

EXPERIMENTAL EVIDENCE FOR MOLECULAR ORBITAL RESULTS

The molecular orbital picture of dioxygen differs from the Lewis picture. Both models predict an oxygen-oxygen double bond, but one model suggests unpaired electrons whereas the other indicates an electron-paired system.

Often, there is experimental evidence available to check the reliability of predictions about structure. These data include measurements of bond lengths and bond strengths as well as magnetic properties.

Bond dissociation energy data tell us how difficult it is to separate one atom from another in a molecule. Bond order is one of the factors that influences bond strength. Thus, measuring a bond dissociation energy is one way to confirm that dioxygen really does contain an oxygen-oxygen double bond.

First, we need something to compare it to. Peroxides (such as hydrogen peroxide, H_2O_2 , or sodium peroxide, Na_2O_2) probably contain oxygen-oxygen single bonds, according to their Lewis structures. These bonds are relatively weak, costing about 35 kcal/mol to break. In contrast, the bond in dioxygen costs about 70 kcal/mol to break. Its bond is about twice as strong; it is a double bond.

- Bond dissociation energies can be used to determine how many bonds there are between two atoms.

Bond dissociation energies can be complicated to measure. They require a comparison of energy changes in numerous chemical reactions so that the energy change resulting from cleavage of a specific bond can be inferred. In contrast, infrared absorption frequencies are easy to measure. They simply require shining infrared light through a sample and measuring what frequencies of the light are absorbed by the material. (A related technique, Raman spectroscopy, gives similar information by measuring subtle changes in the frequency of laser light that is scattered off a sample). The frequencies absorbed depend on what bonds are present in the material. These frequencies vary according to two basic factors: the weights of the atoms at the ends of the bond, and the strength of the bond between them. The stronger the bond, the higher the absorption frequency.

Peroxides absorb infrared light at around 800 cm^{-1} (this unusual frequency unit is

usually pronounced "wavenumbers"). Dioxygen absorbs infrared light around 1300 cm^{-1} . Since the atoms at the ends of the bond in both peroxide and dioxygen are oxygens, we can be sure that this difference in frequency is not due to a difference in mass. It is due to a difference in bond strength. The bond in dioxygen is much stronger than the O-O bond in peroxide, because the former is a double bond and the latter is a single bond.

- Vibrational spectroscopies (IR and Raman spectroscopy) can give information about the bond order between two atoms.

A third measure of bond order is found in bond length measurements. The more strongly bound two atoms are, the closer they are together. An O=O bond should be shorter than an O-O bond. Bond lengths can be measured by microwave spectroscopy (usually for gas-phase molecules), in which frequencies absorbed depend on the distance between the molecules. Alternatively, bond lengths can be measured by x-ray crystallography. X-rays can be diffracted through crystals of solid materials. The interference pattern that is produced can be mathematically decoded to produce a three-dimensional map of where all the atoms are in the material. The distances between these atoms can be measured very accurately.

The O-O bond in peroxides are about 1.49 Angstroms long (an Angstrom is 10^{-10} m ; this unit is often used for bond lengths because it is a convenient size for this task. Covalent bonds are generally one to three Angstroms long). The O-O bond in dioxygen is about 1.21 Å long. The O-O bond in dioxygen is shorter and stronger than in a peroxide.

- Bond length data provides insight into the bond order.

In addition to bond order, there is the question of electron pairing in dioxygen. The Lewis structure suggests electrons are paired in dioxygen. The molecular orbital picture suggests two unpaired electrons.

Compounds with paired electrons are referred to as diamagnetic. Those with unpaired electrons are called paramagnetic. Paramagnetic substances interact strongly with

magnetic fields.

It turns out that oxygen does interact with a magnetic fields. A sample of liquid-phase oxygen can be held between the poles of a magnet. Oxygen has unpaired electrons. This finding is consistent with molecular orbital theory, but not with simple Lewis structures. Thus, MO theory tells us something that the Lewis picture cannot.

- Magnetic information, and measurements of magnetism, give us experimental evidence of spin states.
- We can tell if electrons are paired, unpaired, and how many unpaired spins there are.

A final important source of experimental data is photoelectron spectroscopy. Photoelectron spectroscopy gives information about the electron energy levels in an atom or compound. In this technique, gas-phase molecules are subjected to high-energy electromagnetic radiation, such as ultraviolet light or X-rays. Electrons are ejected from various energy levels in the molecule, and the binding energies of electrons in those levels is determined. Thus, photoelectron spectroscopy provides verification for exactly the sort of information that quantitative molecular orbital calculations are designed to deliver.

- Photoelectron spectroscopy tells how much energy is needed to remove electrons from various energy levels in a molecule.
- This technique gives us an accurate experimental picture of the energy levels that we predict with molecular orbital calculations.

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