Solid Oxygen

DOI: 10.1002/anie.200604410

Dark-Red O_8 Molecules in Solid Oxygen: Rhomboid Clusters, Not S_8-Like Rings

Ralf Steudel and Ming Wah Wong**

Keywords:
π interactions · ab initio calculations · high-pressure chemistry · oxygen · sulfur

Recent high-pressure research has demonstrated that typical nonmetals such as elemental hydrogen, oxygen, and sulfur, that is, prototype insulators at ambient conditions, turn into semiconductors and even into metals at very high pressures.[1] Some of these "metals" become superconductors if the temperature approaches the absolute zero point.[2,3] This behavior, observed by measuring the electrical conductivity, indicates that dramatic structural changes must occur if the density of the material is increased further and further. In the case of oxygen a density of about 10^{23} atoms per cm^3 is needed to reach the metallic state![3] Studying the properties of such samples in the laboratory is not at all trivial since the sample volume is usually very small, the sample is enclosed in a thick-walled high-pressure cell, and the temperature may be far from room temperature. Besides measurement of the electrical conductivity, vibrational and optical spectroscopies have been among the first methods to elucidate the structures of novel high-pressure phases.

Molecular oxygen has now come up with another big surprise. This colorless gas condenses at 90 K (at standard pressure) to a pale-blue paramagnetic liquid, which freezes at 55 K to give blue crystals of γ-O_2, which on further cooling turn into rhombohedral β-O_2 (at 44 K) and eventually into monoclinic α-O_2 (at 24 K), the low-temperature phase. Increasing the pressure produces first orange-colored δ-O_2 (stable at room temperature between 9.6 and 10 GPa), then dark-red ε-O_2 (range 10–96 GPa), and eventually the metallic phase ζ-O_2 (above 96 GPa). Of course, these pressure values depend on the sample temperature; the phase diagram of oxygen is known up to temperatures of about 650 K and to pressures of about 130 GPa.[4]

The structures of the oxygen allotropes that are stable at equilibrium vapor pressures have been known for some time. While the high-temperature γ phase is a disordered arrangement of O_2 molecules, α- and β-O_2 as well as the orthorhombic high-pressure phase δ-O_2 are all of similar structure consisting of planar layers of parallel-oriented O_2 units in differing packing modes, with the molecular axes normal to the layers (see Figure 1).[4]

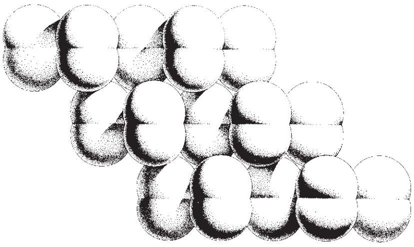

Figure 1. Packing of O_2 molecules in the low-temperature α phase of solid oxygen. Within the layers each molecule is surrounded by six neighbors. The shortest intermolecular distances are (320 ± 12) pm. From reference [20].

The interaction of the molecules within these layers and between them is of the van der Waals type (dispersion forces), but in addition there is a more or less strong magnetic coupling of the spins of the two unpaired electrons in the degenerate π^* levels of neighboring O_2 molecules. Expectedly, this intermolecular interaction is temperature-dependent. Therefore, the low-temperature phase α-O_2 is antiferromagnetic (long-range order; also in δ-O_2), β-O_2 is diamagnetic (short-range order), and the high-temperature phase γ-O_2 is paramagnetic, as is liquid O_2. The magnetic properties of ε-O_2 are not yet known with certainty, but most likely this phase is also diamagnetic.[4]

It has always been an intriguing question whether small sections of the layers in solid dioxygen, that is, oligomers such as O_4, O_6, O_8, and so on, can be prepared or at least detected as distinct species in gaseous oxygen, in analogy to elemental sulfur for which the corresponding molecular sizes are well-known.[5] The dimer O_4 has in fact been observed but as a very weakly bound van der Waals molecule $(O_2)_2$ of D_{2h} symmetry with an interaction enthalpy of just 1.2(1) kJ mol^{-1}.[6] With the first convincing structure determinations of the high-pressure phase ε-O_2 this situation has now changed dramatically since the first true oligomer of O_2 has been discovered. According to two independent X-ray investigations, ε-O_2 consists of layers of well-defined O_8, or $(O_2)_4$, molecules.[7] This phase was first prepared in Germany in 1979,[8] but its molecular composition has long been disputed. O_4, among others, has been proposed as the dominating molecular unit.[9]

