

Advanced Chemistry, 2008
Winter Quarter – Inorganic Chemistry– Week 7 Homework

1. Draw molecular orbital diagrams for the homonuclear diatomics: H₂, He₂, Li₂, Be₂, B₂, C₂, N₂, O₂, F₂, and Ne₂. Draw each molecule on a different page.
2. Label the atomic and molecular orbitals with proper symmetry symbols. Clearly identify the HOMO and LUMO on each diagram.
3. Use these diagrams to determine
 - The bond order
 - Stability
 - Magnetism
 - Electron configuration
4. The following article was taken from the Journal of Chemical Education, Volume 80, Number 12, December 2003. page 1381. After carefully reading this article draw two separate molecular orbital diagrams to show the first and second excited states of O₂.

The Excited States of Molecular Oxygen

An article in this *Journal* nicely discusses the visible spectrum of liquid oxygen in the framework of molecular orbital theory applied to the O₂ molecule (1). It is very interesting that the simultaneous excitation of two O₂ molecules to the first excited state by a single photon accounts for the blue color of oxygen in the liquid and solid phases. Furthermore, the reported results lead to energy values above ground state of 1.576×10^{-19} and 2.62×10^{-19} J per molecule for the first two excited states of the O₂ molecule. Multiplied by Avogadro's number, these values give 94.9 and 157.8 kJmol⁻¹, in excellent agreement with the literature values of 94.72 and 157.85 kJmol⁻¹ (2). Nevertheless, there is a mistake in the electronic structure of the first two excited states. While the ground state electron configuration of the O₂ molecule is

KK (2s)²(2s*)²(2pz)²(2px)²(2py)²(2px*)¹(2py*)¹

with the electrons in the ^{*} orbitals with parallel spins (a triplet 3_g state), in agreement with Hund's first rule, the first excited state (94.72 kJmol⁻¹ above ground state) has the configuration

KK (2s)²(2s*)²(2pz)²(2px)²(2py)²(2px*)²(2py*)⁰

(a singlet 1_g state) and the second excited state (157.85 kJmol⁻¹ above ground state) is

KK (2s)²(2s*)²(2pz)²(2px)²(2py)²(2px*)¹(2py*)¹

with the electrons in the ^{*} orbitals with opposite spins (a singlet 1_g state) (2–4). The two excited states are interchanged in reference (1), as well as in some inorganic chemistry textbooks (5–7), while other textbooks contain the correct ordering (8–12). In the excellent textbook by Greenwood and Earnshaw (5), it is correctly stated that the first excited state of the O₂ molecule corresponds to the singlet 1_g state, but it is incorrectly assigned to a configuration with the ^{*} electrons occupying separate orbitals. It is important that the mistake is corrected in further editions of the textbooks (5–7) in order to avoid the disturbing discrepancies that we put forward a few years ago (4). The very interesting discussions in reference (1) are quite valid just by exchanging the configurations of the singlet-1 and singlet-2 states in Figure 1.

Literature Cited

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