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Topological analysis and Quantum mechanical structure of Ozone

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ABSTRACT

Topological analysis has been performed on the total electron density of the two forms of Ozone molecule, C_2V and D_3H , to investigate the nature of chemical bonds, molecular structure, atomic charges and electrical properties. While these concepts have been completely discussed using classical models the emphasize in this work is based on Quantum Theory of Atoms in Molecules (QTAIM). Because the D_3H form has not been observed experimentally a well defined chemical model, i.e., QTAIM should be used to predict the above chemical properties for this species. The comparison between the atomic and molecular properties between the two forms has been done. Large π character has been assigned to the bonds in D_3H form, classically. This latter concept has also been investigate using the ZZ component of atomic quadrupole moments.

Keywords: Quantum theory; Classical model; π Character.

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INTRODUCTION

The ozone molecule has received considerable attention in recent years because of its pivotal role in atmospheric chemistry. While a hazardous pollutant near the earth surface, ozone protects lives on the earth by absorbing ultraviolet solar rays in stratosphere¹⁻⁶. So many theoretical calculations were concerned on PES of this molecule as well as its spectroscopic properties with high level and sophisticated ab initio methods and basis sets^{1,2,6}. Referring to one of the recent works in this field¹, the most stable form of O₃ in its ground electronic state ($X^1 A_1$) is an open C₂V molecule with O—O bond lengths of 1.2717 Å and an interbond angle of 116.78°, ab initio data also indicated that there should be in addition to stable open (C₂V) minimum a metastable ring (D₃H) minimum which is difficult to characterize empirically due to the lack of experimental data¹. So parallel to these ab initio data it is appropriate to look more precisely to the chemistry of this molecule using descriptive models. One important subject of interest is the nature of chemical bonds in cited two minima. While the classical models such as resonance structures or Lewis model have been used to investigate the structure and bond *qualitatively*⁷ in these forms, a model must be used to describe the chemistry of these molecules *quantitatively* thus the fundamental definition of atom and chemical bond should be proposed. In other words a theory is needed to break the properties of molecules to some fundamental units (Atoms). QTAIM provides this tool, using the fundamental concepts of quantum mechanics.⁸

QTAIM

In this section we present a brief description of the theory of atoms in molecules⁹ that is necessary to understand the results for systems which we present in the main body of this work.

Characteristics of Critical Points.

Trajectories of the gradient vector field of the charge density, $\nabla\rho$, are our device for exploring the three-dimensional topology

of ρ ^{10,11}; critical points, at which $\nabla\rho$ vanishes, are our key to understanding its structure. Each critical point is quantified by its three principal curvatures (eigenvalues of the Hessian matrix), λ_{1-3} , and characterized by the ordered pair of integers, (r, ω) , designating respectively its rank (number of nonzero eigenvalues) and signature (number of positive eigenvalues minus the number of negative eigenvalues). The positions of nuclei coincide with maxima, *i.e.*, (3,-3) critical points in ρ . Two paths originate and ascend in opposite directions from (3,-1) critical points. These paths typically terminate at nearby nuclei and together comprise an “atomic interaction line (AIL)”, a line of maximum electron density. In an equilibrium structure, such an atomic interaction line is referred to as a “bond path (BP)” and the (3,-1) critical point is termed a “bond critical point (BCP)”¹². Their presence meets the necessary and sufficient conditions that the two atoms are bonded to one another⁹ the network of bond paths defines the molecular graph. The fact that bond paths coincide with traditional chemical bonds in almost all cases lends weight to chemical interpretations of the charge density. Pairs of atoms which are linked by bond paths are thus readily identified to be those whose interaction dominates the forces which hold the structure together. The value of ρ at a BCP, ρ_b , gives a loose indication of bond strength⁹ Boyd and Choi found linear relationships between the value of ρ at the H-bond critical point and the H-bond strength¹³ as well as the intermolecular bond length¹⁴ for a set of complexes between organic nitriles and hydrogen halides. Infinitely many trajectories descend from a BCP and define an interatomic surface (which in general is not planar), such that the condition $\nabla\rho \cdot \mathbf{n} = 0$ is obeyed everywhere in it (\mathbf{n} is a vector normal to the surface at a given point). The two negative eigenvalues, λ_{1-2} , quantify curvatures in the interatomic surface, “transverse” to the atomic interaction line, whereas the positive λ_3 denotes the “longitudinal” curvature along the atomic

