

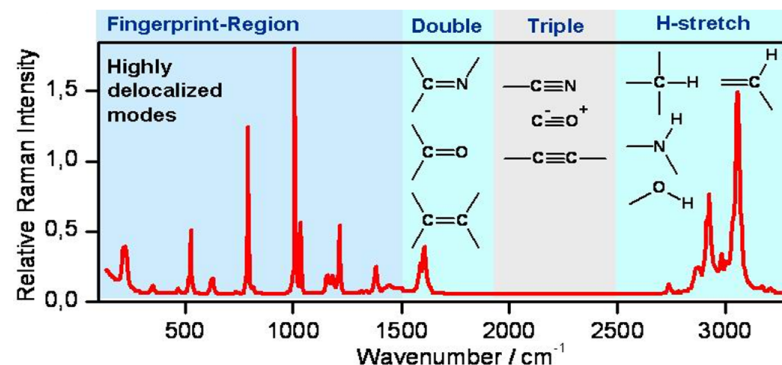
Ch 1b Lecture 7

January 22nd, 2012

Next few lectures – *Light/matter interactions*,
or, An Introduction to Spectroscopy.

Today: Vibrational spectroscopy, with a short
introduction to rotational spectra.

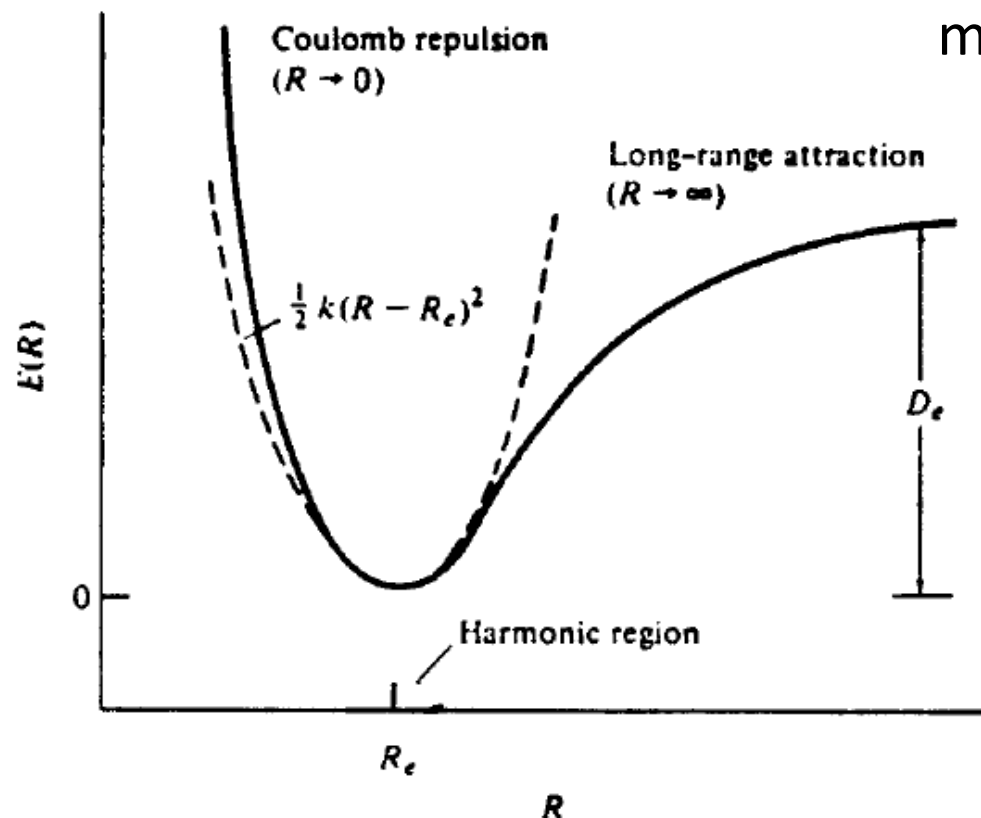
Reading: Review OGC sections 4.5-4.7 as needed, OGC
sections 20.1-20.3; RC Sections 9-4 to 9-7, 9-9



Quick review of last lecture:

- Molecular eigenstates are quantized due to the masses, length scales involved.
- The energies involved for electronic excitation are of order eV, which are $\gg k_B T$; those for the nuclear degrees of freedom less, with populations governed by the Boltzmann distribution (at \sim STP).
- To interact strongly with radiation, the molecular motion/excitation must vary the electric dipole moment periodically.

Simple model of diatomic rotation/vibration:

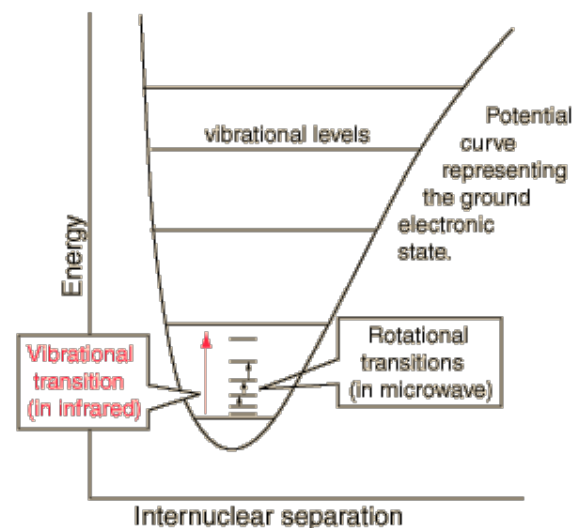


$m_p = 1836m_e$ Born-Oppenheimer
(Section 6.1.2, OGC):

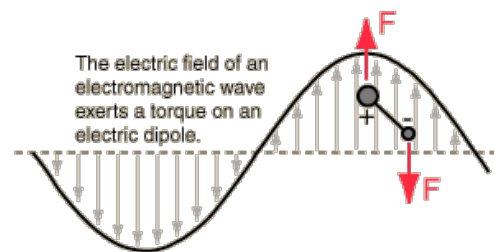
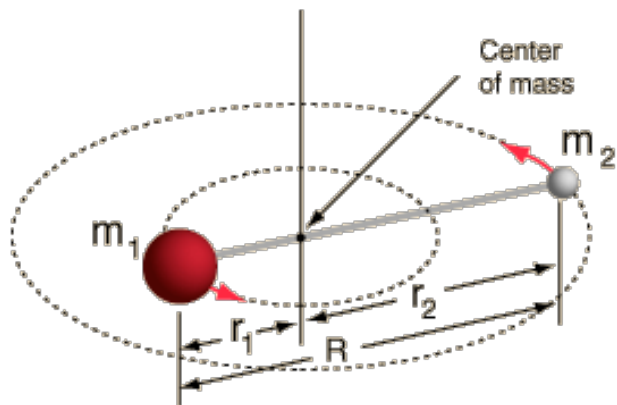
$$\Psi = \Psi^{el} \Psi^{vib} \Psi^{rot}$$

Treat the system as a
harmonic oscillator!

Leads to coupled
equations... Even
simpler?



Rotational Spectroscopy:



Fix bond length at R , moment of inertia, I , is $I = \mu R^2$, where $\mu = m_1 m_2 / (m_1 + m_2)$ is the *reduced mass*.

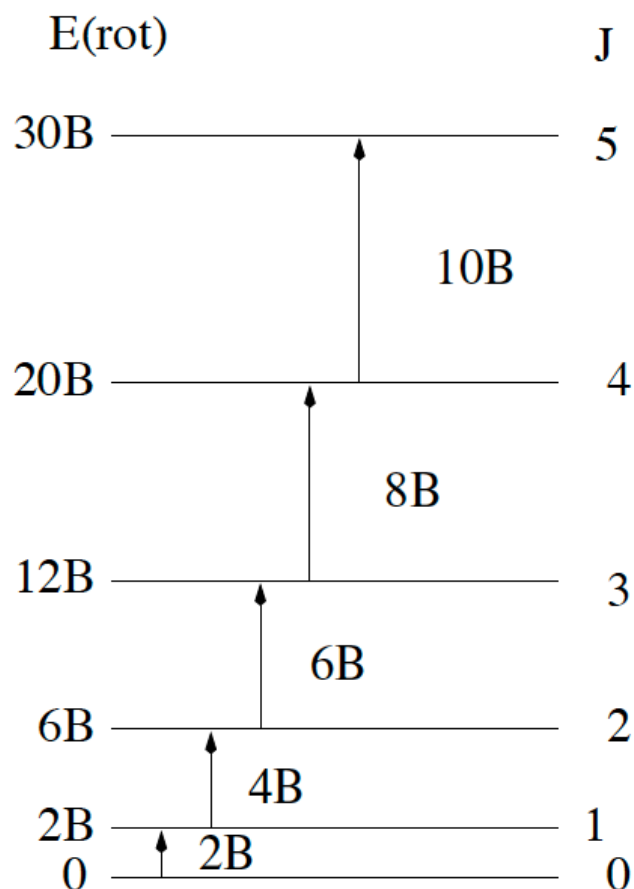
Becomes an angular momentum problem, the math is analogous to the hydrogen atom:

