

Simple Interpretation of the Bond Lengths and Bond Angles in Stratospheric Chlorine Monoxide and Peroxide Based on Atomic and Ionic Radii

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Abstract

Over the last decade, the bond lengths in many molecules including hydrogen bonds and bond angles in small molecules like water and oxides of nitrogen, sulphur and carbon, were interpreted quantitatively in terms of the appropriate atomic and or the Golden ratio based ionic radii. Recently, the structure and formation of stratospheric ozone were explained using the atomic and ionic radii of oxygen. Presented here is a new, precise and simple explanation of the bond lengths and angles of the oxides of chlorine which cause depletion of stratospheric ozone. This work brings the simplest interpretation compared with existing complicated theories.

Keywords: Ozone; Chlorine monoxide; Chlorine peroxide; Additivity of radii; Golden ratio based ionic radii; Atomic structures

1. Introduction

1.1 O₃, ClO and ClOOCl in the stratosphere

Ozone (O₃) is formed by the reaction of atomic oxygen (O) and a molecule of oxygen (O₂) [1],



Ozone molecules present in the stratosphere absorb the ultraviolet (UV) radiation from the Sun which is harmful for the life on Earth. These important molecules are decomposed mainly by the industrial emissions of chlorofluoro carbons (CFC) which cause ozone holes [2]. The CFC molecules break down into fluorocarbon free radicals and chlorine atoms, and the latter react with ozone to produce oxygen and oxides of chlorine like chlorine monoxide ClO and chlorine peroxide ClOOCl [2, 3]. Some main reactions which decompose ozone are as follows:



As ozone gets depleted, the harmful UV light penetrates down to Earth. Therefore, it is important to curb emissions of ozone-depleting chemicals into the atmosphere and protect the life on Earth.

1.2. Bond length and bond angle in O₃ explained using the atomic and ionic radii of O.

Ozone, of chemical formula, O₃, and of structural formula, O⁺OO⁻, where the end atoms are negatively charged and make an angle $\theta = 116.78^\circ$ with the central oxygen, as shown in Fig. 1.

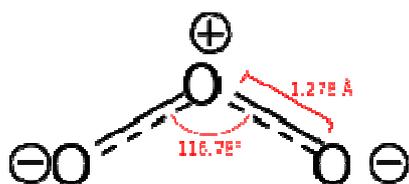


Fig. 1. Structural formula for Ozone, [1].

The observed bond length, $d(\text{O}^-\text{O}^+)_{\text{obs}} = 1.278 \text{ \AA}$ [1], is midway between the bond lengths $d(\text{OO})_{\text{s,b.}} = 1.34$ [4] for a single bond and $d(\text{OO})_{\text{d,b.}} = 1.207 \text{ \AA}$ [5] for a double bond. This mystery has exercised many minds, see e.g. [6]. It was explained recently in a simple way [7] in terms of the additivity of atomic and Golden ratio $[\phi = (1 + 5^{1/2})/2 = 1.618..]$ based ionic radii. See [7, 8] and the literature therein, for an introduction to the Golden ratio based ionic radii. The importance of the latter came into light a decade ago [8], when the author was investigating the ionization potential of hydrogen. The support obtained during the last ten years [9] finally resulted in the article [10] tracing the error to the negative sign [11] in Bohr's equation for the ground state energy of the hydrogen atom.

