States of Oxygen

As far as allotropes go, oxygen as an element is fairly uninteresting, with ozone (O_3, closed-shell and C_{2v} symmetric like SO_2) and O_2 being the stable molecular forms. Most of our attention today will be devoted to the O_2 molecule that is so critically connected with life on Earth.

O_2 has the following valence electron configuration: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$. It is because of the presence of only two electrons in the two π^* orbitals labelled $1\pi_g$ that oxygen is paramagnetic with a triplet (the spin multiplicity "triplet" is given by $2S+1$; here S, the total spin quantum number, is $0.5 + 0.5 = 1$).

There are six possible ways to arrange the two electrons in the two degenerate π^* orbitals. These different ways of arranging the electrons in the open shell are called "microstates". Further, because there are six microstates, we can say that the total degeneracy of the electronic states arising from $(1\pi_g)^2$ configuration must be equal to six. The ground state of O_2 is labeled $^3\Sigma_g^-$, the left superscript 3 indicating that this is a triplet state. It is singly degenerate orbitally and triply degenerate in terms of spin multiplicity; the total degeneracy (three for the ground state) is given by the spin times the orbital degeneracy.

The first excited state of O_2 is labeled $^1\Delta_g$, and this has a spin degeneracy of one and an orbital degeneracy of two for a total degeneracy of two. This state corresponds to spin pairing of the electrons in the same π^* orbital. This is the metastable state referred to by the term "singlet oxygen"; it resides 7882.39 cm^{-1} above the ground state and has a sufficient lifetime to have interesting and important chemistry.

The second excited state of O_2 is labeled $^1\Sigma_g^+$. This state corresponds to having the electrons spin paired with one in each of the two π^* orbitals; there is only one way to do this for a total degeneracy of one. This state resides 13120.9 cm^{-1} above the ground state. Note that in the term symbol for the electronic state the label is derived from the Mulliken symbol for the respective point group. What is the point group for the O_2 molecule? Check the character table for this point group and you will see there the symbols used in describing the electronic states of the O_2 molecule. It is a general feature of open-shell configurations that they give rise to multiple electronic states; we will see this again in studying the properties of coordination complexes that have some number n electrons occupying the five d orbitals.

Liquid and Singlet Oxygen

Liquid oxygen is blue in color and, due to its paramagnetism, is deflected if poured between the poles of a strong permanent magnet. The blue color of liquid O_2 is ascribed to absorption of light by a dimer consisting of two O_2 molecules that are weakly bonded together in the liquid state but nonexistent in the gas phase. This mechanism is called the "one photon two molecule" mechanism.

Also interesting from the point of view of color is singlet oxygen. This can be generated using sodium hypochlorite (bleach) to oxidize hydrogen peroxide in what is called the Mallet reaction (from 1927):

$$H_2O_2 + NaOCl \rightarrow NaCl + H_2O +^1 O_2 \tag{1}$$

Photodynamic Therapy (PDT)

Singlet oxygen can also be generated using a photosensitizer; this is the basis of a form of cancer therapy known as photodynamic therapy (PDT). In PDT, the sensitizer is administered to the patient and during an incubation period accumulates selectively in tumor cells. This type of therapy is best for tumors located just under the skin; irradiation with long-wavelength visible light capable of penetrating tissue is then used to excite the sensitizer. The excited singlet sensitizer undergoes intersystem crossing (ISC) to transition to a long-lived triplet state which, in turn, can collide with triplet O_2 to produce excited, singlet oxygen, together with returning the sensitizer to its singlet ground state. This type of collision where one electronically excited molecule interacts with a ground state molecule in a manner that transfers the excitation from one to the other is known as energy transfer. Photochemical processes (excitation, ISC, fluorescence, luminescence) are typically portrayed schematically in a Jablonski diagram.

Appreciating Oxygen

Some very interesting insight can be obtained concerning the chemistry of solar energy storage on our planet by taking into consideration the heat of combustion, ΔH_{comb}, and its relation to the chemical bonds that are formed and broken in a combustion reaction. Key to understanding this point is that the O-O bond of the O_2 is relatively weak, coming in at 496 kJ/mol for the bond dissociation enthalpy (BDE). Upon combustion, however, oxygen is able to form two *strong* bonds in the combustion products CO_2 and H_2O. If a fossil fuel undergoes combustion (combination with oxygen) the carbon and hydrogen atoms form strong bonds already in the starting materials, just the same as in the products. In other words, the driving force for combustion resides in the conversion of a weak oxygen bond into strong chemical bonds in the combustion products. For this reason, it is possible to predict a value for ΔH_{comb} that is based solely on the number of moles of oxygen consumed in the balanced equation for the combusion reaction (460 kJ/mol O_2). Thus, for the combustion of methane that uses two moles of O_2 for every molecule of CH_4, the prediction would be $\Delta H_{\text{comb}} = -920$ kJ/mol. Similarly, for the heat of combustion of ethanol consuming three moles of O_2, we predict -1380 kJ/mol.

The foregoing insight is profound. Photosynthesis on Earth uses energy from the sun not only to fix carbon dioxide and generate carbohydrates, but also to store vast amounts of energy in the form of atmospheric oxygen molecules. This is how nature stores solar energy by driving an uphill reaction, conversion of water (two strong bonds to each oxygen) to O_2, with its weak bond representing a vast storehouse of chemical potential. Many kinds of substances support combustion, but the combining power of oxygen is due to its weak bond, not due to any special chemical characteristic of the "fuel". In principle, any weak chemical bond that can be formed from a strong one under the action of solar energy can be the basis for energy storage in chemical bonds. One example is the weak bond in a halogen molecule such as Br_2. The energy stored in a weak chemical bond is recovered upon combination with a "fuel".

Another illustration of the importance of oxygen is to consider the fact that glucose metabolism provides enough energy to drive the formation of 38 ATP molecules if it is aerobic, meaning that the metabolism involves the combination with oxygen, but only enough for formation of 2 ATP molecules if it is anaerobic as in muscle or yeast. Anaerobic metabolism involves rearrangemtn of the chemical bonds to a lower-energy form, not combination with oxygen. Metabolism in muscle rearranges glucose to 2 molecules of lactic acid, whereas glucose metabolism in yeast rearranges the bonds to form 2 molecules each of ethanol and CO_2.