$$\left\{ \frac{J^2}{2\mu R_e^2} - E^{rot} \right\} Y_{JM}(\hat{R}) = 0.$$

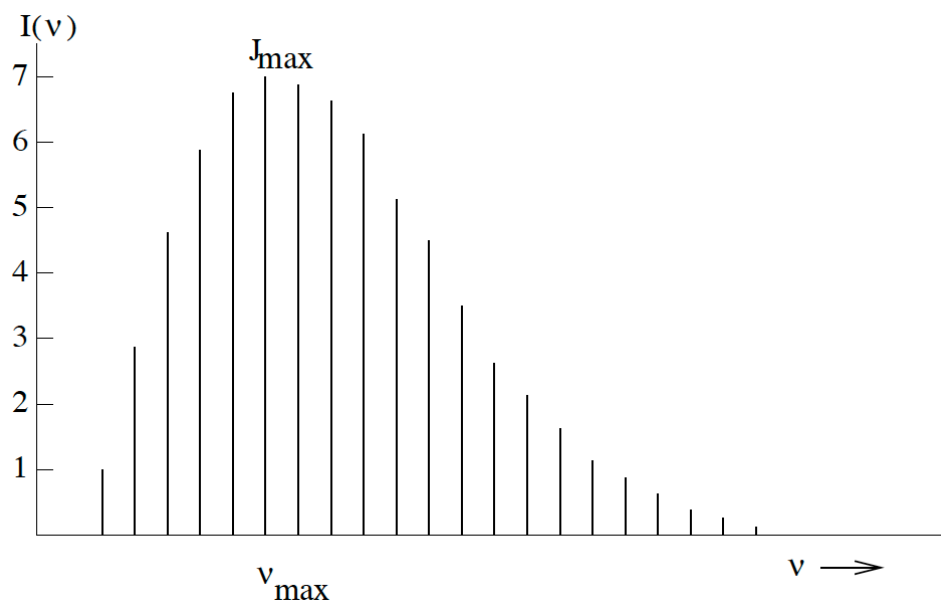
$$J^2 Y_{JM}(\hat{R}) = 2\mu R_e^2 E^{rot} Y_{JM}(\hat{R}) = J(J+1) Y_{JM}(\hat{R}).$$

Rotational Spectroscopy:

$$E^{rot} = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2\mu R_e^2} J(J+1) = B_e J(J+1)$$



Light can only change J by ± 1 , which leads to evenly spaced lines. The degeneracy is $(2J+1)$ (why?), envelope of intensities is thus temperature dependent.



Rotational Spectroscopy:

What can we do with this

Absorption intensity is not the same for all of the absorption lines



$$B_{\text{LiF}} \approx 0.67 \text{ cm}^{-1}$$

$$\frac{n'}{n''} = \frac{g'}{g''} e^{\frac{-\Delta E}{k_B T}}$$

The absorption intensity reflects the thermal population of the rotational energy levels

Energy Levels

— 30B

— 20B

— 12B

— 6B

— 2B

— 0B

If we measure the spectrum, we get B. If we know B, we know the moment of inertia, I. If we know what molecule we are measuring, we can get the bond length.

Powerful route to structures, requires gas phase.
Some diatomic numerical examples follow...

Rotational Spectroscopy:

For molecules, always consider the μ when considering the moment of inertia.

Diatomic molecules

$$\mu = \frac{m_{\text{atom1}} \times m_{\text{atom2}}}{m_{\text{atom1}} + m_{\text{atom2}}}$$

$$I_{\text{mol}} = \mu R_{\text{bond}}^2$$

Example: Calculate the moment of inertia for Li-F:

mass Li = 7 g/mol

mass of F = 19 g/mol

Bond length = 2.2 Å.

(this is a guess!)

$$\mu = 8.53\text{E-}27 \text{ kg}$$

$$I = (8.53\text{e-}27 \text{ kg})(2.2\text{e-}10 \text{ m})^2 = 4.1\text{E-}46 \text{ kg m}^2$$

Convert bond length to meters for mks units

Rotational Spectroscopy:

What are the first 4 rotational energy levels of LiF?

$$B_{\text{LiF}} = \frac{\hbar^2}{2I} = 1.36 \text{E} - 23$$

$$J = 0$$

$$E_0 = 0$$

For $J = 1$

$$E_1 = 1(1+1)B_{\text{LiF}} = 2.72\text{E}-23 \text{ J}$$

For $J = 2$

$$E_1 = 2(2+1)B_{\text{LiF}} = 8.15\text{E}-23 \text{ J}$$

For $J = 3$

$$E_1 = 3(3+1)B_{\text{LiF}} = 1.63\text{e}-22 \text{ J}$$

For $J = 4$

$$E_1 = 4(4+1)B_{\text{LiF}} = 20B$$

$$E_J = J(J + 1)B_{\text{LiF}}$$

$$J=0,1,2,3\dots$$

$$\lambda = hc/E$$

$$= 7.4 \text{ millimeters}$$

$$= 2.5 \text{ millimeters}$$

$$= 1.2 \text{ millimeters}$$

Vibrational Spectroscopy:

$$H_{\text{vib}} \Psi = E_{\text{vib}} \Psi$$

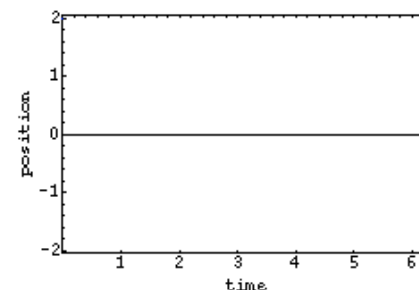
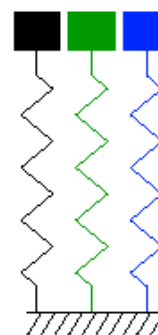
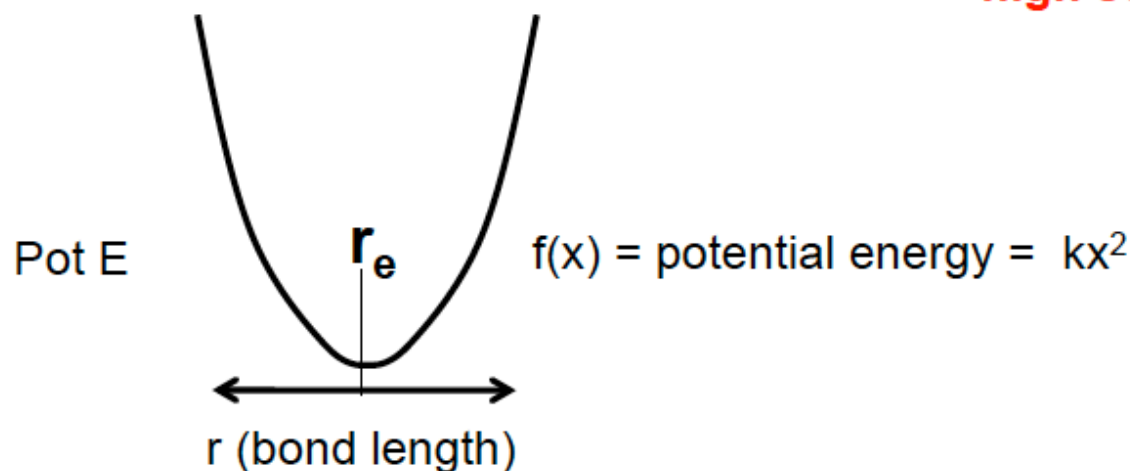
Kinetic E + Potential E

$$-\frac{\hbar^2}{2\mu} \frac{d^2\Psi}{dx^2} + \frac{1}{2} kx^2 \Psi = E\Psi$$



The molecule is modeled as two atoms connected together by a spring

Potential energy term from Hooke's Law (remember high school physics)



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modified by D. Russell, 1997

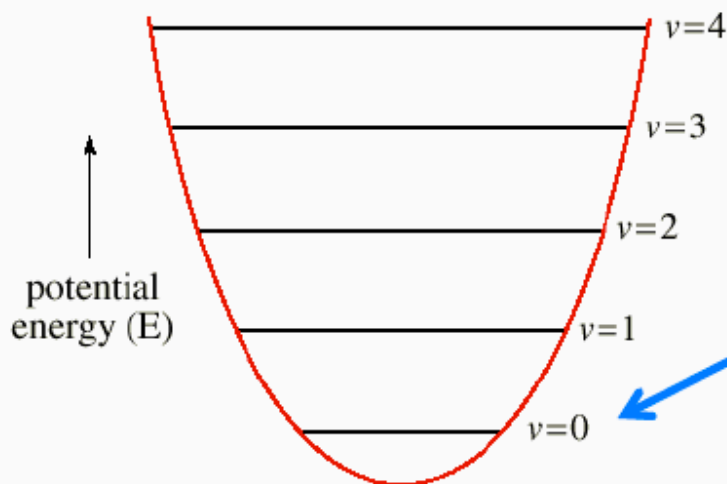
Vibrational Energy Levels:

$$E(\nu_e \text{ or } \omega_e) = h\nu_e(\nu + 1/2) \quad \nu = 0, 1, 2, 3, \dots$$