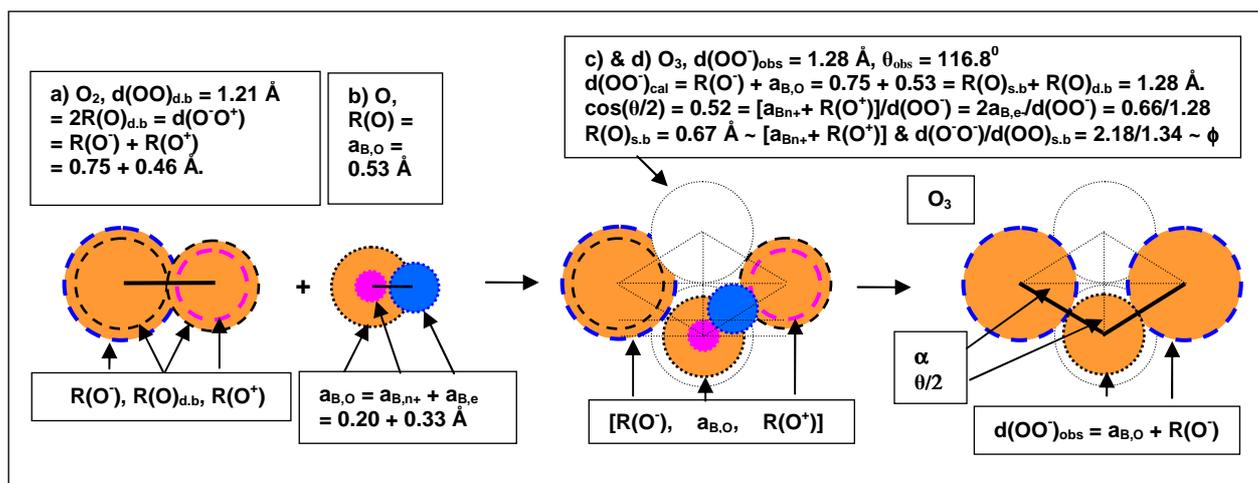


Fig. 2. Formation of ozone (O_3) from O_2 and atomic oxygen, O , [7]. In Figs. c) and d) the bond length, $d(\text{OO}^+) = R(\text{O})_{\text{d,b.}} + a_{\text{B,O}} = 1.28 \text{ \AA}$, [1]. The two empty dotted circles (absent oxygen) touching each other in c) & d) have the single bond radii, $R(\text{O})_{\text{s,b.}} = 0.67 \text{ \AA}$.

Fig. 2a shows the oxygen molecule (O_2) with a bond length $d(\text{OO})_{\text{d,b.}} = 1.21 \text{ \AA} = 2R(\text{O})_{\text{d,b.}}$, is also the sum of its Golden sections [7], as shown below:

$$d(\text{OO})_{\text{d.b.}} = 2R(\text{O})_{\text{d.b.}} = d(\text{O}^-\text{O}^+) = R(\text{O}^-)_{\text{d.b.}} + R(\text{O}^+)_{\text{d.b.}} \quad (7)$$

$$R(\text{O}^-)_{\text{d.b.}} = d(\text{OO})_{\text{d.b.}}/\phi = 0.75 \text{ \AA} \text{ and } R(\text{O}^+)_{\text{d.b.}} = d(\text{OO})_{\text{d.b.}}/\phi^2 = 0.46 \text{ \AA} \quad (8)$$

The ratio, $R(\text{O})_{\text{s.b.}}/d(\text{OO}^-) = 0.67/1.278 = 0.524 = \cos(\theta/2)$ and $(\theta/2) = 58.4^\circ$. This explains precisely the observed angle [1], $(\text{O}^-\text{OO}^-) = \theta = 116.8^\circ$. The angle, $\alpha = \text{OO}^-\text{O}^- = 90 - (\theta/2) = 31.6^\circ$. $R(\text{O})_{\text{d.b.}}$ is the covalent double bond radius [4], $\phi = (1+5^{1/2})/2 = 1.618..$, is the Golden ratio [12], $R(\text{O}^-)_{\text{d.b.}}$ and $R(\text{O}^+)_{\text{d.b.}}$ are the Golden ratio based radii [8] of O^- and O^+ (resonance forms of O) [4] respectively. An oxygen atom (O), with the atomic radius as the Bohr radius, $a_{\text{B,O}} = 0.53 \text{ \AA}$ obtained from its 1st ionization potential [13] is shown in Fig. 2b. The latter, $a_{\text{B,O}}$ is the sum of its Golden sections, $a_{\text{B,e}^-}$ and $a_{\text{B,n}^+}$ pertaining to the electron (e^-) and nucleus (n^+). Note that the single bond radius $R(\text{O})_{\text{s.b.}} = d(\text{OO})_{\text{s.b.}}/2 = 0.67 \text{ \AA}$ and that $R(\text{O})_{\text{s.b.}}/R(\text{O})_{\text{d.b.}} \sim (5^{1/2}/2) = \phi - 1/2 = 1.118$.