interaction line itself. Consequently, a pair of atoms which share an interatomic surface (IAS) are also linked by an atomic interaction line which intersects that surface perpendicularly at a (3,-1) critical point. The molecular graph may be regarded as a set of primary attractors (the nuclei) linked by secondary attractors (the BCPs). Whereas the location and number of these features are dictated by the physics of the system, occasions demand the existence of "ring" (or (3,+1)) critical points for which one curvature is negative and two positive. Two oppositely oriented trajectories descend perpendicular to the plane of the ring. (Additionally, "cage" (or (3,+3)) critical points which are minima found in cavities surrounded by three or more rings, may also arise, for example in Tetrahedron C_4H_4) It was pointed out by Collard and Hall¹⁵ that the number of critical points of all types is governed by a fundamental theorem of topology, the Poincaré-Hopf relationship,

$$n-b+r-c=1$$

where n is the number of nuclei and b , r , and c are the numbers of bond, ring, and cage critical points, respectively. Sometimes, as a result of this counting rule (in concert with point-group symmetry, if present), it becomes inevitable that certain critical points must exist. In particular, the action of bringing two molecules together to form a complex demands the existence of at least one new "intermolecular" BCP. Furthermore, for any "intramolecular" rearrangement in which one net extra BCP arises, a corresponding ring critical point must also be created. Conversely, atomic interaction lines in formally "intermolecular regions" persist as a complex is split into infinitely separated monomer units, whereas atomic interaction lines between sterically hindered atoms (in intramolecular environments) may change in nature (and may cease to exist or may be replaced by others) under certain conformational changes^{16,17}. It should be stressed, though, that the topology of ρ is not dictated by geometry alone; given only a set of primary attractors (nuclei), there is no requirement that any scalar field should adopt the form that ρ does. In fact there is a

homeomorphism between ρ and the virial field¹⁸. A molecular graph is mirrored by a corresponding virial graph in such a way that lines of maximum density linking bonded nuclei are matched by lines of maximally negative potential energy density.

Laplacians. The nature of BCPs in H-bonded, van der Waals, and ionic species needs to be reconciled with that of their counterparts in "regular" molecules. Bader and Essén made the first comprehensive study of the observed categories of BCPs¹² and uncovered the distinction between "shared" and "closed-shell" interactions. They concluded that the hallmark of "shared" (*i.e.*, covalent) interactions is a high value of the charge density at the BCP, ρ_b ($>10^{-1}$ a.u.). In addition, the curvatures of the charge density are usually large. The Laplacian, $\nabla^2\rho_b$, may be positive or negative and is usually of the same order of magnitude as ρ . A negative Laplacian denotes a perpendicular contraction of charge toward the atomic interaction line which is more significant than the longitudinal depletion of charge away from the BCP, toward the nuclei. This is in accord with one's intuitive understanding of the nature of chemical bonding in regular molecules. A positive Laplacian may occur for polar covalent bonds, *e.g.*, the double bonds between C and O or S. By contrast, in hydrogen-bonded systems, noble-gas dimers, and also ionic systems, ρ_b is quite small ($\sim 10^{-2}$ a.u. or less and $\sim 10^{-3}$ a.u. in van der Waals complexes^{9,19,13,17}) and the Laplacian is positive. These two observations appear to have no exceptions and are indicative of a "closed-shell" interaction. Subsequent comprehensive studies of H-bonded systems by Carroll *et al.* verified this description and added the observation that ρ_b was only very slightly greater than the sum of unperturbed monomer densities, $\sum\rho_b$, at that point. We conclude that in the weaker interactions between closed-shell molecules the longitudinal curvature is such as to squeeze electron density away from the BCP much more dramatically than the concomitant radial

compression of charge toward it. There is an energetic interpretation of these observations which derives from the local statement of the virial theorem,

$$\frac{\hbar^2}{2m} \nabla^2 \rho(r) = 2G(r) + V(r)$$

which relates the Laplacian to the values of the potential and kinetic energy densities, $V(\mathbf{r})$ and $G(\mathbf{r})$, respectively. Regions where the Laplacian is negative are such that the potential energy is dominant (in magnitude), whereas regions where it is positive are such that the kinetic energy dominates.