The vibrational frequency, or energy of vibration, is:

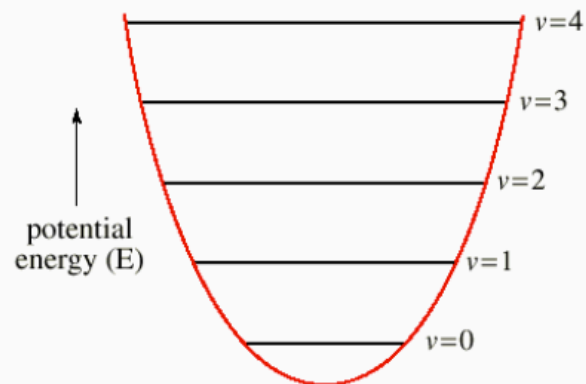
$$\nu_e = 1/2\pi (k/\mu)^{1/2}$$

k = bond force constant (spring constant from Hooke's Law)
 μ = reduced mass



Note that $\nu=0$ is NOT
at the bottom of the
potential energy well

(Zero Point Energy, or ZPE)



The allowed energies are:

$$E_v = h \nu_e (v + 1/2)$$

ν_e — vibration frequency
 v — vibrational quantum number

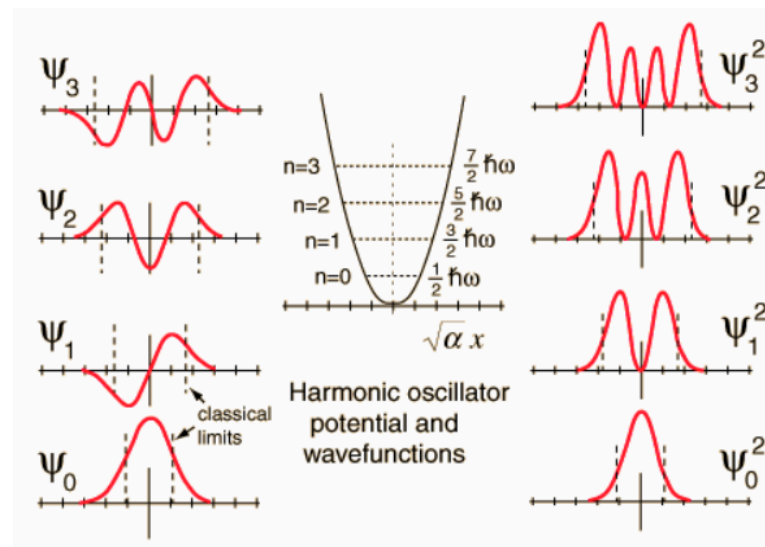
$$v = 1, 2, 3$$

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

k — bond force constant / N m^{-1}

μ — reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$



Selection rule?

$$\Delta v = \pm 1$$

What are units of k ?

Equating both sides of the equation,

$$\text{s}^{-1} = (\text{k/kg})^{1/2}$$

So

$$\text{s}^{-2} = \text{k/kg} \text{ and } \text{kg s}^{-2} = \text{k} = \text{Newton m}^{-1}$$

Because the spring constant has units of (Force/unit length), we often call it a **force constant**.

Vibrational Spectroscopy, Some Numerical Examples:

$$\nu_e = (1/2\pi)(k/\mu)^{1/2}$$

Problem:

Based on the above equation, and the fact that a C-H has a characteristic resonance wavelength of vibration of $\lambda = 3$ micrometers ($= 3.45 \times 10^{-6}$ meters), estimate the resonance frequencies of C-O, O-H, N-H, and C-C single bonds.

$$\text{Since } c/\lambda = \nu \quad \frac{1}{\lambda} \propto \left(\frac{k}{\mu} \right)^{1/2}$$

Since all molecules are single bonds, let's assume that

$$k_{\text{C-O}} \approx k_{\text{O-H}} \approx k_{\text{N-H}} \approx k_{\text{C-C}}$$

$$\mu_{\text{CH}} = \frac{1 \times 12}{1+12} = 0.923$$

And so

$$\boxed{\frac{1}{\lambda} \propto \left(\frac{1}{\mu} \right)^{1/2}}$$

Vibrational Spectroscopy, Some Numerical Examples:

$$\nu_e = (1/2\pi)(k/\mu)^{1/2}$$

Problem:

Based on the above equation, and the fact that a C-H has a characteristic resonance wavelength of vibration of $\lambda = 3$ micrometers ($= 3.45 \times 10^{-6}$ meters), estimate the resonance frequencies of C-O, O-H, N-H, and C-C single bonds.

Since $c/\lambda = \nu$ $\frac{1}{\lambda} \propto \left(\frac{k}{\mu}\right)^{1/2}$

Since all molecules are single bonds, let's assume that the force constants are the same, thus

$$\frac{1}{\lambda} \propto \left(\frac{1}{\mu}\right)^{1/2}$$

$$\mu_{\text{CH}} = \frac{1 \times 12}{1+12} = 0.923$$

$$\mu_{\text{OH}} = \frac{1 \times 16}{1+16} = 0.94$$

$$\mu_{\text{NH}} = \frac{1 \times 14}{1+14} = 0.94$$

All vibrate at about the same frequencies

$$\mu_{\text{CC}} = \frac{12 \times 12}{12+12} = 6$$

$$\mu_{\text{CO}} = \frac{12 \times 16}{12+16} = 6.86$$

Vibrational Spectroscopy, Some Numerical Examples:

$$\nu_e = (1/2\pi)(k/\mu)^{1/2}$$

Problem:

Based on the above equation, and the fact that a C-H has a characteristic resonance wavelength of vibration of $\lambda = 3$ micrometers ($= 3.45 \times 10^{-6}$ meters), estimate the resonance frequencies of C-O, O-H, N-H, and C-C single bonds.

$$\frac{\frac{1}{\lambda_{CH}} \propto \left(\frac{1}{\mu_{CH}}\right)^{1/2}}{\frac{1}{\lambda_{CC}} \propto \left(\frac{1}{\mu_{CC}}\right)^{1/2}} \text{ or } \frac{\lambda_{CH}}{\lambda_{CC}} \approx \left(\frac{\mu_{CH}}{\mu_{CC}}\right)^{1/2}$$

$$(0.92/\mathbf{6})^{0.5} = \mathbf{0.39}$$

$$3.45 \times 10^{-6} / \mathbf{0.39} = 9.1 \times 10^{-6} \text{ m} = \lambda_{CC} \text{ (} \approx 1100 \text{ cm}^{-1} \text{)}$$

$$\text{Real Answer: Vib } E_{C-C} = 700\text{-}1250 \text{ cm}^{-1}$$

$$\mu_{CH} = \frac{1 \times 12}{1+12} = 0.923$$

$$\mu_{OH} = \frac{1 \times 16}{1+16} = 0.94$$

$$\mu_{NH} = \frac{1 \times 14}{1+14} = 0.94$$

$$\mu_{CC} = \frac{\mathbf{12} \times \mathbf{12}}{\mathbf{12} + \mathbf{12}} = \mathbf{6}$$

Vibrational Spectroscopy, Some Numerical Examples:

$$\nu_e = (1/2\pi)(k/\mu)^{1/2}$$

Problem:

Based on the above equation, and the fact that a C-H has a characteristic resonance wavelength of vibration of $\lambda = 3$ micrometers ($= 3.45 \times 10^{-6}$ meters), estimate the resonance frequencies of C=O vibrations.

$$\text{Since } c/\lambda = \nu \quad \frac{1}{\lambda} \propto \left(\frac{k}{\mu} \right)^{1/2}$$

From Table 12.3, p. 511, OGC (6th edition), the average bond enthalpies are:

C-H **413** kJ mol⁻¹

C=O **728** kJ mol⁻¹

$$728/413 = 1.76$$

$$\text{Assume } k_{\text{C=O}} = 1.76 \times k_{\text{C-H}}$$

Vibrational Spectroscopy, Some Numerical Examples:

Problem: $\nu_e = (1/2\pi)(k/\mu)^{1/2}$

Based on the above equation, and the fact that a C-H has a characteristic resonance wavelength of vibration of $\lambda = 3$ micrometers ($= 3.45 \times 10^{-6}$ meters), estimate the resonance frequencies of C=O vibrations.

Since $c/\lambda = \nu$ $\frac{1}{\lambda} \propto \left(\frac{k}{\mu}\right)^{1/2}$

$$\mu_{CH} = \frac{1 \times 12}{1+12} = 0.923$$

$$\mu_{CO} = \frac{12 \times 16}{12+16} = 6.86$$

$$\left(\frac{1}{\lambda_{C-H}} \right) \propto \left(\frac{k_{C-H}}{\mu_{C-H}} \right)^{1/2} = \frac{\lambda_{C=O}}{3.38 \times 10^{-6} \text{ m}} \propto \left(\frac{k_{C-H}}{\mu_{C=O}} \right)^{1/2} = 1.9$$

$$\lambda_{C=O} = 6.41 \times 10^{-6} \text{ m} = 1560 \text{ cm}^{-1}$$

Real Answer $\sim 1640\text{--}1780 \text{ cm}^{-1}$

Vibrational Spectroscopy, Polyatomics:

How many vibrational modes will a molecule have?