The oxygen atom (O) combines with the oxygen molecule (O_2) as shown in Fig.2c, which results in the formation of $\text{O}_3 = \text{O}^-\text{OO}^-$ as in Fig. 2d. This explains precisely the observed bond length $d(\text{O}^-\text{O})_{\text{obs}} = 1.28 \text{ \AA}$ in ozone as the simple sum,

$$d(\text{O}^-\text{O}) = R(\text{O}^-)_{\text{d.b.}} + a_{\text{B,O}} = 0.75 + 0.53 = 1.28 \text{ \AA} \quad (9)$$

The observed O^-OO^- bond angle, $\theta = 116.8^\circ$ (see Fig. 1) is shown in Figs. 2c,d. This is explained exactly by the ratio, $\cos(\theta/2) = 0.524 = R(\text{O})_{\text{s.b.}}/d(\text{O}^-\text{O})_{\text{obs}} = 0.67/1.28$, where $\theta/2 = 58.4^\circ$. The distance, $d(\text{O}^-\text{O}^-) = 2d(\text{O}^-\text{O})\sin(\theta/2) = 2*1.28*0.852 = 2.18 \text{ \AA}$. The bond lengths and angles in other simple molecules like H_2O , NO_2 , CO_2 , SO_2 , H_2CO_3 etc were similarly interpreted quantitatively in terms of the appropriate radii similarly in [14,15], for the first time. This previous work gave the author the enthusiasm to extend the method to ozone and chlorine oxides, described here.

2. Bond length in ClO in terms of the atomic and ionic radii of Cl and O:

The bond length, $d(\text{ClO})_{\text{obs}}$ is known to be 1.49 \AA , [4]. The covalent radius [4] of chlorine, $R(\text{Cl}) = d(\text{ClCl})/2 = 1.988/2 = 0.99 \text{ \AA}$ [4 LP] and the covalent double bond radius, $R(\text{O})_{\text{d.b.}} = d(\text{OO})_{\text{d.b.}}/2 = 0.60 \text{ \AA}$. Since $d(\text{ClO})_{\text{obs}} < [R(\text{Cl}) + R(\text{O})_{\text{d.b.}}] = 1.59 \text{ \AA}$, this bond length also has not found a simple explanation [4,16]. In this work, a new and simple explanation is given for the formation and structure of chlorine monoxide in terms of the atomic and Golden ratio based ionic radii of Cl and O.

The covalent bond length $d(\text{ClCl}) = 1.988 \text{ \AA}$ in the Cl_2 molecule is also the sum of the Golden ratio based ionic radii, $R(\text{Cl}^-)$ and $R(\text{Cl}^+)$ as shown:

$$d(\text{ClCl}) = 2R(\text{Cl}) = R(\text{Cl}^-) + R(\text{Cl}^+) \quad (10)$$

$$R(\text{Cl}^-) = d(\text{ClCl})/\phi = 1.23 \text{ \AA} \text{ and } R(\text{Cl}^+) = d(\text{ClCl})/\phi^2 = 0.76 \text{ \AA}. \quad (11)$$