All Topological analysis were performed by MORPHY99²²⁻²⁷ program. This software is equipped with powerful integral algorithms for dealing with unusual topology of ρ (When the Gap is appeared between IASs²⁶).

DETAILS OF CALCULATIONS

Geometry optimizations were done at C_{2V} and D_{3H} symmetry spaces using RHF/cc-pVDZ level of calculations. The small size correlation consistent basis set²⁰ was chosen in regards to computational resources and desired accuracy of calculations. The nature of optimized structures were determined by frequency calculations. All these calculations were performed using PCGAMESS software²¹. Two local minima with cited symmetries were found. Structural parameters and total energies are shown in Table 1.

This corresponds to the idea that normal molecules are bound together as a consequence of increased electronic potential energy in the interatomic binding region. Conversely, interactions between closed-shell species suffer from Pauli exclusion of electrons from those very regions, and instead the potential energy is separately increased within one or both of the atomic basins. We can acknowledge that they denote significant atom-atom interactions while differentiating them from the intramolecular bonds which define the structure of the individual monomers.

RESULTS AND DISCUSSION

I. Atomic shapes and Molecular Graphs(MG)

A good descriptive model must readily shows the difference between the chemistry of any system at first glance.

Gradient vector field and contour map of molecules is the first suitable facility which AIM theory provides for us. The maps of two O_3 forms are shown in Fig1. They are obtained at the symmetry plane of each structure containing every three oxygen nuclei. The characteristics of CPs were gathered in Table 2. Poincare-Hopf relation is satisfied for both structures.

Critical points(CPs), Interatomic surfaces(IASs) and Atomic interaction lines(AILs) of each molecule were also shown in the maps.

Table 1. Bond lengths, Bond angles, Total dipole moments and Total energies of two local minima of O_3 in its (X^1A_1) ground electronic state at RHF/cc-pVDZ

	Bond length (Å)			Bond angle (o)	Diople moment (Debye)	Total energy (a.u)
	01-02	01-03	02-03	02-01-03		
C_{2V}	1.1968	1.1968	2.0625	119.0	0.8478	-224.28068
D_{3H}	1.3652	1.3652	1.3652	60.0	0.0000	-224.25999