The answer lies in the numbers of degrees of freedom that are necessary to describe everything about a molecule

Each atom has x,y,z

So **3N** degrees of freedom for **N** atoms

3 degrees of freedom → describe translation of molecule through space

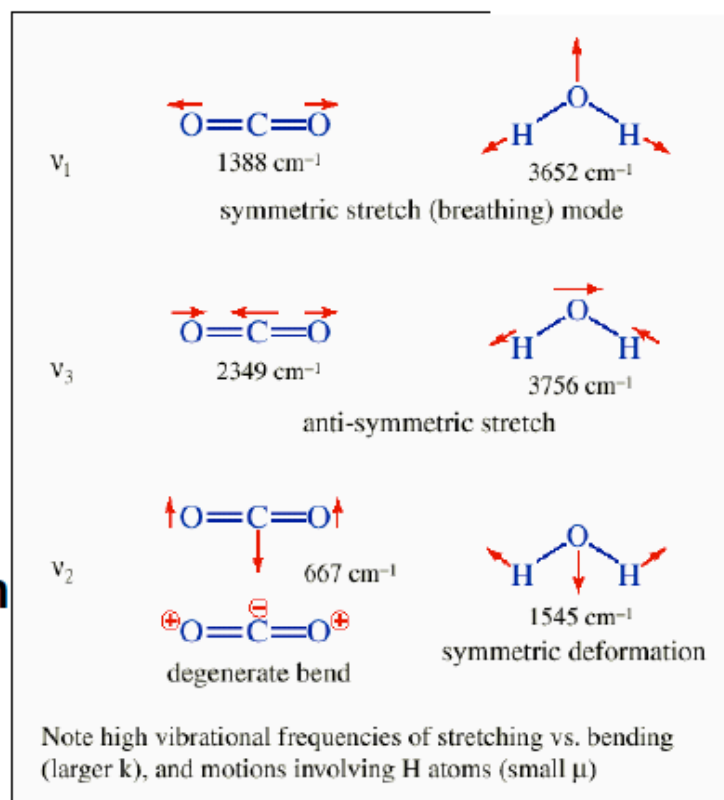
3 (or **2** for linear molecules) describe rotation of molecule through space

Everything else describes vibration

3N – **3** – **3** (or **2** for linear molecules) =
3N-6 (or 5) degrees of freedom

Linear molecule
vibrational modes

Nonlinear
molecule
vibrational
modes



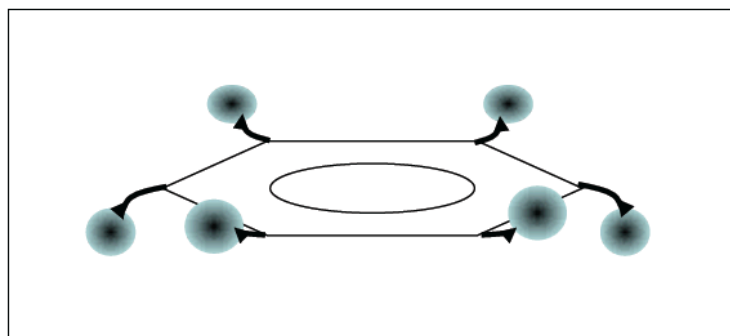
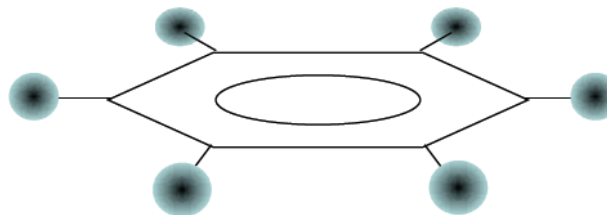
Vibrational Spectroscopy, Polyatomics:



Asymmetric stretch



Asymmetric stretch



Remember, the molecular motion must alter the dipole moment in order for the absorption or emission to be allowed. These modes do just that, for OCS, OCO and C₆H₆.

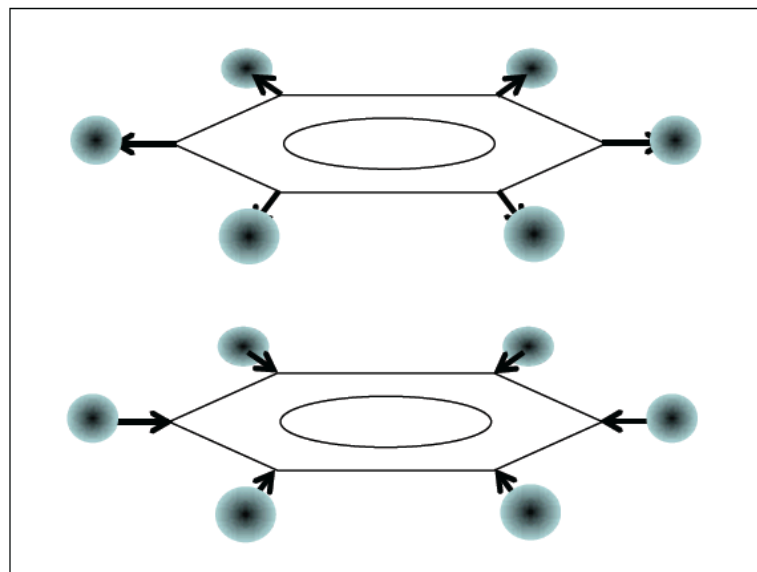
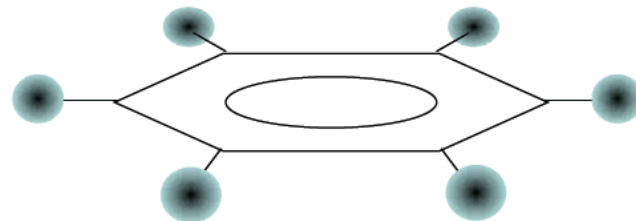
Vibrational Spectroscopy, Polyatomics:



Symmetric stretch



Symmetric stretch

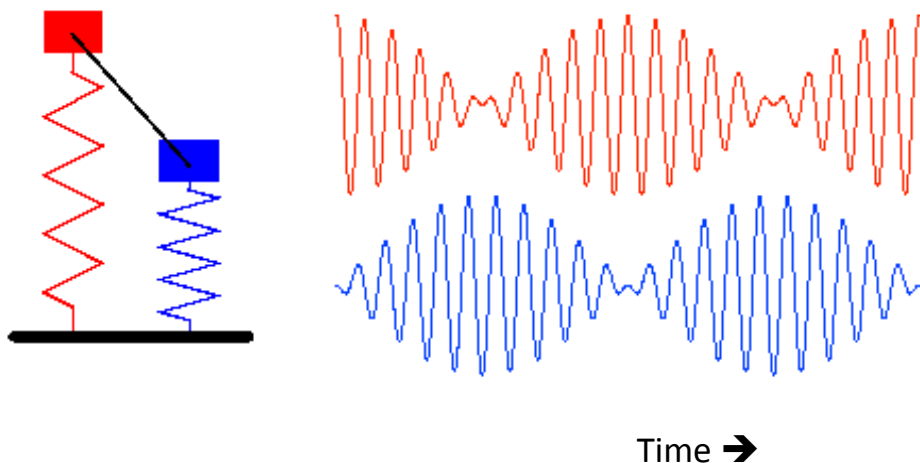


Remember, the molecular motion must alter the dipole moment in order for the absorption or emission to be allowed. These modes shown for OCO and C₆H₆ are *not* seen in the IR. Why?

Vibrational Spectroscopy, Functional Groups:

Clearly, the previous examples show that IR spectra depend on the force constants and reduced masses involved. How, then, can such spectra be used to help constrain the functional groups that are present in a wide range of molecules?

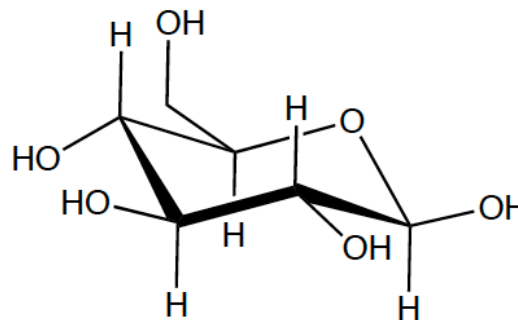
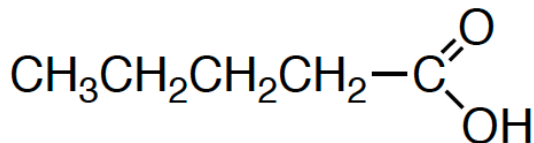
One good way to start thinking about things is to look at coupled classical harmonic oscillators:



Notice how the energy is exchanged between the oscillators (no damping).

Vibrational Spectroscopy, Functional Groups:

Clearly, the previous examples show that IR spectra depend on the force constants and reduced masses involved. How, then, can such spectra be used to help constrain the functional groups that are present in a wide range of molecules?

