The Molecular Oxygen Tetramer: Intermolecular Interactions and Implications for the $\epsilon$ Solid Phase

Massimiliano Bartolomei and Estela Carmona-Novillo, Marta I. Hernández, Jesús Pérez-Ríos, José Campos-Martínez

Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain

Ramón Hernández-Lamoneda

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, 62210 Cuernavaca, Mor. México

(Dated: January 15, 2013)

Abstract

Recent data have determined that the structure of the high pressure $\epsilon$ phase of solid oxygen consists of clusters composed of four O$_2$ molecules. This finding has opened the question about the nature of the intermolecular interactions within the molecular oxygen tetramer. We use multi-configurational ab initio calculations to obtain an adequate characterization of the ground singlet state of (O$_2$)$_4$ which is compatible with the non magnetic character of the $\epsilon$ phase. In contrast to previous suggestions implying chemical bonding, we show that (O$_2$)$_4$ is a van der Waals like cluster where exchange interactions preferentially stabilize the singlet state. However, as the cluster shrinks, there is an extra stabilization due to many-body interactions that yields a significant softening of the repulsive wall. We show that this short range behavior is a key issue for the understanding of the structure of $\epsilon$-oxygen.
The nature of the bonding in molecular oxygen clusters has been a subject of debate for nearly a century starting with the suggestion by Lewis of formation of dimers to explain the deviations from Curie’s law observed in liquid oxygen \[1\]. A chemically bound dimer was expected considering the open shell \(3\Sigma_{g}^{-}\) character of \(O_2\) where two unpaired electrons occupy degenerate \(\pi^*_g\) orbitals. However, a number of experimental \[2–4\] and theoretical \[5–7\] works clarified that in the gas phase \((O_2)_2\) has the typical features of a van der Waals complex: a well depth of tens of meV and retention of the molecular properties within the complex. In fact it has been shown \[5, 6\] that a singlet species of \(D_{2h}\) symmetry is stabilized due to exchange interactions but not in a sufficient extent to lead to chemical bonding. On the other hand, formation of a \(O_4\) molecule with four equivalent single bonds has been theoretically predicted \[8\] but roughly 4.3 eV above its \((O_2)_2\) van der Waals counterpart. This \(O_4\) molecule is structurally closer to the naturally occurring sulfur rings \(S_8\) and in fact an analogous crown-shaped \(O_8\) cluster has been predicted \[9\] but again, as a very high energy isomer.

Recently, the determination of the structure of the high pressure \(\epsilon\) phase of oxygen \[10, 11\] has risen the interest in the study of molecular oxygen oligomers. In contrast to previously proposed structures based on the dimer \[12\] and herringbone chains \[13\], two independent x-ray diffraction experiments \[10, 11\] definitively concluded that \(\epsilon\)-O\(_2\) consists of layers of well-defined \((O_2)_4\) aggregates. They were found to form prisms with the \(O_2\) axes perpendicular \[10\] or nearly perpendicular \[11\] to a rhombic, nearly squared, base. There is a hierarchy of distances in this phase, the \(O_2\) bond length which nearly keeps the gas phase value \((\approx 1.21\ \text{\AA})\) at all pressures, and the intra- and inter-cluster distances \((2.34\ \text{and}\ 2.66\ \text{\AA}, \text{at 11.4 GPa})\), which decrease monotonically with pressure up to the boundary with the metallic \(\zeta\)-phase \[11\]. Other key properties of this phase, suggesting increasing intermolecular interactions, are a dark-red color, a strong infrared absorption and a magnetic collapse \[12, 14, 16\]. Further evidence for a new intermolecular bonding has come from inelastic x-ray scattering \[17\] where, at the lower pressure boundary of this phase \((10\ \text{GPa})\), a discontinuous shift of about 1.1 eV in the electronic transitions from \(1s\) to \(1\pi^*_g\) orbitals was found.