---

[*] Prof. Dr. R. Steudel
Institut für Chemie
Technische Universität Berlin, Sekr. C2
10623 Berlin (Germany)
Fax: (+49) 30-3142-6519
E-mail: steudel@sulfur-research.de

Prof. Dr. M. W. Wong
Department of Chemistry
National University of Singapore
3 Science Drive 3
Singapore 117543 (Singapore)
Fax: (+65) 67-791-691
E-mail: chmwmw@nus.edu.sg

However, as part of an international team, Lundegaard et al. have now succeeded in growing single crystals of ε-O_2 from a mixture of helium and O_2 (2.6 mol%) in a diamond anvil cell at 450 K and a pressure of 22.5 GPa. Dark-red monoclinic crystals were obtained which allowed a definite structure determination by X-ray crystallography despite the twinning of the crystals.[7a] Simultaneously, a Japanese group has proposed essentially the same structure on the basis of angle-dispersive powder X-ray diffraction experiments and a Rietvield refinement.[7b]

The ε-O_2 phase comprises layers of collinear O_2 molecules, the axes of which are oriented perpendicular to the layers, but in contrast to the structures of the α–δ phases the distances between the O_2 units within these layers are not equal, but distinct O_8 units can be identified. The symmetry of the rhomboid-shaped O_8 molecular units is D_{2h} with three characteristic shortest interatomic distances: 120–121 pm within the O_2 units, 218–219 pm between neighboring O_2 units within the O_8 molecules, and 257–261 pm between neighboring O_8 units (see Figure 2).[7a] The shortest interlayer distance is 250 pm. For comparison, the van der Waals distance between two oxygen atoms is listed as 300 pm. The characteristic bond angles in the O_8 units are 84° (O3-O1-O3 and O3-O2-O3), 96° (O1-O3-O2), and the trivial value of 90° (e.g. O3-O1-O2).

There is a large volume contraction when δ-O_2 is transformed into ε-O_2.[4] This observation can now be explained by the reduction of the intermolecular O–O distance from 257 pm within the layers of δ-O_2[10] to 219 pm within the O_8 units of ε-O_2. Evidently, a kind of pressure-induced Peirls distortion takes place. The very substantial density increase (ca. 10%) not only favors the formation of ε-O_2 at high pressure but is also responsible for its stability over a remarkably large range of pressures. Despite the unpolar nature of both O_2 and O_8, the latter gives rise to a strong infrared absorption.[4,7,9]

How can the bonding in these spectacular O_8 molecules be understood? Previous theoretical studies on O_8 have focused only on the crown-shaped eight-membered ring, a valence isoelectronic analogue of the well-established molecular structure of S_8.[11] Interestingly, the crown-shaped O_8 molecule is highly unstable with respect to four O_2 molecules, by more than 500 kJ mol^{-1}.[11a] Density functional calculations suggest that this D_{4d}-symmetric O_8 structure is likely to lie in a very shallow potential well.[11c]

However, in the case of S_8 a hypothetical cuboid-shaped isomer of D_{4h} symmetry has been proposed with a structure similar to that of rhomboid O_8 (Figure 3).[12] This singlet cuboid structure was calculated to be a local energy minimum at the MP2/6-31G* level. The structure is characterized by four parallel-oriented S_2 molecules held together by some attractive force, as indicated by the calculated S–S bond length of 281 pm between the S_2 dumbbells (Figure 3).[13] The bond lengths within the S_2 moieties (194 pm) are almost identical to that of the diatomic S_2 molecule (192 pm, at the same level of theory). This unusual molecular geometry was explained in terms of π*–π* interactions. However, this elusive structure is not a stable species at higher levels of theory.