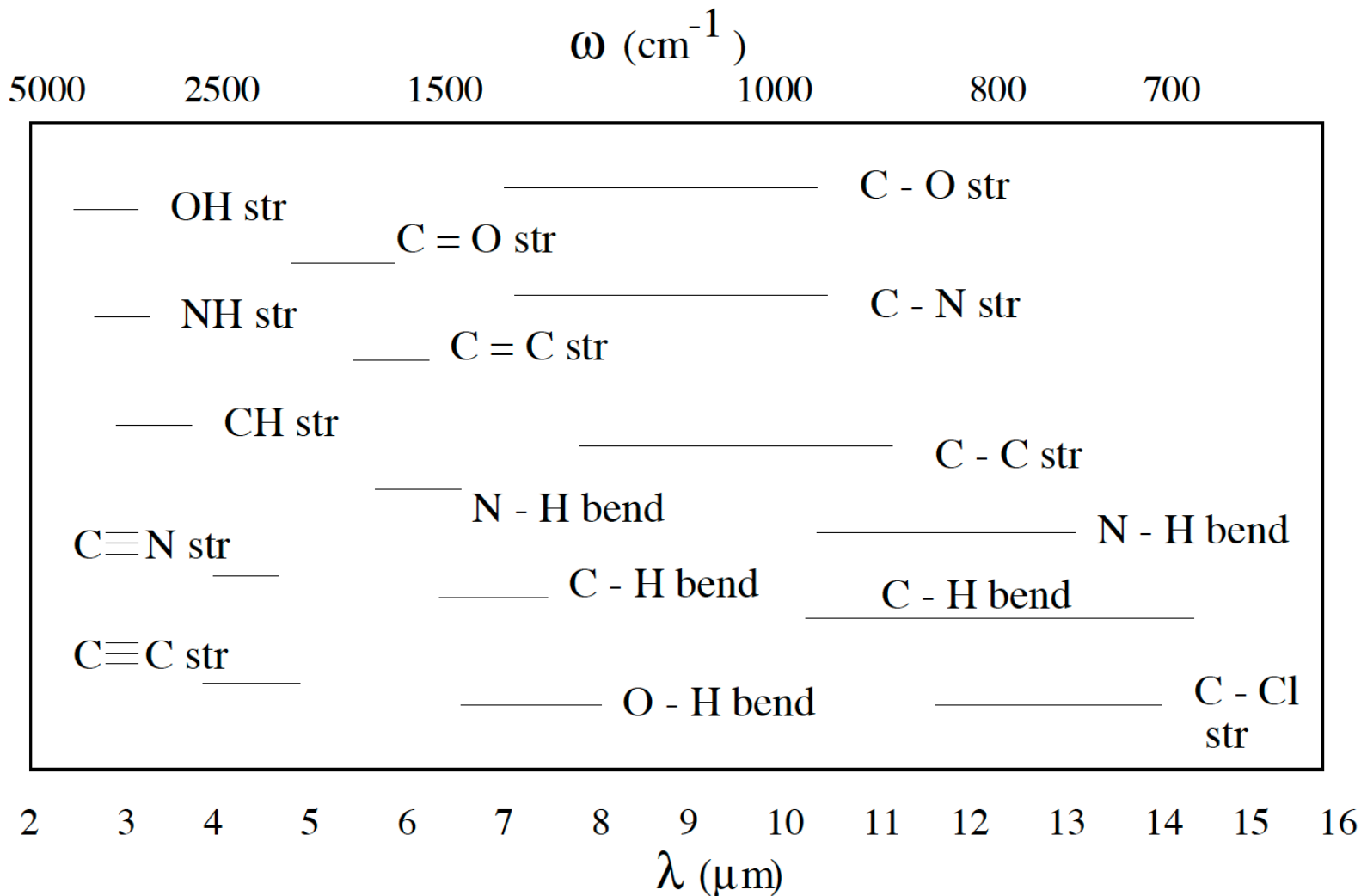


Two key insights from coupled classical harmonic oscillators:

- If the resonant frequency of a vibration is quite distinct from the remaining frequencies, it remains close to the pseudo-diatomic value (reduced mass & hydrides).
- If the force constants for a bond/group are distinct from those around it, the frequency remains ~close to the pseudo-diatomic value (most important for carbonyl groups).

Vibrational Spectroscopy, Functional Groups:

How best to read/decipher IR spectra?

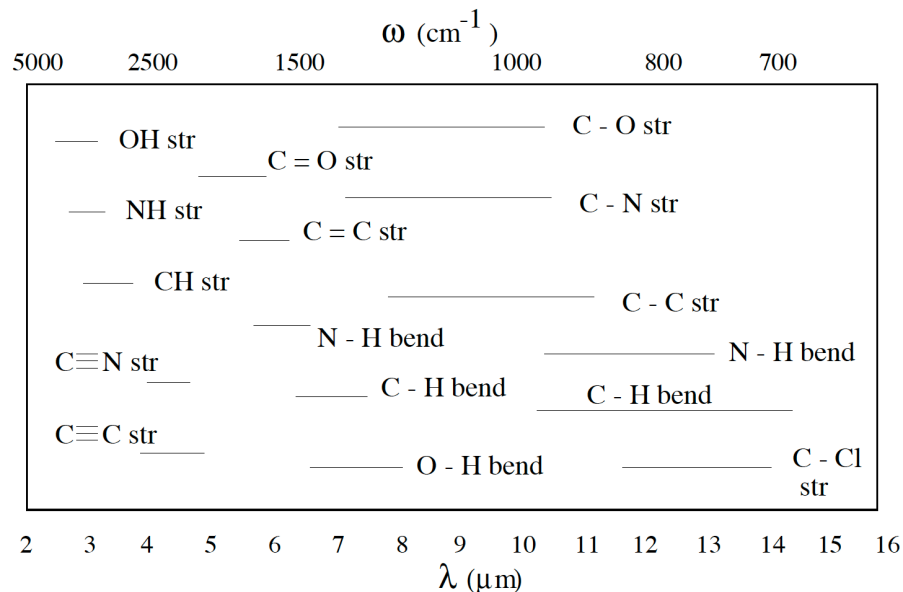


Extensive databases are now on-line, see for example:

<http://webbook.nist.gov/chemistry/name-ser.html>

Vibrational Spectroscopy, Functional Groups:

How best to read/decipher IR spectra?

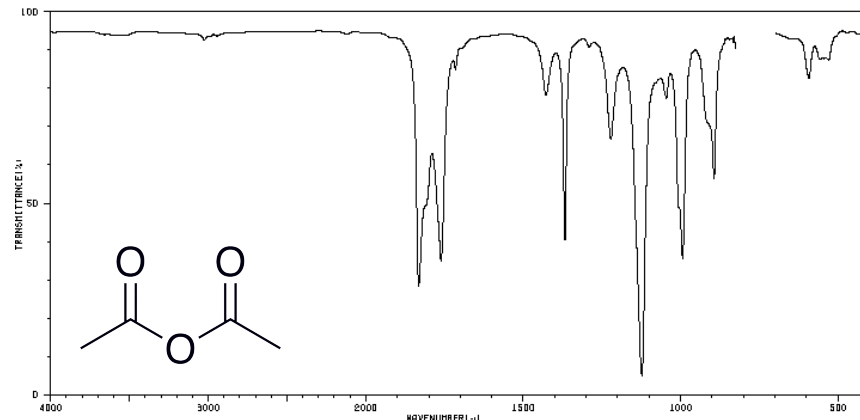
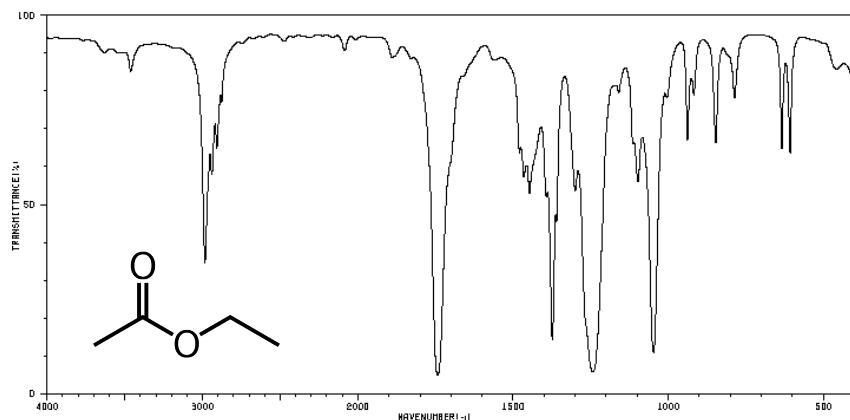


- Wavelength increases to right, hydride stretches to far left (reduced mass more important than k). Shape tells you about hydrogen bonding.

- Other important group typically involves carbonyls, frequency fairly insensitive to $R-(C=O)-R'$.

