464	14	836	84			
2952	13	2461	86	1432	23	786	49			
2891	34	2460	86	1387	68	767	77			