A few works \[10, 18–20\] have attempted to rationalize the stability and the bonding of the \((O_2)_4\) species in the framework of the density functional theory (DFT), but with unclear results. Thus, authors of Ref. \[18\] found that the \(D_{4h}\) cuboid structure corresponds to a
local energy minimum that they recognized as unstable when higher levels of theory were applied. Furthermore, DFT calculations in Ref. [19] failed to show that the experimental \((O_2)_4\) geometry is the most stable one compared with other chain structures [13], showing the need for additional studies. Then, it is apparent that despite recent progress [21–23] made in DFT methodologies for treating dispersion forces, the multiconfigurational character of molecular oxygen clusters still remains a serious challenge for such techniques.

We report here high level supermolecular ab initio calculations of the \((O_2)_4\) cluster. Our goal is a reliable characterization of the singlet ground state which is consistent with the magnetic collapse [16] and spectroscopy [12, 14, 15] of the \(\epsilon\) phase. To this end, we use a multiconfigurational ansatz which is unavoidable for spin multiplicities of \((O_2)_4\) lower than the maximum one (nonet). We proceed in analogy to our previous work on the dimer [6, 7] and treat the highest spin complex by means of a restricted coupled cluster theory with singles, doubles and perturbative triple excitations [RCCSD(T)]. In addition, the singlet-nonet splitting can be well described at the multiconfigurational complete active space second order perturbation (CASPT2) theory. Finally, the \((O_2)_4\) singlet energy is obtained by adding to the RCCSD(T) nonet potential, the singlet-nonet CASPT2 splitting. The aug-cc-pVQZ [24] basis set has been used at all levels of theory. For the CASPT2 calculations the active space is defined by distributing 8 electrons in 8 molecular orbitals correlating asymptotically with the \(O_2 \pi^*\) shell. As customary, these orbitals have been previously optimized with the Complete Active Space Self Consistent Field (CASSCF) method. The counterpoise method [25] was applied to correct interaction energies for the basis set superposition error. As for the \((O_2)_4\) geometry, we use a cuboid structure with \(D_{4h}\) symmetry. The centers of mass of \(O_2\) form a square whose side is changed in the range \([1.5 - 25]\) Å while the intramolecular distance is kept fixed to \(1.2065\) Å. Calculations have been performed with the MOLPRO2006.1 package [26]. In addition and in order to study the role of many body interactions, we compare the supermolecular calculations just described with estimations based on the summation of pure pair interactions. In the pairwise approach we have obtained expressions for the \((O_2)_4\) energy which are compatible with a well-defined total spin of the complex, resulting in specific combinations of the \((O_2)_2\) singlet, triplet and quintet potentials. For a faithful comparison, the pair potentials were obtained at the same level of theory than those of \((O_2)_4\). It must be noted that there are three singlet states [27] asymptotically correlating with four \(O_2(3\Sigma_g^-)\), and that here we are reporting the calculations of the ground singlet
FIG. 1: Upper panel: Interaction energies (in meV) for the nonet and ground singlet states of $(O_2)_4$ as functions of the square side $d$ (in Å). Supermolecular approach is represented in solid lines while the pairwise approach in dashed lines. Lower panel: many-body interaction energy for the singlet state, $\Delta V(d)$, obtained as the difference between supermolecular and pairwise energies. The large values of $\Delta V$ at small $d$’s might be a key feature to explain the clustering of O$_2$ molecules in the $\epsilon$ phase.