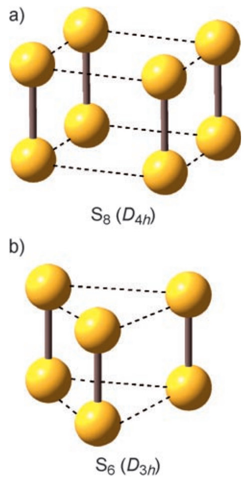

Figure 3. Structures of a) the theoretically predicted cuboid S_8 molecule (D_{4h})[12] and b) the prism-shaped S_6 isomer (D_{3h}).[13] The π*–π* interactions between the S_2 units are indicated by broken lines.

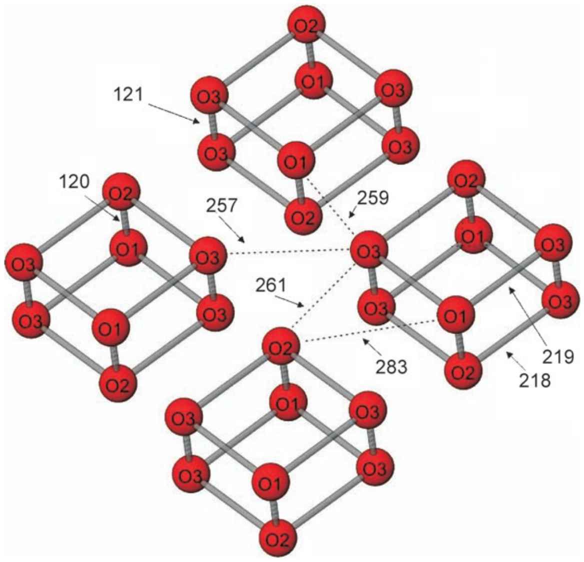

Figure 2. Geometry and packing of the O_8 molecules in the high-pressure ε phase of solid oxygen (internuclear distances in pm, at 17.6 GPa; modified from reference [7a]). The bond lengths within the O_2 units (standard deviation: 1 pm) are identical to the gas-phase value.

But in the case of S_6 a similar oligomer, $(S_2)_3$ of D_{3h} symmetry, was predicted as a local energy minimum on the potential hypersurface (see Figure 3). Essentially, this species consists of three S_2 molecules connected by weak π*–π* interactions, with predicted S–S bond lengths of 190 and 276 pm. The existence of these π*–π* interactions was supported by an analysis of the molecular orbitals and by a topological analysis of the charge density (ρ) and its Laplacian ($\nabla^2\rho$). A bond order of 0.28 was estimated for the π*–π* bonds.[13] The energy of this prism-shaped structure is 51 kJ mol^{-1} above that of the chair-shaped *cyclo*-S_6 form of D_{3d} symmetry.

On the basis of the above theoretical findings for S_6 and S_8, one would anticipate a cuboid O_8 structure to be a potential high-energy species for oxygen also. Indeed, preliminary G3X(MP2) calculations indicate that a similar rhomboid O_8 structure of D_{2h} symmetry is a stable species, that is, a local energy minimum.[14] Remarkably, this structure is 281 $\mathrm{kJ\,mol^{-1}}$ more stable than the crown-shaped isomer of D_{4d} symmetry mentioned above. The calculated O–O bond lengths (120 and 212 pm) and bond angles (82.3 and 96.7°) are in accord with the X-ray results on the ε-O_2 phase. This molecular geometry is close to a cuboid structure of D_{4h} symmetry.[14]

What is then the spin state of the rhomboid O_8? The π*–π* interaction is a two-electron stabilizing interaction involving the two open-shell π* orbitals of the O_2 molecule. In the case of $(O_2)_4$ four sets of π*–π* interactions involving eight degenerate (singly occupied) π* orbitals of four O_2 molecules will lead to eight molecular orbitals, four bonding and four antibonding. The eight electrons occupy the four bonding orbitals, resulting in an overall spin-paired molecule (Figure 4). Our quantum chemical calculations have confirmed that the ground state of rhomboid $(O_2)_4$ is a singlet.[14] This theoretical finding is consistent with the experimental suggestion that the ε-O_2 phase is diamagnetic. The crucial role of π*–π* interactions in rhomboid $(O_2)_4$ is readily reflected in the shapes of the four highest occupied molecular orbitals shown in Figure 5.

