**ATOC 3500/CHEM 3151**

**Problem “Final 1”**

**Formation of O(1D)**

In Problem 11 we saw that it takes 105 kJ of energy to break apart a mole of ozone molecules (i.e. for O3 🡪 O + O2, Ho = 105 kJ mol-1). For a single molecule of ozone, this worked out to be equivalent to a photon with a wavelength of 1140 nm, which is in the infrared. However, throughout the semester we have talked about how ozone does not photolyze in the atmosphere unless the wavelength of light is < 300 nm, which is on the edge of the visible/ultraviolet spectrum. This problem examines where the extra energy goes.

The absorption of light by ozone is explained by quantum mechanics. The ozone molecule can only absorb a photon if the sum of the “electronic spins” of the two fragment species is conserved. Spectroscopists say that the way to visualize this is that the absorption process occurs in a very short time – less than a picosecond (10-12 seconds), and that isn’t long enough for the electron spin to change states. Therefore, if the sum of the electron spins in the ozone molecule prior to absorption is zero (same number of “up” spins as “down” spins), the sum of the electron spins in the fragments following absorption must also be zero.

In the case of ozone photolysis, the two products that are formed are O(1D) (called “O singlet D”) and O2(1) (called “O2 singlet delta”). These two products contain an additional 190 kJ mol-1 and 95 kJ mol-1, respectively, than their 'ground state' counterparts O and O2. That is, it takes 190 kJ mol-1 to raise the energy of a ground-state oxygen atom into the O(1D) electronic state, and it takes 95 kJ mol-1 to raise O2 from the ground state to the O2(1) state. Therefore, in order to calculate the energy that is needed to break the O3 bond, we need to include these energies into the calculation.

1. Add the additional energy for the photolysis fragments O(1D) and O2(1) to the bond strength of ozone (i.e., 105 kJ mol-1), and determine the wavelength of light that is required to dissociate ozone with enough total energy to produce O(1D) and O2(1).
2. Find an absorption spectrum of the ozone. Is this spectrum consistent with the value you calculate in (a)? Why or why not?