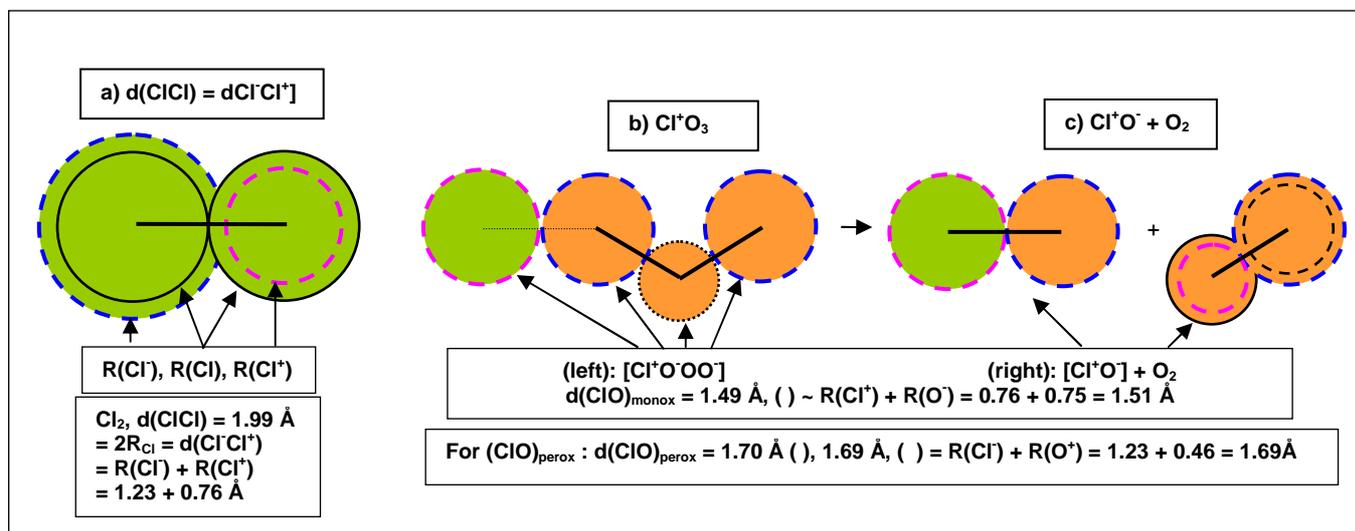


Fig. 3. Formation of ClO and degradation of ozone. a) the relative sizes of the Cl ion pair and covalent atomic radii; b) shows how the Cl^+ attaches to O^- of O_3 and c) shows how Cl^+O_3 splits into Cl^+O^- and O_2 . All the radii and bond lengths are given in the figure.

The ion pairs (which are Pauling's resonance forms) of the chlorine molecule are shown in Fig. 3e. It can be seen from Fig. 3f that Cl^+ combines with O^- of ozone and thereby breaks the latter and results in the formation of ClO and O_2 , see Fig. 3g. The sum of the ionic radii, $R(\text{Cl}^+)$ and $R(\text{O}^-)_{\text{d.b.}}$ is close to the observed value [4],

$$d(\text{ClO})_{\text{monox}} = R(\text{Cl}^+) + R(\text{O}^-)_{\text{d.b.}} = 0.76 \text{ \AA} + 0.75 \text{ \AA} = 1.51 \text{ \AA} \quad (12)$$

It is pointed out here that the radicals of Cl in the stratospheric reactions mentioned in [2] and elsewhere are treated here as the ionic resonance forms. All the ions have definite Golden ratio based radii, which account exactly for the known bond lengths.

3. Bond lengths and angles in ClOOCl in terms of the atomic and ionic radii of Cl and O.

Chlorine peroxide, ClOOCl , is another depleter of ozone and the paths of the reactions have been extensively studied [2,3,17-19]. The formation of this molecule from the ion pairs of molecules of chlorine and oxygen as shown,



is demonstrated in Fig. 4. This conforms with the known [2,3,17] bond lengths, $d(\text{ClO})_{\text{perox}} = 1.704 \text{ \AA}$ and $d(\text{OO}) = 1.426 \text{ \AA}$.

Figs. 4a, b show the ion pairs of both O_2 and Cl_2 . In Figs. 4c,d, they combine together as shown to form ClO and ClOOCl . The radii sum below is closest to the observed [2,3,17] bond length, $d(\text{ClO})_{\text{perox}} = 1.70 \text{ \AA}$,

$$d(\text{Cl}^-\text{O}^+)_{\text{perox}} = R(\text{Cl}^-) + R(\text{O}^+)_{\text{d.b.}} = 1.23 + 0.46 = 1.69 \text{ \AA} \quad (14)$$

and the distance $d(\text{O}^+ \text{O}^+) = 1.426$ [2,3,17] is close to the radii sum,

$$d(\text{O}^+ \text{O}^+) = R(\text{O})_{\text{s.b.}} + R(\text{O}^-)_{\text{d.b.}} = 0.67 + 0.75 = 1.42 \text{ \AA} \quad (15)$$