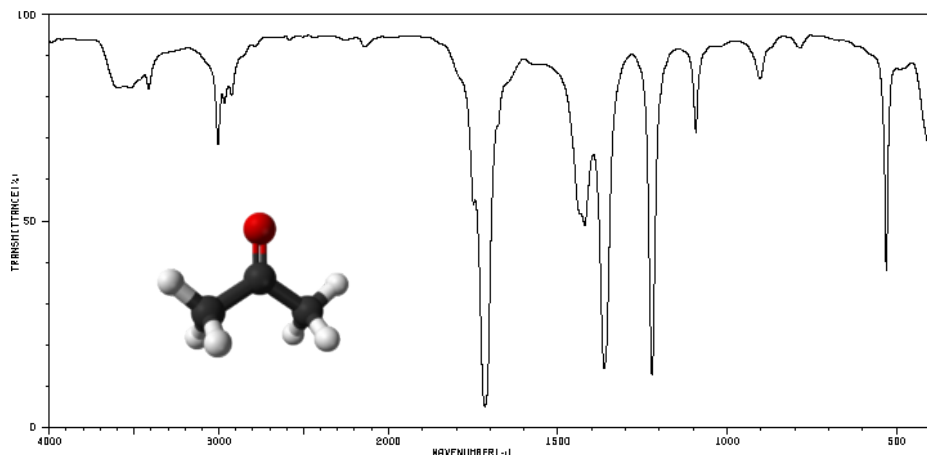
- Mid-IR very sensitive to structure (the springs are nicely resonant), but hard to assign by eye. This is called “the fingerprint region.”

Extensive databases are now on-line, see for example:
<http://webbook.nist.gov/chemistry/name-ser.html>

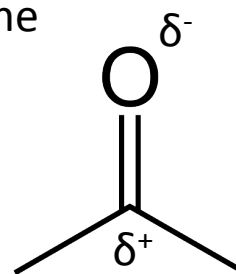


Vibrational Spectroscopy, Functional Groups:

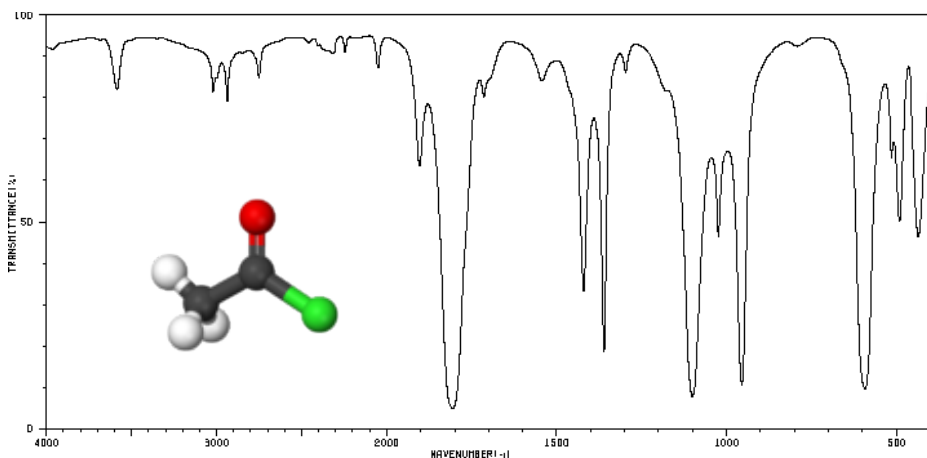
Let's think a bit more about the carbonyl group & bonding. I.



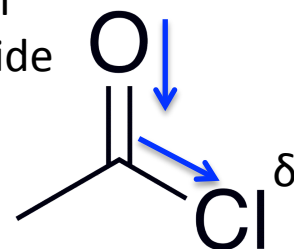
Acetone



Typical ketone carbonyl stretching frequencies are $\sim 1715 \text{ cm}^{-1}$.



Acetyl Chloride



Electron withdrawing groups increase δ^+ character of carbonyl carbon atom.

Such effects typically *increase* the carbonyl stretching frequency:

1810
Anhydride (I)

1800
Acid Chloride

1760
Anhydride (II)

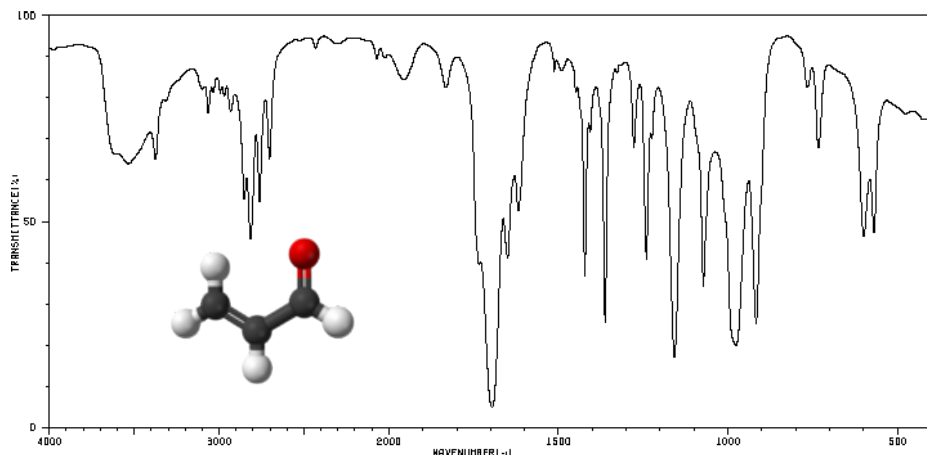
1735
Ester

1725
Aldehyde

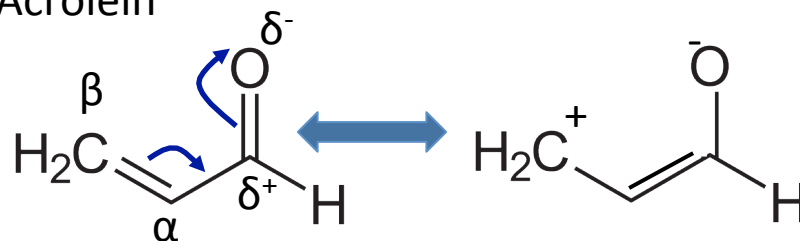
1715 cm^{-1}
Ketone

Vibrational Spectroscopy, Functional Groups:

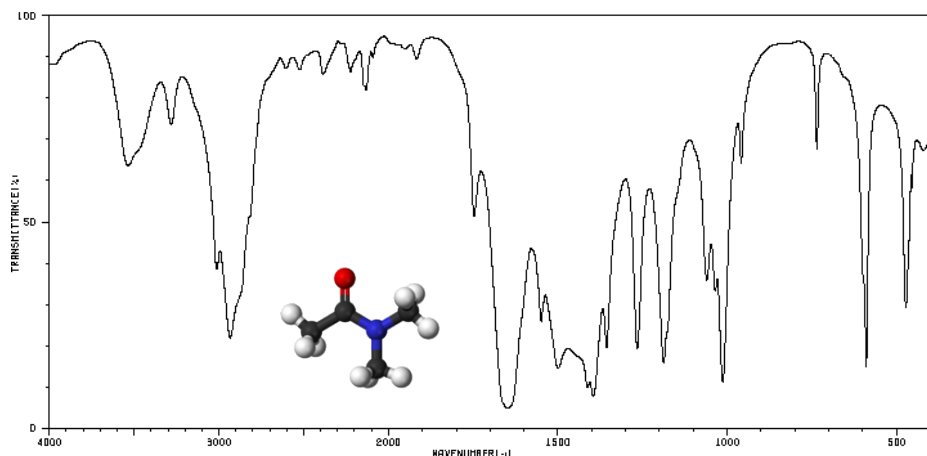
Let's think a bit more about the carbonyl group & bonding. II.



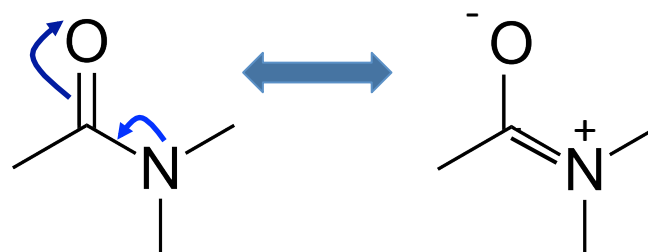
Acrolein



α,β Conjugation weakens C=O bond



N,N-dimethylacetamide



Ground state resonance contributions to the amide bond weaken the C=O bond

Both effects lead to a *lowering* of the carbonyl functional group vibrational frequency.