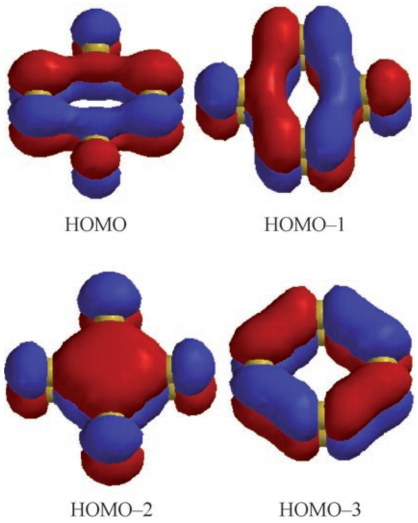

Figure 5. The four highest occupied molecular orbitals of the rhomboid $(O_2)_4$ molecule.[14]

The remarkable formation of the O_8 species in solid oxygen is the first case in which compression of an element results in a novel small molecule that was not observed or even speculated about before. Theoretical calculations may assist in the further characterization and understanding of this surprising species. The concept of π*–π* bonding between the open-shell O_2 molecules explains the formation of closed-shell O_8. Such bonds are widespread in chalcogen chemistry[15] and have already been identified between four sulfur atoms in a rectangular arrangement in the dimers of heterocyclic radicals and radical cations containing a disulfane group.[16] The seemingly omnipresent π*–π* bonding interaction also provides the fundamental understanding of the structures and conformations of all binary sulfur-rich oxides.[17] In halogen chemistry π*–π* bonds are also well-known.

From these findings it is to be expected that more exciting species related to O_8 will be discovered experimentally or computationally in the near future, probably also for the higher homologues selenium and tellurium. For example, Raman spectra of the metallic phase of oxygen clearly show that this material also consists of molecular entities based on O_2.[4] Since the volume decrease at the $\varepsilon \rightarrow \zeta$ transition is less than 1.4%, it can be assumed that metallic oxygen is also built of $(O_2)_n$ molecules ($n > 2$).

Further possible candidates for π*–π* bonding in Group 16 of the periodic table are mixed clusters of dioxygen with either dinitrogen or carbon monoxide such as $(N_2)(O_2)_3$ and $(N_2)_2(O_2)_2$. In the case of the solid N_2/O_2 system there is already evidence from the phase diagram as well as from X-ray diffraction measurements that two incongruently melting phases of composition $(N_2)_3(O_2)$ and $(N_2)(O_2)_2$ exist at high pressures, but most probably these do not consist of molecular entities of the same composition.[18]

Another chalcogen compound likely to undergo π*–π* interactions is sulfur monoxide, the valence isoelectronic congener of O_2. The hypothetical complex $(SO)_4$ with neighboring molecules in an antiparallel orientation could be held together not only by four π*–π* bonds but also by Coulomb forces resulting from the opposite atomic charges on oxygen and sulfur. This cluster may help to explain the extreme reactivity of SO, which is a very short-lived species in the gas phase.[19]

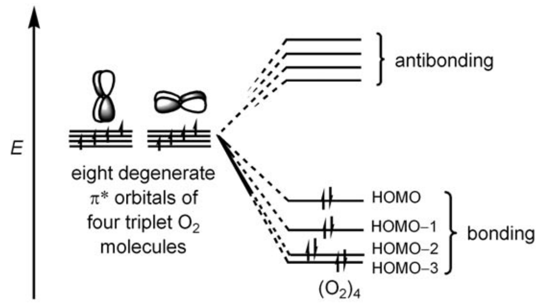

Figure 4. Schematic energy diagram showing the interactions of eight degenerate π* orbitals of four O_2 molecules to form the bonding and antibonding molecular orbitals of the rhomboid $(O_2)_4$ species.[14]

---

[1] A forthcoming review on high-pressure chemistry: W. Grochala, R. Hoffmann, J. Feng, N. W. Ashcroft, *Angew. Chem.*, DOI: 10.1002/ange.200602485; *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200602485.

[2] a) R. Steudel, *Chemie der Nichtmetalle*, 2nd ed., deGruyter, Berlin, **1998**; b) M. Bastea, A. C. Mitchell, W. J. Nellis, *Phys. Rev. Lett.* **2001**, *86*, 3108.

