Homework Week 9:
Exercises 20-22

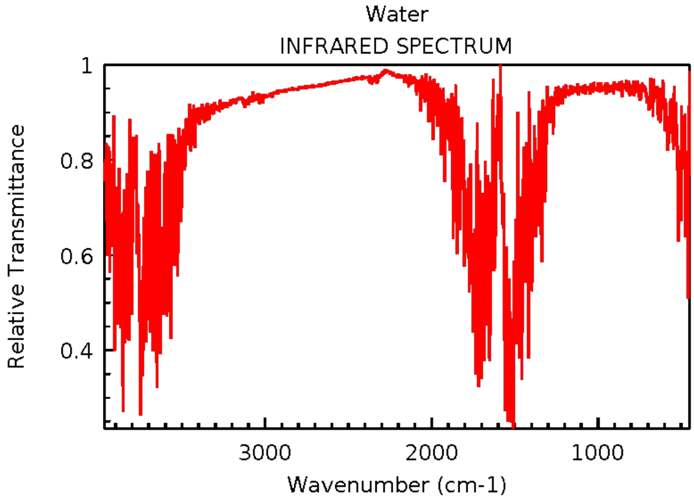
Material to study for next week:
Lecture Notes
Atkins 19.15b)

List of constants:

Boltzmann constant: k = 1.38 x 10^{-23} m^2 kg s^{-2} K^{-1}
Plancks' constant: *h* = 6.626068 × 10^{-34} m^2 kg s^{-1}

20.

The vibrational spectra of gas phase and liquid water are given below. The IR spectrum reports on the vibrational and rotational energy states of water. The energies that correspond to vibrational or rotational states can be seen in the spectrum as adsorption bands. Rotational modes have small energies (and appear as narrow spikes), while vibrational states have higher energies (and appear as broader bands). The Y-axis displays the transmitted intensity of light relative to the incoming intensity, and the X-axis displays the photon energy in wavenumbers at which this happens. Wavenumber is a quantity that is equivalent to wavelength and has the unit of [1/cm]. The wavenumber unit can be related to the energy by using $E = h\nu$, with h Plancks' constant and ν the frequency of the light [s^{-1}]. The speed of light, c = 3 x 10^8 [m/s].



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Figure 2: Gas phase IR spectrum of water

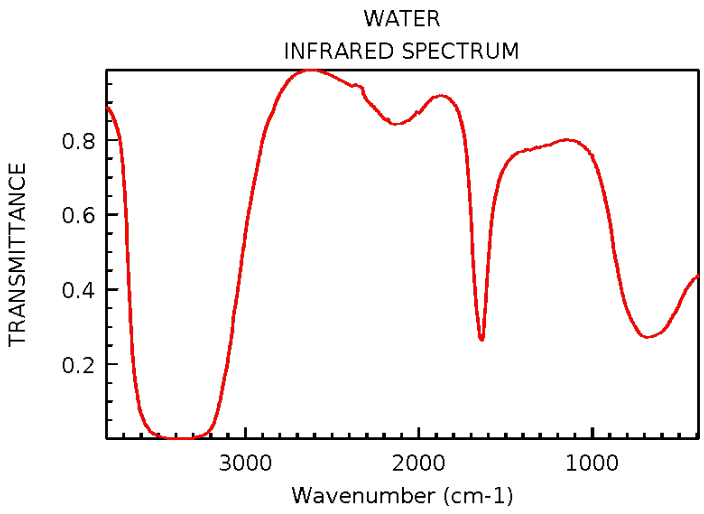


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Figure 3: Liquid phase IR spectrum of water

a. Show by unit conversion that

(1) An equivalent unit for Plancks' constant is [J·s],

(2) A wavenumber can be converted to frequency, and energy.

(3) 1 kT is equivalent to 219 cm^{-1}

Fig. 2 displays the gas phase IR spectrum of water vapor. Fig. 3 displays the liquid phase IR spectrum of water. The band at ~ 3400 cm^{-1} (liquid) and ~3750 cm^{-1} (vapor) represent the energies of the H-O-H vibrational stretch modes and the rotational modes. Fig. 2 consists of a series of sharp spikes, while Fig. 3 consists of a broad band.

b. Draw the structure of water molecules in the gas and liquid phase, indicating the most relevant interaction. What is the major difference between the water molecules in the gas and liquid phase?

c. How does that difference appear in the IR spectrum? Can you explain why Fig. 2 has sharp spikes and Fig. 3 does not?

d. For the liquid water spectrum in fig. 3, what is the approximate width in cm^{-1} of the band at ~3400 cm^{-1} in the liquid phase? How much would the energy difference be in J? How many kT does this correspond to?

e. The average energy per H bond in liquid water at room temperature is 22 kJ/mol. Use the IR spectrum to predict what the highest and lowest H bond energy will be. Can we use the liquid IR spectrum to learn something about the water structure in its liquid phase?

21.