The interaction energies of $(O_2)_4$ in the singlet and nonet states as functions of the square side $d$ are reported in the upper panel of Fig. 1 together with the pairwise estimations of the corresponding interactions. Equilibrium parameters of these potentials are given in Table I. As can be seen from the parameters of the singlet and nonet potential wells, $(O_2)_4$ is a van der Waals like complex in the gas phase, mainly stabilized by dispersion interactions. Exchange interaction, however, plays a role making the potential well of the singlet state deeper and shifted at shorter intermolecular distances than that of the nonet state. As in the dimer[6,7], the exchange interaction favors the states of lowest spin multiplicity.
More insight is gained when comparing the supermolecular calculations with the pairwise estimations. For the nonet state, the pairwise approximation reproduces very well the supermolecular energies indicating that many-body effects are not particularly relevant. However, for the singlet state, an analogous agreement is only achieved for the larger \( d \) sizes of the cluster. Around the minimum of the singlet well, the supermolecular energies are already lower than the pairwise ones (see Table I) but it is for shorter distances where a remarkable softening of the repulsive wall is found. This is due to a many-body effect, as shown in the lower panel of Fig. 1 where it can be noticed that the many-body interaction energy for the singlet state increases dramatically as \( d \) decreases, being about 1.2 eV at \( d = 2 \text{ Å} \). The origin of this effect must be in the exchange interactions\[^{28}\] since polarization contributions to many-body interaction energies, if important, should be shown also for the nonet state, that is not the case.

In a molecular crystal the first response to pressure is the “squeezing out of van der Waals space”, in other words, the penetration to the repulsive region of the intermolecular potentials\[^{29}\]. Therefore the peculiar behavior reported above can be relevant indeed for understanding the structure of the high pressure \( \epsilon \) phase\[^{10, 11}\]. For this reason, in the following we will focus on the features of \((O_2)_4\) at short cluster \( d \) sizes.

Some clues for the softening of the repulsive wall of the ground singlet state are given in Fig. 2, where we report CASSCF calculations of the molecular orbitals arising from the interaction of the eight half-occupied \( \pi^*_g \) orbitals of \( O_2 \). An analogous calculation for the singlet \((O_2)_2\) is shown for the sake of comparison. The properties of these optimized orbitals barely change from the asymptote up to the equilibrium distance \((d \approx 3 \text{ Å})\), but for shorter \( d \)'s the interaction does give rise to bonding and antibonding orbitals. Interestingly, the four bonding orbitals in \((O_2)_4\) are more stable than the bonding orbitals of \((O_2)_2\) and the associated occupation numbers increase faster as \( d \) decreases, as a result of many-body
exchange effects. However, a double occupancy only occurs for very short distances ($d < 1.8 \, \text{Å}$). Moreover, the $(\text{O}_2)_4$ orbital stabilization is much smaller than the electron-electron Coulomb repulsion contribution to the total interaction. Thus, the result is not a minimum but a softening of the repulsive region of the potential, as obtained in Fig. 1. This multiconfigurational analysis differs from those of Refs. [17, 18] where, based on a simpler monoconfigurational picture, it was suggested that all the bonding orbitals were doubly occupied leading to large binding energies with respect to the isolated O$_2$ molecules. The present analysis also gives a qualitative insight into the observation of a $\approx 1 \, \text{eV}$ shift in the $\pi_g^* \leftrightarrow 1 \, s$ transitions at the boundary of the $\epsilon$ phase[17], since the splitting between the $(\text{O}_2)_4$ antibonding energies and the isolated $\pi_g^*$ orbitals is of the same order of magnitude ($\approx 1.5 \, \text{eV}$) in the relevant range ($d \approx 2.4 \, \text{Å}$).

We have also checked that the energy of the ground singlet state is significantly lower than those of the other singlet states and different spin multiplicities as well, particularly in the
FIG. 3: Upper panel: Energy of a layer of $\epsilon$-O$_2$ (Eq. 1) as a function of the cluster size, $d$, for a pressure of 18.3 GPa (solid line). In the inset, the model unit cell is shown where the O$_2$ axes are perpendicular to the a-b plane and the inter-cluster distances, $r_{ij}$, are displayed by dashed lines, being $D$ the shortest one among them. A minimum of the energy is obtained for the intra-cluster distance $d_m$. Lower panel: Pressure dependence of $d_m$ and $D_m$ (lines) compared with data of Ref.[11](circles). See text for details.