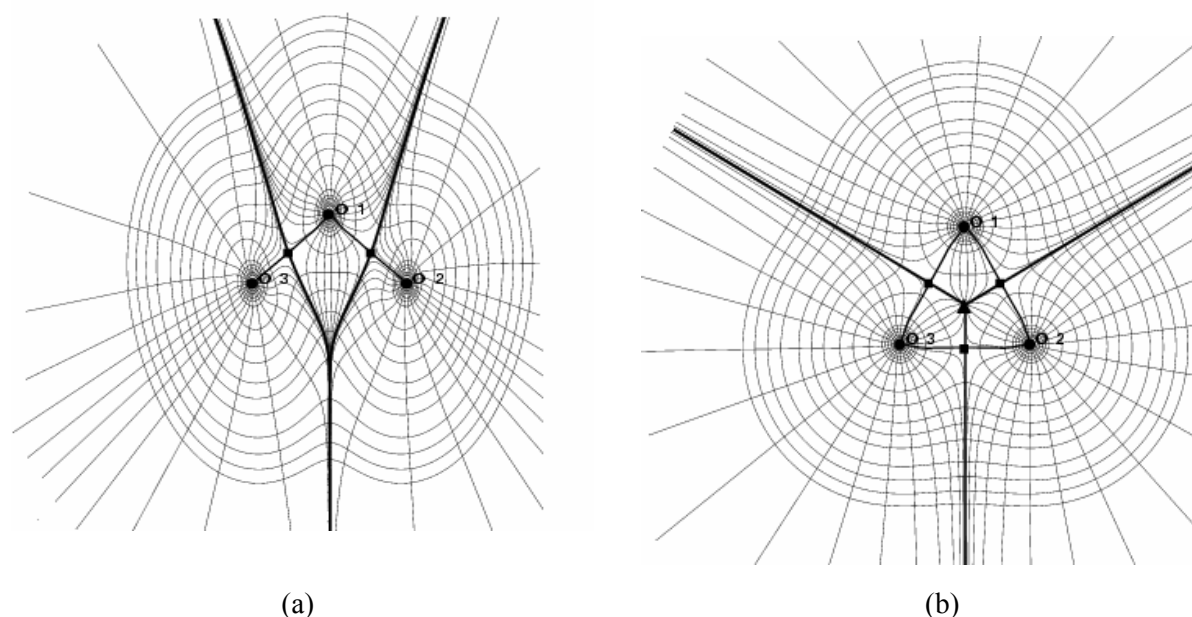


Fig. 1. Gradient vector field and contour map for (a) O_3 in its open C_{2V} and (b) for its ring D_{3H} form .Black squares are BCPs and Black triangle is RCP. AILs are black lines passing through BCP and ending at nucleus . Dark Black lines which pass through BCPs and slice the whole molecule in to three regions are the intersections of IASs with the plane of molecules.

Table 2. Characteristics of critical points in ρ function at RHF/cc-pVDZ

	(r, ω)	kind	ρ_b (a.u)	$\nabla^2 \rho_b$	λ_1	λ_2	λ_3	ϵ	
C_{2V}									
	O1-O2	(3, -1)	BCP	0.55408	-1.00743	-1.48253	-1.38653	1.86163	0.06924
	O1-O3	(3, -1)	BCP	0.55408	-1.00743	-1.48253	-1.38653	1.86163	0.06924
$n-b+r-c=3-2+0+0=1$									
D_{3H}									
	O1-O2	(3, -1)	BCP	0.34822	-0.36259	-0.84666	-0.81493	1.29899	0.03893
	O1-O3	(3, -1)	BCP	0.34822	-0.36259	-0.84666	-0.81493	1.29899	0.03893
	O2-O3	(3, -1)	BCP	0.34822	-0.36259	-0.84666	-0.81493	1.29899	0.03893
	O2-O1-O3	(3, +1)	RCP	0.24545	0.97520	-0.57958	0.77739	0.77739	
$n-b+r-c=3-3+1+0=1$									

As Fig 1 shows the MGs of these two structures establish the open and ring nature of two minima (a ring point exists for D_{3H} minimum) which we could only guess by the spatial orientation of Oxygen

nuclei before. With the ab initio LCAO-MO approximation (distribution of all electrons among all nuclei) one can not predict whether any interaction(Chemical bond) exist between O2 and O3 in C_{2V}

form or not. It is not acceptable to judge about the existence of chemical bonds on the basis of distances between nuclei because we can find lots of examples in which the nuclei are far apart from each other than normal distances but we propose the existence of bond between them (Transition Metal Complexes , Van der Waals complexes , ...).As Fig 1 shows , in ring form the AILs are not exactly straight lines but they show small deviations outward the ring.These deviations of AILs in ring systems were described as strain effects (example: cyclopropane ²⁸).O₃ in its ring form shows little strain and this effect rises the total energy of molecule (Table 1).Both structures are sliced in three regions (Quantum Mechanical Oxygen atoms) by IASs. These atoms are bounded by IASs and low electron density ($\sim 10^{-6}$ a.u) contour surface.The Basin of O1 essentially has the same pattern in both structures, this basin has been more squeezed in open C_{2V} structure. The great differences between the basins' pattern of O2 and O3 in two forms can be seen form Fig1.