Vibrational Spectroscopy, Functional Groups:

A Simplified Correlation Chart for IR Spectra

Group	Vibration	Frequency (cm^{-1})	Wavelength (μm)	Intensity
C–H	Alkanes (stretch)	3000-2850	3.33-3.51	s
	-CH ₃ (bend)	1450, 1375	6.90, 7.27	m
	-CH ₂ - (bend)	1465	6.83	m
	Alkenes (stretch)	3100-3000	3.23-3.33	m
	(out-of-plane bend)	1000-650	10.0-15.3	s
	Aromatics (stretch)	3150-3050	3.17-3.28	s
	(out-of-plane bend)	900-690	11.1-14.5	s
	Alkynes (stretch)	ca. 3300	ca. 3.03	s
	Aldehydes	2900-2800	3.45-3.57	w
		2800-2700	3.57-3.70	w
C–C	Alkanes	1400-700	~7-14	m-w
C=C	Alkene	1680-1600	5.96-6.25	m-w
	Aromatic	1600, 1475	6.25, 6.78	m-w
C≡C	Alkyne	2250-2100	4.44-4.76	m-w
C=O	Aldehyde	1740-1720	5.75-5.81	s
C=O	Ketone	1725-1705	5.80-5.87	s
C=O	Carboxylic acid	1725-1700	5.80-5.88	s
C=O	Ester	1750-1730	5.71-5.78	s
C=O	Amide	1670-1640	6.00-6.10	s
C=O	Anhydride	1810, 1760	5.52, 5.68	s
C=O	Acid Chloride	1800	5.56	s

A Simplified Correlation Chart for IR Spectra

Group	Vibration	Frequency (cm^{-1})	Wavelength (μm)	Intensity
C-O	Alcohols, ethers, esters	1300-1000	7.69-10.0	s
	Carboxylic acids, anhydrides			
O-H	Alcohols, Phenols			
	Free	3650-3600	2.74-2.78	m
	H-Bonded	3500-3200	2.86-3.13	m
	Carboxylic acids	3400-2400	2.94-4.17	m
N-H	Prim. & Sec. Amines, amides (stretch)	3500-3100	2.86-3.23	m
	(bend)	1640-1550	6.10-6.45	m-s
C-N	Amines	1350-1000	7.4-10.0	m-s
C=N	Imines & Oximes	1690-1640	5.92-6.10	w-s
C \equiv N	Nitriles	2260-2240	4.42-4.46	m
X=C=Y	Allenes, Ketenes, Isocyanates	2270-1950	4.40-5.13	m-s
	Isothiocyanates			
N=O	Nitro (R-NO_2)	1550, 1350	6.45, 7.40	s
S-H	Mercaptans	2550	3.92	w
S=O	Sufoxides	1050	9.52	s
	Sulfones, Sulfonyl Chlorides	1375-1300 &	7.27-7.69	s
	Sulfates, Sulfonamides	1200-1140	8.33-8.77	s
C-X	Fluoride	1400-1000	7.14-10.0	s
	Chloride	800-600	12.5-16.7	s
	Bromide, Iodide	<667	>15.0	s

Vibrational Spectroscopy, Functional Groups:

In trying to understand the spectrum of some unknown (or known) compound, it is best to first try and determine whether certain major functional groups are present or not. Peaks from C=O, O-H, N-H, C-O, C=C, C \equiv C, C \equiv N, and NO₂ groups are often the most conspicuous and provide immediate structural information when they are present. It can be difficult to extract detailed information from the C-H stretching absorptions near 3000 cm⁻¹ since almost all compounds have these features. Here's a handy check list:

1. Is a carbonyl group present?

The C=O group gives rise to a strong absorption feature in the 1820-1660 cm⁻¹ region (λ =5.5-6.1 μ m). This peak is often the strongest in the spectrum and is of medium width. You can't miss it!

2. If C=O is present, check for the following types (if absent, go to 3.):

ACIDS. Is OH also present? This will give rise to broad absorption near 3400-2400 cm⁻¹ (which usually overlaps with the C-H stretching bands).

AMIDES. Is NH also present? Here you'll find medium absorption near 3500 cm⁻¹ (2.85 μ m), which is sometimes split into a doublet.

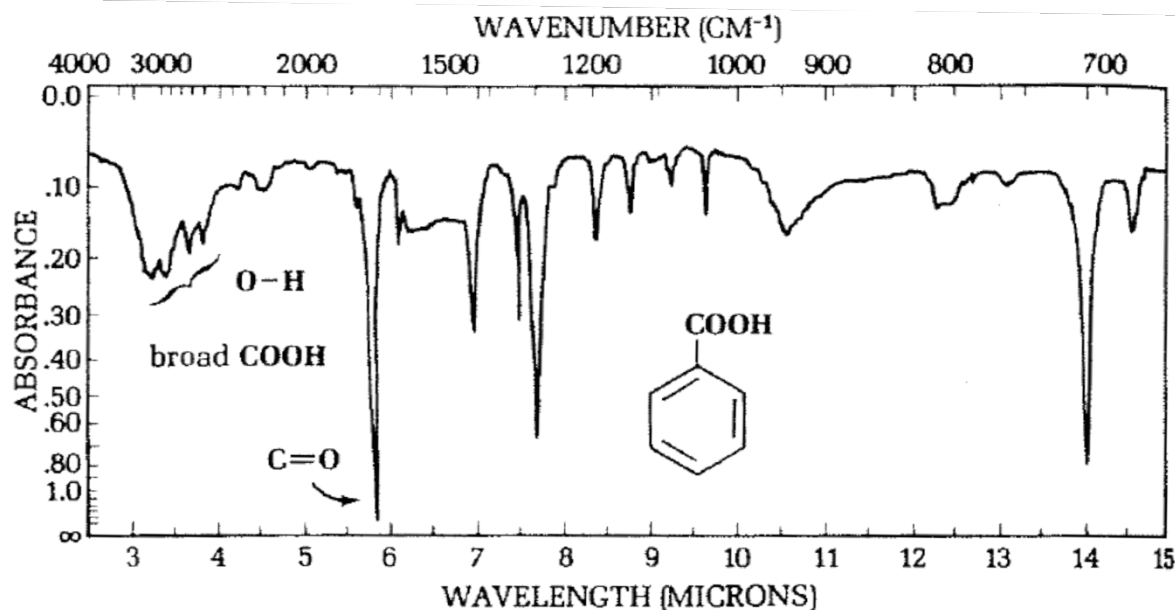
ESTERS. Is C-O also present? These will be manifest as strong absorptions near 1300-1000 cm⁻¹.

ANHYDRIDES. These have two carbonyl stretches from 1900-1700 cm⁻¹ and a C-O feature near 1300-1000 cm⁻¹ (7.7-10.0 μ m).

ALDEHYDES. Is the aldehyde C-H stretch present? These are the longest wavelength C-H stretching features near 2850 and 2750 cm⁻¹.

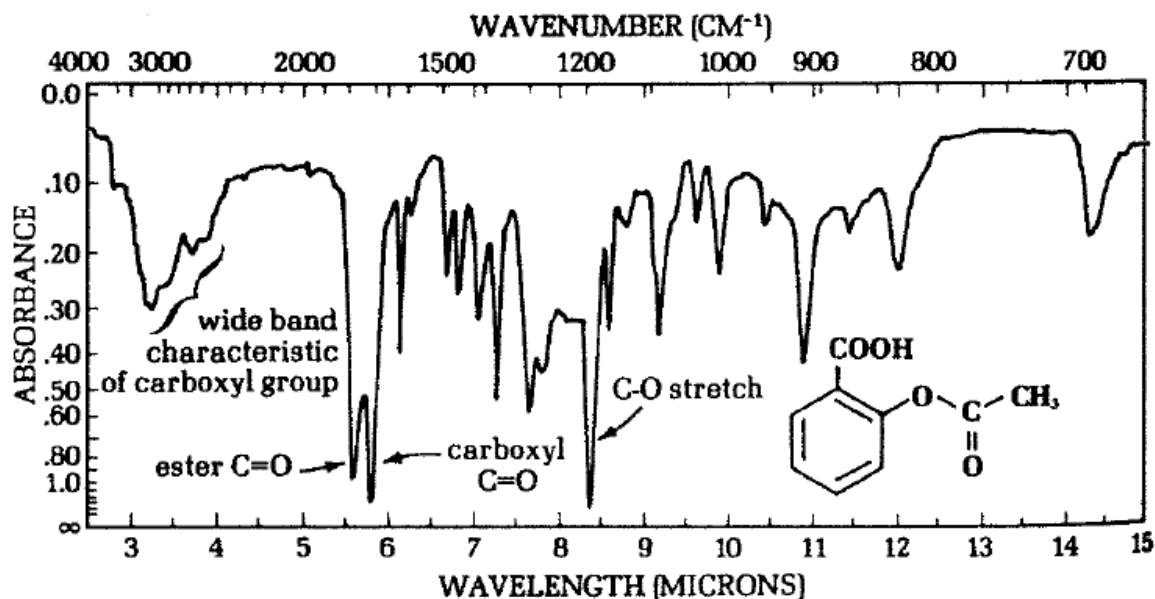
KETONES. The above five choices have been eliminated.

Vibrational Spectroscopy, Functional Groups:



Benzoic acid – Note the strong C=O stretch and the broad O-H vibrational band characteristic of carboxylic acids. The mode near 14 microns involves bending of the molecule.

Here, for acetylsalicylic acid (aspirin), there are two carbonyl groups and the strong C-O stretch from the ester now appears. Note the increased complexity in the fingerprint region.



Vibrational Spectroscopy, Functional Groups:

3. If C=O is absent, check for:

ALCOHOLS, PHENOLS. Check for O–H, which gives broad absorptions over 3600-3300 cm^{-1} and C–O stretches near 1300-1000 cm^{-1} . Note that the hydrogen bonded broadening is not as great as for carboxylic acids.