repulsive region of the interaction. Albeit in a very intuitive manner, the emerging picture can give some hints on the formation and structure of the $\epsilon$ phase and its non-magnetic character. To illustrate this point and also in order to study whether present results are adequate for a description of the $\epsilon$ phase, we consider a very simple model for the energy of a layer of (O$_2$)$_4$ clusters. A basic unit cell is shown in Fig.[3] where the tetramers form rhombuses of length $d$ and angle $\alpha$. It is assumed that, at a given pressure, the centers of mass of the clusters are fixed and determined by the lattice parameters $a$ and $b$. Values of these parameters as functions of pressure were taken from Ref.[11]. In addition, the angle $\alpha$ is fixed to 81.4$^\circ$ as derived from data reported at 11.4 GPa[11]. We assume that all clusters increase/decrease their size $d$ at a time and study the subsequent modification of the cell
energy. This energy is given as a sum of intra- and inter-cluster contributions

\[ E(d) = V^{\text{intra}}(d) + \frac{1}{2} \sum_{i,j} V^{\text{inter}}(r_{ij}), \]  

(1)

where \( V^{\text{intra}} \) is the already reported supermolecular \((\text{O}_2)_4\) singlet potential and \( V^{\text{inter}} \) is a pair potential between molecules \( i \) and \( j \) belonging to different clusters. The corresponding intermolecular distance \( r_{ij} \) is determined by \( d, a, b \) and \( \alpha \). A spin-averaged \((\text{O}_2)_2\) potential was used for \( V^{\text{inter}}_{ij} \) because the nonmagnetic character\([10]\) of the \( \epsilon \) phase suggests that dependence on spin must be washed out. In Fig.3 (upper panel) it is shown that, within the cell, the optimum size of the cluster is considerably reduced with respect to the gas phase equilibrium distance. For 18.3 GPa, a minimum in the total energy is obtained at about \( d_m = 2.17 \text{ Å} \), in agreement with the observed intra-cluster distance of 2.185 Å\([11]\) as well as with the value obtained at 17.6 GPa in other independent experiment\([10]\). In the lower panel of Fig. 3 we show that the pressure dependence of the optimized intra- and inter-cluster distances \( d_m \) and \( D_m \) agrees fairly well with the observations\([11]\) \((D_m \) is the shortest inter-cluster distance, obtained as a function of \( d_m, a, b \) and \( \alpha \)).

We would like to stress that, despite the simplicity of the model, the key element is the behavior of the repulsive wall of the ground singlet state, adequately calculated at a multiconfigurational level of theory. Indeed, substitution of the the ground singlet energy \( V^{\text{intra}}(d) \) with that corresponding to a different spin multiplicity (or an excited singlet state) would lead to an optimum intracluster size far less compatible with the measurements (e.g., \( d_m \approx 2.35-2.40 \text{ Å} \) at 18.3 GPa). As discussed in Ref.\([10]\), the fact that both intra- and inter-cluster distances compress at nearly the same rate is a clear indication of a rather weak interaction between the \( \text{O}_2 \) molecules. Present finding of a van der Waals cluster with a very incipient chemical bond for short sizes is consistent with the observations. More refined models and extended calculations should be developed to account for the intriguing spectroscopy of \( \epsilon \)-oxygen\([12, 14, 15]\). Since at the cluster sizes relevant to the \( \epsilon \) phase the energy of the \((\text{O}_2)_4\) unit is not a minimum, including both intra and inter-cluster degrees of freedom in such models is unavoidable, especially for the lower frequency vibrational modes.

We thank Yuichi Akahama for sending us the structure data of Ref.\([11]\) and funding by Ministerio de Ciencia e Innovación (Spain, FIS2010-22064-C02-02). RHL was supported by a sabbatical grant by the Ministerio de Educación (Spain, SAB2009-0010) and by Conacyt
(Mexico, Ref. 126608). J.P.-R. is a JAE CSIC predoctoral fellow.

