Comment on "Insights into the Electronic Structure of Ozone and Sulfur Dioxide from Generalized Valence Bond Theory: Bonding in O_3 and SO_2"

Kalemos Apostolos*

Department of Chemistry, Laboratory of Physical Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Hellas

The nature of the chemical bond in O_3 is a topic of some interest that dates back in the early 70s. Goddard and co-workers concluded on the basis of generalized valence bond (GVB) calculations that "...the ground state of ozone is well-represented as a biradical[8] with weak bonding between the singly occupied π orbitals on the terminal oxygen atoms."[1] The biradical hypothesis was challenged by Kalemos and Mavridis[2] who proposed that the ground O_3 state is a genuine closed-shell molecule formed from the perpendicular attack of $O(^1D)$ to $O_2(^1\Delta_g)$. Miliordos and Xantheas[3] concluded quite recently that "the ground state of O_3 does indeed originate from the excited-state fragments $O_2(^1\Delta_g) + O(^1D)$ as first proposed by Kalemos and Mavridis[7]" and they finally proposed a ground state of 82% closed shell and 18% diradical character originating from the interaction of $O(^3P)$ to $O_2(^3\Sigma_g^-)$. The 18% diradical character found was based on a restructuring of the two main configuration state functions producing orbitals that are not localized on the terminal O atoms but rather on the O_2 moiety of the O_3 species. So, their conclusions concerning the 18% diradical character are at least questionable. Takeshita et al.,[4] based on the recoupled pair model built upon the GVB wave function, presented a study on the bonding nature of O_3 with conclusions in line with those presented in ref 1. There are a number of points though that make their conclusions questionable.

First, the Takeshita et al.[4] study builds upon a GVB wave function that is specifically designed solely for the $O(^3P) + O_2(^3\Sigma_g^-)$ interaction as admitted even by the authors (vbL Scheme 1, Figure 1): "It should, however, be noted that since we only use one set of orbitals and the overall GVB wave function must be consistent with the symmetry of the molecule, our calculations would not be able to describe the asymmetric

bonding pattern associated with formation of a dative bond at R_e." So, a closed-shell bonding pattern as suggested in ref 2 is not and cannot be described from the outset (vbL Scheme 2, Figure 1).

Second, the ground O_3 state correlates at linearity with the $^1\Delta_g$ symmetry.[2] This is not the case though with the GVB wave function constructed in ref 4, since it correlates to either a Σ^+ or a Π symmetry because it conforms to the $O(^3P) + O_2(^3\Sigma_g^-)$ electronic distribution at all points of the configurational space.

Third, the active space adopted in the GVB calculations is incomplete as shown in the Appendix section of ref 4. As the authors explain its change results into two recoupled π bonds between the central and the terminal O atoms, and this is in qualitative disagreement with their conclusions on the diradical character of O_3. This means that a different Hartree product per spin function is needed to accommodate for such different bonding scenarios. Moreover, it has been stressed out that in cases where two or even more bonding situations are energetically close, they should be included in the wave function with the orbitals reoptimized in the presence of each other.[5]

Fourthly, the $D_e(O-O_2) = 23.8$ kcal/mol and $D_e(O_2) = 118.0$ kcal/mol, although not required to be identical, are so different that they cannot be consistent with the proposed equivalent σ bonds between the central and the terminal O atoms.[4] On the contrary, in the SO_2 molecule both SO bonds are energetically extremely close, that is, 127 and 125 kcal/mol.[4] If we consider the bonding mechanism depicted in vbL Scheme 2 we have $D_e(O_2, {}^1\Delta_g) = D_e(O_2, {}^3\Sigma_g^-) - T_e(^1\Delta_g \leftarrow {}^3\Sigma_g^-) = 96.34$ kcal/mol,[6] while based on the numerical values of ref 4, the $D_e(O-O_2$, with respect to $O_2(^1\Delta_g) + O(^1D)) = 91.6$ kcal/mol, in practical agreement with the $D_e(O_2, {}^1\Delta_g)$ and the interaction energy shown in Figure 2.