[3] P. P. Edwards, F. Hensel, *ChemPhysChem* **2002**, *3*, 53 (a critical discussion of the insulator–metal transition in fluid oxygen).

[4] Y. A. Freyman, H. J. Jodl, *Phys. Rep.* **2004**, *401*, 1 (a review on solid oxygen with more than 400 references).

[5] a) R. Steudel, B. Eckert, *Top. Curr. Chem.* **2003**, *230*, 1; b) R. Steudel, Y. Steudel, M. W. Wong, *Top. Curr. Chem.* **2003**, *230*, 117.

[6] a) F. Cacace, G. de Petris, A. Troiani, *Angew. Chem.* **2001**, *113*, 4186; *Angew. Chem. Int. Ed.* **2001**, *40*, 4062; b) V. Aquilanti, D. Ascenzi, M. Bartolomei, D. Cappelletti, S. Cavalli, M. de Castro Vitores, F. Pirani, *J. Am. Chem. Soc.* **1999**, *121*, 10794; c) K. Pfeilsticker, H. Boesch, R. Fitzenberger, C. Camy-Peyret, *NATO Sci. Ser. IV* **2003**, *27*, 273.

[7] a) L. F. Lundegaard, G. Weck, M. I. McMahon, S. Desgreniers, P. Loubeyre, *Nature* **2006**, *443*, 201; b) H. Fujihisa, Y. Akahama, H. Kawamura, Y. Ohishi, O. Shimomura, H. Yamawaki, M. Sakashita, Y. Gotoh, S. Takeya, K. Honda, *Phys. Rev. Lett.* **2006**, *97*, 085503.

[8] M. Nicol, K. R. Hirsch, W. B. Holzapfel, *Chem. Phys. Lett.* **1979**, *68*, 49.

[9] F. A. Gorelli, L. Ulivi, M. Santoro, R. Bini, *Phys. Rev. B* **2001**, *63*, 104110.

[10] D. Schiferl, D. T. Cramer, L. A. Schwalbe, R. L. Mills, *Acta Crystallogr. Sect. B* **1983**, *39*, 153.

[11] a) K. S. Kim, J. H. Jang, S. Kim, B.-J. Mhin, H. F. Schaefer, *J. Chem. Phys.* **1990**, *92*, 1887; b) M. Zhao, B. M. Gimarc, *J. Phys. Chem.* **1993**, *97*, 4023; c) P. Politzer, P. Lane, *Int. J. Quantum Chem.* **2000**, *77*, 336.

[12] M. W. Wong, Y. Steudel, R. Steudel, *Chem. Phys. Lett.* **2002**, *364*, 387.

[13] M. W. Wong, Y. Steudel, R. Steudel, *J. Chem. Phys.* **2004**, *121*, 5899.

[14] M. W. Wong, R. Steudel, unpublished results, **2006**; a cuboid structure with D_{4h} symmetry is a local energy minimum at the DFT level of theory, but not stable at higher levels of ab initio theory.

[15] a) I. Krossing, *Top. Curr. Chem.* **2003**, *230*, 135; b) W. A. S. Nandana, J. Passmore, P. S. White, C.-M. Wong, *Inorg. Chem.* **1990**, *29*, 3529.

[16] a) R. Gleiter, *Angew. Chem.* **1981**, *93*, 442; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 444; b) R. T. Oakley, *Prog. Inorg. Chem.* **1988**, *36*, 299; c) R. T. Oakley, *Can J. Chem.*, **1993**, *71*, 1775.

[17] a) M. W. Wong, R. Steudel, *Chem. Commun.* **2005**, 3712; b) M. W. Wong, R. Steudel, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1292; c) M. W. Wong, Y. Steudel, R. Steudel, *Chem. Eur. J.* **2007**, *13*, 502.

[18] D. Sihachakr, P. Loubeyre, *Phys. Rev. B* **2004**, *70*, 134105.

[19] R. Steudel, *Gmelin Handbuch der Anorganischen Chemie*, 8th ed., Sulfur Oxides, Springer, Berlin, **1980**, pp. 1–69.

[20] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**, p. 319.