* Electronic address: maxbart@iff.csic.es

[1] G. N. Lewis, J. Am. Chem. Soc. 46, 2027 (1924).
[2] C. Long and G. Ewing, J. Chem. Phys. 58, 4824 (1973).
[3] L. Biennier, D. Romanini, A. Kachanov, A. Campargue, B. Bussery-Honvault, and R. Bacis, J. Chem. Phys. 112, 6309 (2000).
[4] V. Aquilanti, D. Ascenzi, M. Bartolomei, D. Cappelletti, S. Cavalli, M. de Castro Vitores, and F. Pirani, Phys. Rev. Lett. 82, 69 (1999).
[5] P. Wormer and A. van der Avoird, J. Chem. Phys. 81, 1929 (1984).
[6] M. Bartolomei, M. I. Hernández, J. Campos-Martínez, E. Carmona-Novillo, and R. Hernández-Lamoned, Phys. Chem. Chem. Phys 10, 5374 (2008).
[7] M. Bartolomei, E. Carmona-Novillo, J. Campos-Martínez, M. I. Hernández, and R. Hernández-Lamoned, J. Chem. Phys. 133, 12431 (2010).
[8] M. Caffarel, R. Hernández-Lamoned, A. Scemama, and A. Ramírez-Solís, Phys. Rev. Lett. 99, 153001 (2007).
[9] P. Politzer and P. Lane, Int. J. Quantum Chem. 77, 336 (2000).
[10] L. F. Lundegaard, G. Weck, M. I. McMahon, S. Desgreniers, and P. Loubeyre, Nature 443, 201 (2006).
[11] H. Fujihisa, Y. Akahama, H. Kawamura, Y. Ohishi, O. Shimomura, H. Yamawaki, M. Sakashita, Y. Gotoh, S. Takeya, and K. Honda, Phys. Rev. Lett. 97, 085503 (2006).
[12] F. A. Gorelli, L. Ulivi, M. Santoro, and R. Bini, Phys. Rev. Lett. 83, 4093 (1999).
[13] J. B. Neaton and N. W. Ashcroft, Phys. Rev. Lett. 88, 205503 (2002).
[14] Y. A. Freiman and H. J. Jodl, Phys. Rep. 401, 1 (2004).
[15] Y. Akahama and H. Kawamura, Phys. Rev. B 61, 8801 (2000).
[16] I. N. Goncharenko, Phys. Rev. Lett. 94, 205701 (2005).
[17] Y. Meng, P. J. Eng, J. S. Tse, D. M. Shaw, M. Y. Hu, J. Shu, S. A. Gramesh, C. Kao, R. J. Hemley, and H. K. Mao, Proc. Nati. Acad. Sci., USA 105, 11640 (2008).
[18] R. Steudel and M. W. Wong, Angew. Chem. Int. Ed. 46, 1768 (2007).
[19] B. Militzer and R. J. Hemley, Nature 443, 150 (2006).
[20] Y. Ma, A. R. Oganov, and C. W. Glass, Phys. Rev. B 76, 064101 (2007).

[21] A. Becke and E. Johnson, J. Chem. Phys. 127, 124108 (2007).

[22] E. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. Cohen, and W. Yang, J. Am. Chem. Soc. 132, 6498 (2010).

[23] J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Angyan, Phys. Rev. Lett. 102, 096404 (2009).

[24] R. Kendall, J. T. H. Dunning, and R. Harrison, J. Chem. Phys. 96, 6796 (1992).

[25] J. van Lenthe, J. van Duijneveldt-van de Rijdt, and F. van Duijneveldt, Adv. Chem. Phys. 69, 521 (1987).

[26] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al., Molpro, version 2006.1, a package of ab initio programs (2006), see http://www.molpro.net/.

[27] H. V. Gomonay and V. M. Loktev, Phys. Rev. B 76, 094423 (2007).

[28] C. C. Díaz-Torrejón and I. G. Kaplan, Chem. Phys. 381, 67 (2011).

[29] W. Grochala, R. Hoffmann, J. Feng, and N. W. Ashcroft, Angew. Chem. Int. Ed. 46, 3620 (2007).