Fifthly, the rather large $\Delta E(^3B_2 \leftarrow {}^1A_1) = 29.7$ kcal/mol energy gap is rather inconsistent with the statement "...weakly interacting singlet coupled pair $(S = 0.16)$ must be broken to form the corresponding $^3B_2$ triplet state."[4]

Finally, the mixed covalently/datively bonded system advocated in ref 2 is strongly supported by the smooth and continuous asymmetric dissociation curve at both the RHF and RCCSD(T) levels of theory as shown in Figure 2. It is very well-
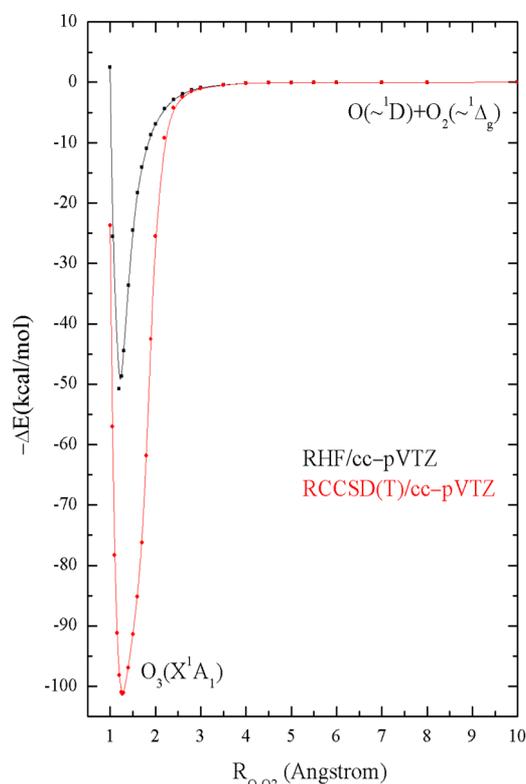

$O_2(^3\Sigma_g^-) + O(^3P) \rightarrow O_3(^1A_1)$

(vbL Scheme 1)

$O_2(^1\Delta_g) + O(^1D) \rightarrow O_3(^1A_1)$
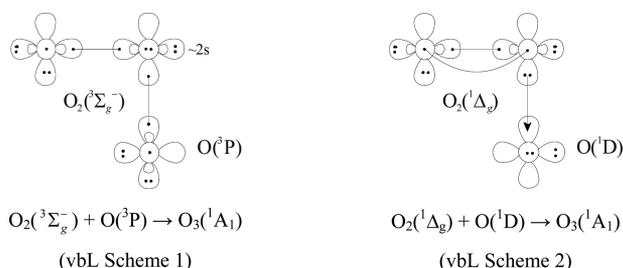
(vbL Scheme 2)

Figure 1. Valence bond Lewis (vbL) Schemes representing two different bonding situations. In vbL Scheme 2, the σ_v mirror image should also be included.

Figure 2. Potential energy curves at the RHF and RCCSD(T) computational levels for the asymmetric dissociation of the ground O_3 state.

known that the breaking of a regular covalent bond entails a spin decoupling, and its breaking cannot be described by any single reference method.

To unequivocally conclude on the bonding nature within the premises of the GVB methodology, the authors of ref 4 should have enlarged their active space, included more bonding patterns, and used a different Hartree product per spin function. We feel that their work is inconclusive or in other words their conclusions are consistent with their working hypothesis, that is, the consideration of only one configuration compatible with the $O(^3P) + O_2(^3\Sigma_g^-)$ interaction.

■ **AUTHOR INFORMATION**

Corresponding Author
*E-mail: kalemos@chem.uoa.gr.

Notes
The authors declare no competing financial interest.

■ **REFERENCES**

(1) Hay, P. J.; Dunning, T. H., Jr.; Goddard, W. A., III Configuration Interaction Studies of O_3 and O_3^+. Ground and Excited States. *J. Chem. Phys.* **1975**, *62*, 3912−3924.

(2) Kalemos, A.; Mavridis, A. Electronic Structure and Bonding of Ozone. *J. Chem. Phys.* **2008**, *129*, 054312.

(3) Miliordos, E.; Xantheas, S. S. On the Bonding Nature of Ozone (O_3) and its Sulfur−Substituted Analogues SO_2, OS_2, and S_3: Correlation Between their Biradical Character and Molecular Properties. *J. Am. Chem. Soc.* **2014**, *136*, 2808−2817.

(4) Takeshita, T. Y.; Lindquist, B. A.; Dunning, T. H., Jr. Insights into the Electronic Structure of Ozone and Sulfur Dioxide from Generalized Valence Bond Theory: Bonding in O_3 and SO_2. *J. Phys. Chem. A* **2015**, *119*, 7683−7694.

(5) Penotti, F. E.; Cooper, D. L. Combining Symmetry Separated and Bent−Bond Spin−Coupled Models of Cylindrically Symmetric Bonding. *Mol. Phys.* **2015**, *113*, 1690−1694.

(6) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Company: New York, 1979.