II. Bonds' nature and Atomic Properties

Referring to Table 2 and Fig 1,O₃ in its open form has two equal shared chemical bonds and has three equal shared chemical bonds in ring form between Oxygen atoms. As was detected by MORPHY99 , O1 , O2 and O3 are topologically connected to form a ring in D_{3H} structure and a ring critical point is appeared. As a result of forming a chemical bond between O3 and O2 ,it is expected that the electron density between O1,O2 and O1,O3 become lesser in ring form in comparison to open form. This effect can be detected in ρ_b values of BCPs(Table2). The ρ_b values for BCPs between O1,O2 and O1,O3 in ring form become ~ 0.2 a.u lesser than open form. As a result it is safe to say that the shared bonds in open form of Ozone are stronger than in ring form .A useful quantity which is used to characterizing the shape of ρ around BCP is ellipticity(\mathcal{E}),This quantity is defined as $(\frac{\lambda_1}{\lambda_2})-1$ and ranges from zero to infinity.

Table 3. Atomic properties(in atomic units) from AIM analysis at RHF/cc-pVDZ

	Vol[0.001] [†]	q _‡	Q ₁ [*]	Q ₂₀	E(Ω) ^{**}	L(Ω) [#]	
C _{2V}	O1	70.08	0.2151	0.4330	-0.3645	-74.7335	0.00062
	O2	107.00	-0.1074	0.5689	-0.3841	-74.7737	0.00003
	O3	107.00	-0.1074	0.5689	-0.3841	-74.7737	0.00003
D _{3H}	O1	92.14	-0.0006	0.5260	-1.0282	-74.7534	-0.00091
	O2	92.16	0.0001	0.5270	-1.0285	-74.7533	0.00014
	O3	92.14	0.0000	0.5269	-1.0285	-74.7533	0.00001

[†] Atomic volume is integrated over atomic basin(Ω) to the contour surface of 0.001 a.u

[‡] Total atomic charge

^{*} Total intra Atomic Dipole Moment

^{**} Total atomic energy which is calculated by integrating over atomic basin(Ω)

[#] Total integration error over atomic basin (Ω) for calculating atomic properties

Lewis resonance structures of O₃ in Open form, gave a positive formal charge to O1 and negative formal charges to O2 and O3. AIM atomic charges reveal the same pattern but these charges are obtained from electronic charge density of each AIM oxygen atom. It is apparent from Fig1 that O1 volume must be smaller than O2 and O3 in Open form, this also is

For cylindrical bonds (Diatomic molecules, ethane, acetylene,...) ϵ is equal to zero at BCP. Comparing the ϵ values in Table 2, denotes that the bonds in D_{3h} form, have more cylindrical shape at BCPs than in open form. Complete integration over atomic basins were performed by MORPHY99 to obtain all atomic properties. These data were gathered in table 3 revealed in reported atomic volumes. Total atomic energies of O2 and O3 in C_{2v} form are more negative than O1 as a result of charge accumulation in the atomic basins of these atoms. Intra atomic dipole moment or first moment measures the extent, direction and sense of the shift of the atom's electronic charge cloud with respect to the nucleus so O2 and O3 are more polarized than O1 atom in open structure. All calculated atomic properties are the same in ring structure as is expected from its symmetry (D_{3h}). All atomic charges are Zero (in regarding to small integration errors) and all atoms have the same total energies. Total molecular volume of ring form is 7.64 a.u smaller than open form as result of charge concentration between three O nuclei and accumulation of charge density at RCP ($\rho = 0.24545$ a.u). All three O atoms were similarly polarized as their first moments imply, this is because of zero value of total molecular dipole moment and nuclear permutation symmetry. One of the five irreducible atomic quadrupole moments called Q₂₀ measures how much the electronic charge distribution is protruding (when negative) along Z axis (Usually perpendicular to the molecular plane) or how much it is flattened (When positive) in that direction. It acts as the electron density analogue of a π population of Orbital Model²⁹. All Q₂₀ values are negative for O atoms in both forms of ozone, but Q₂₀

for each O atom in ring form is twice larger than Q₂₀ values in Open form. This implies that the charge density of each O atom is largely elongated along Z axis (The direction Orthogonal to molecular plane). Comparison of O atoms' Q₂₀ values (-1.03 a.u) in this form with the reported Q₂₀ values of C atoms in benzene (-1.64) and ethene (-1.70)²⁹ reveals the similarity between electronic charge distribution in cyclic ozone and these well known π systems.