AMINES. Look for N–H via medium absorptions near 3500 cm^{-1} , or 2.85 μm .

ETHERS. Check for the presence of C–O near 1300-1000 cm^{-1} , and no O–H.

4. Double bonds and/or aromatic rings.

By itself, a C=C double bond produces a weak absorption feature near 1650-1450 cm^{-1} . A series of absorptions in the 6-7 μm range often imply an aromatic ring.

5. Triple Bonds.

C \equiv N is a sharp, medium absorption near 2250 cm^{-1} , C \equiv C is a weak but sharp absorption near 2150 cm^{-1} .

6. Nitro Groups.

R-NO₂ is characterized by two strong features at 1600-1500 & 1390-1300 cm^{-1} .

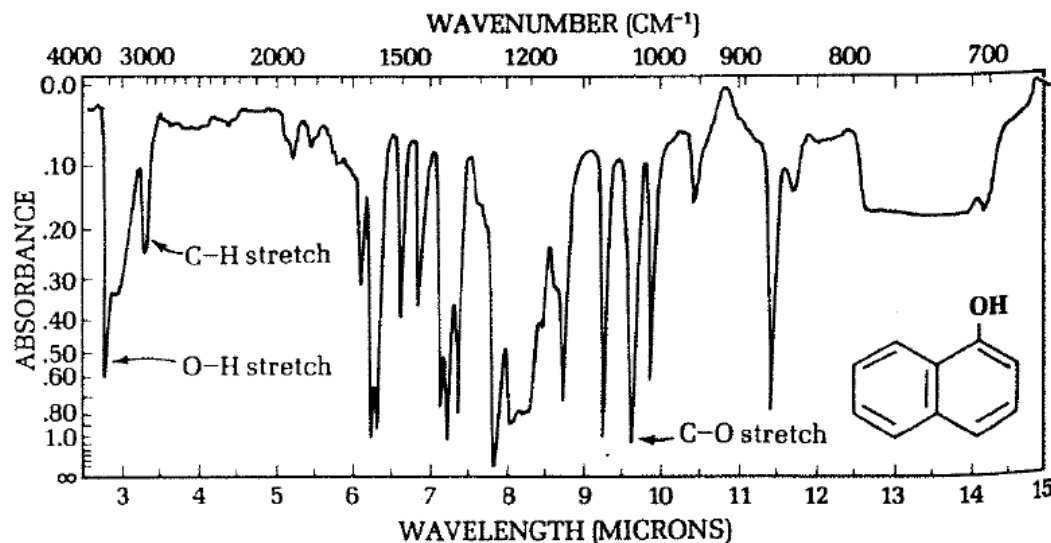
7. Halogen Atoms.

The presence of F, Cl, and Br is manifest as *strong* features longward of 8-10 μm ,

8. Hydrocarbons (non-aromatic).

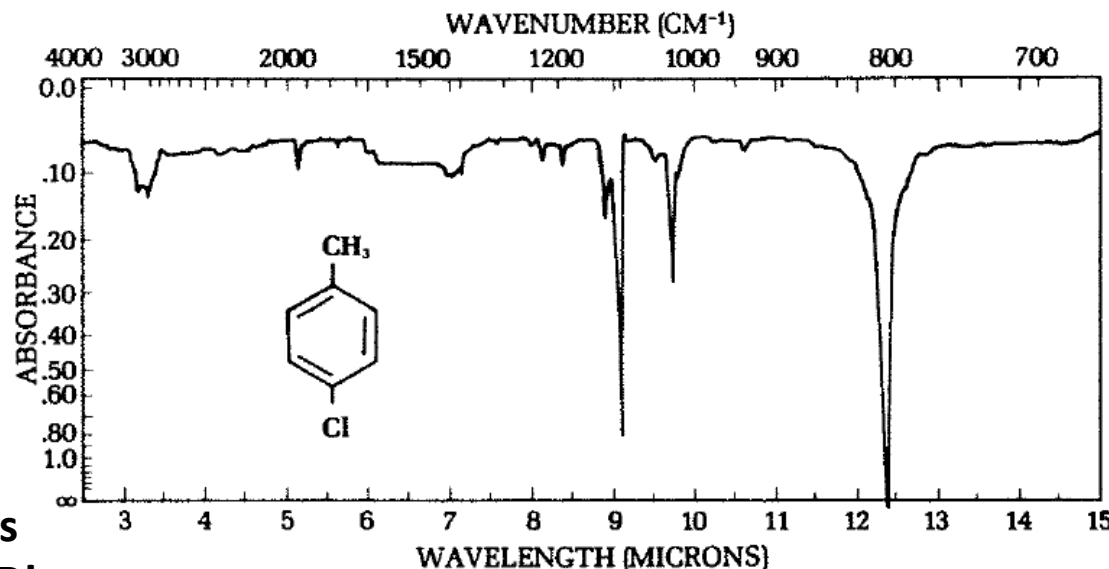
If none of the above features are found, you're probably dealing with a hydrocarbon.

Vibrational Spectroscopy, Functional Groups:



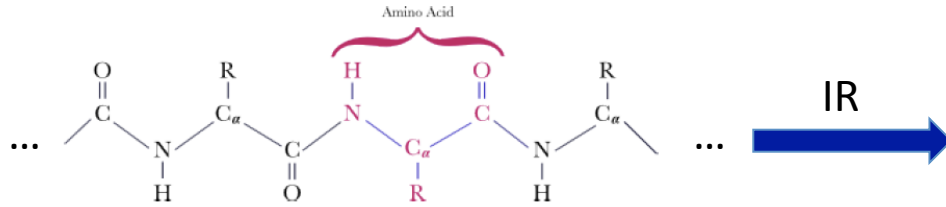
α Naphthol – Here the O-H vibrational stretching mode is still broadened by hydrogen bonding, but not to the extent characteristic of carboxylic acids.

Para chloro-toluene – Not a great deal going on here, except for the *intense* the C-Cl stretch near 12.5 μm (true in general, important aspect of CFC and HCFC use).



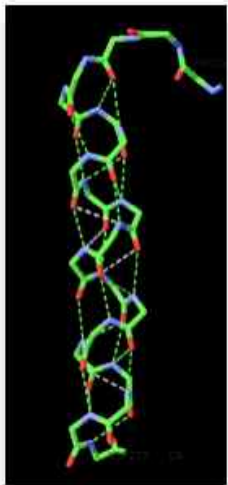
Clearly, more data are better. Let's come back to structures after NMR!

Vibrational Spectroscopy, Polymers/Proteins:

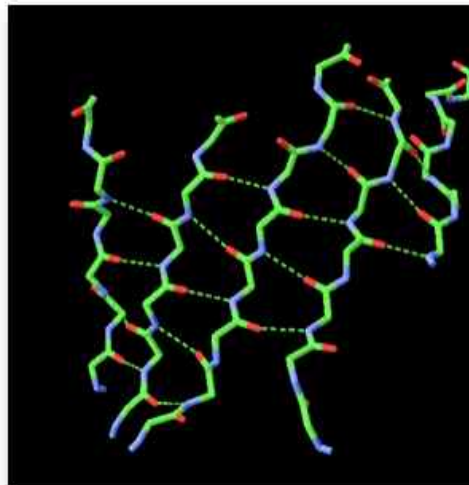


Many copies of functional groups, can lead to complex, broadened spectral features. For proteins, the amino acid order is called the primary structure (more later).

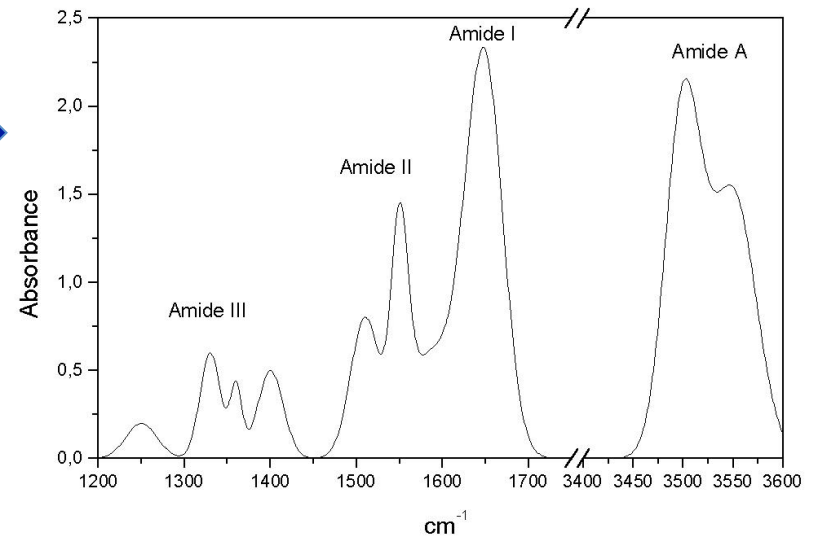
The local environment can be critical, esp. if hydrogen bonding is involved. For proteins, two important secondary structure motifs (stay tuned!) are:



α Helix



β Sheet



Can correlate amide (C=O) spectral shifts with secondary structure, in optimal cases.