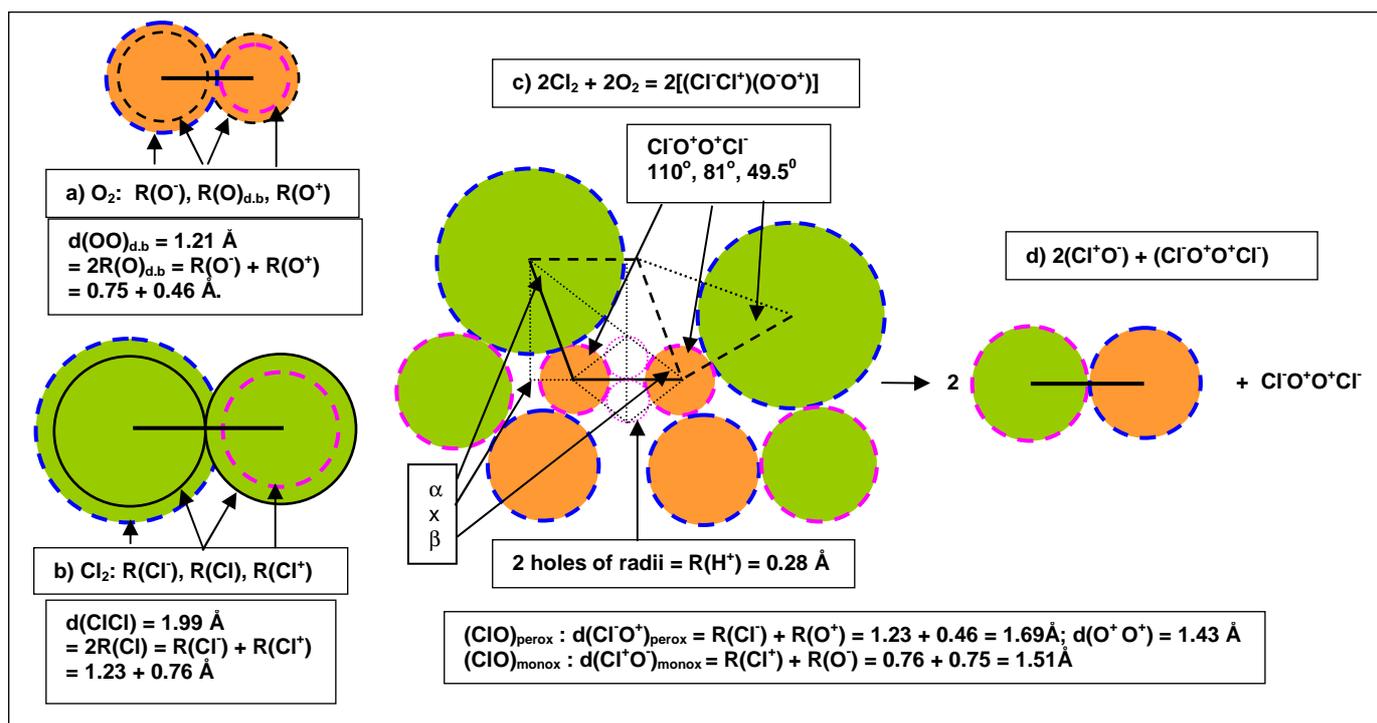


Fig. 4. a) oxygen (O_2), b) chlorine (Cl_2), c) combination of the ion pairs of O_2 and Cl_2 , to form ClOOCi (upper half) and 2ClO (lower half) and d) decomposition into 2ClO and ClOOCi . All the radii and bond distances are given in the Figure. The angle $\text{ClOO} = 110^\circ$ and the angle of the second ClO bond with the plane (marked by broken lines) of the ClOO group is 81° as per the data in [2,17].

The two holes at the centre marked by the dotted circles of radii $R(\text{H}^+) = d(\text{HH})/\phi^2$ (= the Golden ratio based cationic radius of H, [8]) suggest that the OO bond formation in chlorine peroxide takes place by the elimination (or assistance by hydrogen bridging [20]) of two H^+

ions as if from 2 molecules of hypochlorous acid HOCl. In the latter, the OCl bond length is 1.693 Å, [21] as in Eq. (14).

On denoting ClOOCl from left to right with the subscripts, Cl_aO_aO_bCl_b, the observed angle ClO_aO_b = 110⁰, makes the external angle XO_aCl_a = 180 - 110 = 70⁰ and the angle XCl_aO_a = 90 - 70 = 20⁰. The perpendicular distance, Cl_aX = d(ClO)_{perox} sin 70⁰ = 1.70*0.940 = 1.60 Å and XO_a = d(ClO)_{perox} cos 70⁰ = 1.70*0.342 = 0.58 Å. The distance XO_b = d(O_aO_b) + XO_a = 1.426 + 0.58 = 2.01 Å. The ratio, Cl_aX/XO_b = tan β = 1.60/2.01 = 0.796 and the angle β = 38.52⁰. Note that the ratio Cl_aX / Cl_aO_b = sin 38.52⁰ = 0.623 ~ 1/φ. Also, the ratio 2R(H⁺)/[d(O_aO_b)/2] = tan β = 0.56/0.713 = 0.785, β = 38.15⁰. The average value is β = 38.35⁰. The angle, α = O_aCl_aO_b = 180 - 110 - 38.35 = 31.65⁰. This is the same value as the angle, α = OO⁻O⁻ in ozone (see Fig. 2d).

Regarding the out of plane dihedral angle [17], 81⁰ (see Fig. 4c) in the isosceles triangle, with the base angles equal to (180 - 81)/2 = 49.5⁰, it is interesting that 49.5 + α = 81.15⁰.

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