CONCLUSION

Two local minima of O₃ at its (X¹ A₁) electronic state were obtained at RHF/cc-pVDZ level of calculations in according to previous calculations. The molecular graphs of these two minima were obtained Using AIM analysis on their RHF wavefunctions. The open and ring nature of these minima were then established by investigating their gradient vector field and contour maps of ρ . Chemical bonds' nature were also investigated by the aid of analyzing the CPs in ρ . Integration over each oxygen atomic basin was performed to obtain all atomic properties (atomic charge, atomic volume, atomic energy, Intra atomic moment and atomic quadrupole moment) in two structures. The full comparison between atomic properties were reported for each form separately and between two forms. The calculated atomic charges for C_{2v} form resemble the same pattern as Lewis resonance structures. The strain effect in ring form was demonstrated through the deviation of its AILs from straight line. The electronic charge polarizations and the total shape of ρ for each O atom were investigated using Intra-atomic dipole moment (first moment) and quadrupole moments. Using Q₂₀ the similarity between Ozone in its ring form and well known π systems like Benzene and ethene was also established.

REFERENCES

1. Kirk A. Peterson et al , *J.Chem.Phys.*,2000,**112**,8378.
2. Yutaka Matsumi , *Chem. Rev.*, 2003, **103**, 4767.
3. Zhou, Sh. et al. *J. Phys. Chem. A.*,. 2006; **110**,7386.
4. Elliott, R. et al. *J. Phys. Chem. A.*, 2005; **109**, 11304.
5. Vacha, R et al *J. Phys. Chem. A.*, 2004; **108**,11573.
6. A.H. Pakiari, F. Nazari , *Journal of Molecular Structure (Theochem)*, **2003**, 640,109.
7. Gillespie , Popelier , *Chemical bonding and molecular Geometry*, New York, Oxford,2001.
8. R.F.W. Bader et al , *J.Chem.Phys.*,1996,**100**,10892.
9. R.F.W. Bader, *Atoms in Molecules*, Clarendon, Oxford, 1990.
10. R.F.W. Bader, *Acc. Chem. Res.*, 1985, **18** , 9.
11. R.F.W. Bader, *Chem.Rev.*,1991,**91**,893.
12. R.F.W. Bader et al , *J.Chem.Phys.*,1984,**80**,1943.
13. Boyd , Choi ,*Chem.Phys.Lett.*,1986,**129**,62.
14. Boyd , Choi ,*Chem.Phys.Lett.*,1985,**120**,80.
15. Collard , Hall , *Int.J.Quantum Chem.*,1977,**12**,623.
16. Cioslowski , Mixon, *J.Am.Chem.Soc.*,1992,**114**,4382.
17. Cioslowski , Mixon, *Can.J.Chem.*,1992,**70**,443.
18. R.F.W. Bader et al, *Int.J.Quantum Chem.*,1996,**57**,183.
19. R.F.W. Bader et al, *Mol.Phys.*,1988,**65**,695.
20. Thom H. Dunning, Jr., *J. Chem. Phys.*,1989, **90** ,1007.
21. Alex A. Granovsky, <http://classic.chem.msu.su/gran/gamess/index.html> ,
22. M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.*,1993, **14**, 1347.
- 22."MORPHY99, a topological analysis program written by PLA Popelier with a contribution from RGA Bone (UMIST,Engl,EU)"
23. PLA Popelier, *Comp. Phys. Comm.*,1996, **93**, 212
24. PLA Popelier, *Theor. Chim. Acta.*,1994, **87**, 465.
25. PLA Popelier, *Mol. Phys.*,1996, 87,169.
26. PLA Popelier, *Comp. Phys. Comm.*,1998, **108**,180.
27. PLA Popelier, *Can. J. Chem.*, 1996,**74**,829.
28. R.F.W. Bader, *Can. J. Chem.*, 1977,**55**,3040.
29. Paul Lode Albert Popelier, *Atoms in Molecules*, Prentice Hall, UMIST, 2000.