We want to examine the selection rules for IR and Raman spectroscopy for linear di- and triatomic molecules.

a. What are the selection rules for infrared and Raman spectroscopy in terms of the dipole moment and polarizability? Give expressions and explain what they mean.

b. For a linear molecule such as N_2, consider the symmetric stretch vibration and sketch $\frac{d\mu}{dQ}$ and $\frac{d\alpha}{dQ}$ as a function of Q, the normal coordinate for this vibration. Is the mode Raman/IR active?

c. Same as in b. but then for HCl.

d. Consider the molecule CO_2. Answer the same question as in b. but now for the symmetric stretch vibration, the asymmetric stretch vibration and the bending vibration.

Additional Spectroscopy question:

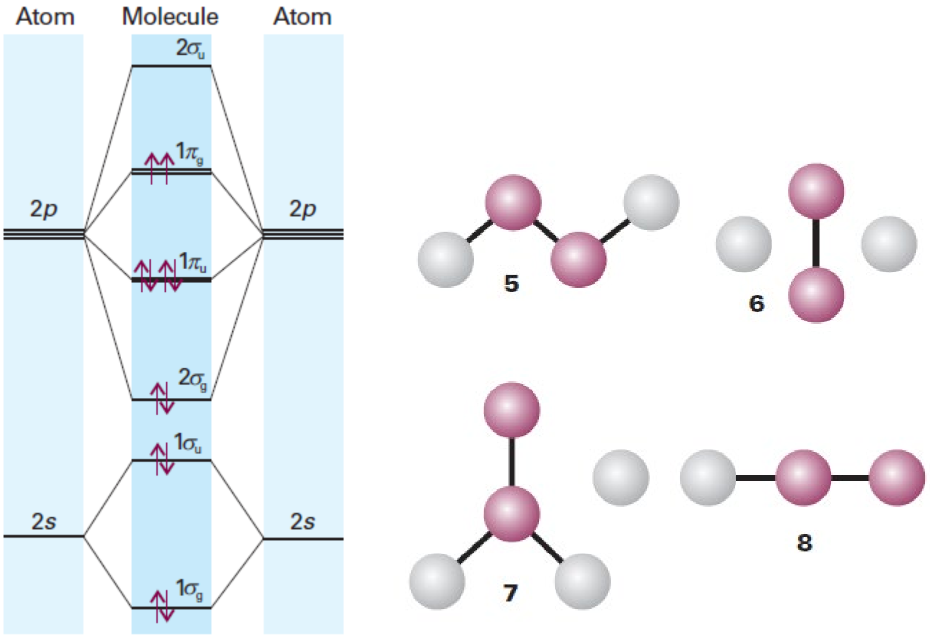

Figure 4: Left: The molecular orbital energy level diagram for O_2. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. Levels below that of the individual atoms are bonding orbitals while energy levels above that of the individual atoms are antibonding orbitals. Arrows pointing up represent spin up electrons, arrows pointing down represent spin down electrons. Each energy level can at most accommodate a pair of electrons. Right: Possible structures for the Fe complex in haemerythrin.

Question I

The protein haemerythrin is responsible for binding and carrying O_2 in some invertebrates. Each protein molecule has two Fe^{2+} ions that are in very close proximity and work together to bind one molecule of O_2. The Fe_2O_2 group of oxygenated haemerythrin is colored and has an electronic absorption band at 500 nm. The resonance Raman spectrum of oxygenated haemerythrin obtained with laser excitation at 500 nm has a band at 844 cm^{-1} that has been attributed to the O-O stretching mode of bound $^{16}O_2$.

a. How many normal modes does O_2 have and what is the vibrational motion of each?

b. Why is resonance Raman spectroscopy and not infrared spectroscopy the method of choice for the study of the binding of O_2 to haemerythrin?

c. Prove that the 844 cm^{-1} band arising from a bound O_2 species may be obtained by conducting experiments on samples of haemerythrin that have been mixed with $^{18}O_2$, instead of $^{16}O_2$. Predict the fundamental vibrational wavenumber of the ^{18}O-^{18}O stretching mode in a sample of haemerythrin that has been treated with $^{18}O_2$.

d. The fundamental vibrational wavenumbers for the O-O stretching modes of O_2, O_2^- (superoxide anion), and O_2^{2-} (peroxide anion) are 1555, 1107, and 878 cm^{-1}, respectively. Explain this trend in terms of the electronic structures of O_2, O_2^- (superoxide anion), and O_2^{2-}. Use the energy level scheme of neutral O_2 given in Fig.4 to explain this change in resonance frequency.

e. Based on the data given above, which of the following species best describes the Fe_2O_2 group of haemerythrin: $Fe_2^{2+}O_2$, $Fe^{2+}Fe^{3+}O_2^-$, or $Fe_2^{3+}O_2^{2-}$? Explain your reasoning.

f. The resonance Raman spectrum of haemerythrin mixed with $^{16}O^{18}O$ has two bands that can be attributed to the O-O stretching mode of bound oxygen. Discuss how this observation may be used to exclude one or more of the four proposed schemes in Fig. 4 (right side) (**5–8**) for binding of O_2 to the Fe_2 site of haemerythrin.