New interpretation of the structure and formation of ozone based on the atomic and Golden ratio based ionic radii of oxygen

(Dedicated to Mario J. Molina, N. L., a pioneer in ozone research)

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*"Geometry has two great treasures: one is the theorem of Pythagoras, the other the division of a line into mean and extreme ratio. The first we may compare to a mass of gold, the second we may call a precious jewel. - On the Golden ratio, by **Johannes Kepler**, "*

Abstract

A decade ago, the Bohr radius of hydrogen atom was interpreted as the sum of two Golden sections pertaining to the electron and proton, and those of the bond length of a hydrogen molecule as the cationic and anionic radii. Subsequently, this result was shown to be applicable to other elements as well. Further, the bond lengths in the structures of molecules were found to be sums of the appropriate atomic and or the Golden ratio based ionic radii. Here, the formation and structure of ozone have been explained in terms of the atomic and ionic radii of oxygen.

Keywords: Ozone; oxygen; atomic radii; ionic radii; Golden ratio; bond length; bond angle

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1. Introduction

1.1. <u>O_3, an important guardian molecule in the stratosphere</u>

Ozone (O_3), named so in Greek for its smell, has been known for over two centuries [1]. It is formed by the reaction of atomic oxygen (O) with molecular oxygen (O_2) assisted by electric discharge or ultraviolet light [1],

$$O_2 + O ----> O_3 \tag{1}$$

The presence of ozone in the stratosphere, 10 - 50 km above the earth, protects the life on Earth from the harmful effects of the ultra violet (UV) radiation from the Sun [2, 3].

It was found [2, 3] that these important molecules are decomposed by terrestrial emissions of chlorofluoro carbons (CFC) which reach the stratosphere. The ozone depleted regions, called ozone holes let the harmful UV light penetrate down to Earth. Similar effects are caused also by other halo-carbons [2, 3]. As it is important to understand the chemical steps involved in the production and depletion of ozone, this work contributes to a simple and precise knowledge of the formation and structure of ozone at the atomic level.

Ozone is of chemical formula, OO_2 and structure, O^-OO^-, where the end atoms are negatively charged, see Fig. 1. They are both at equal distances, $d(OO^-)_{obs} = 1.278$ Å from the central oxygen, with which they form an obtuse angle of 116.78^o as shown in Fig. 1. A proper explanation of this bond length, $d(OO^-)_{obs}$ has long been a puzzle [1] since it is the mean of the covalent bond length $d(OO)_{s.b.} = 1.34$ Å [4] for a single bond (subscript, s.b.) and $d(OO)_{d.b.} = 1.21$ Å [5] for a double bond (subscript, d.b.),

$$d(OO^-)_{obs} = R(O)_{s.b.} + R(O)_{d.b.} = 0.67 + 0.61 = 1.28 \text{ Å} \tag{2}$$

where $R(O)_{s.b.} = d(OO)_{s.b.}/2$ and $R(O)_{d.b.} = d(OO)_{d.b.}/2$ are the single bond and double bond

covalent radii [4], respectively, of oxygen. The various reported values of the bond lengths and

bond angle for ozone are within about +/- 0.02 Å and +/- 1° respectively of the above values.

In this work, a new and simple explanation at the atomic level is given for the formation of

ozone as per Eq. (1) and for its bond length and angle (shown in Fig. 1) in terms of the Golden

ratio based ionic radius for oxygen; see [6, 7] for previous work. At the outset, a brief

introduction is provided here in sections 1.2 - 7 for the Golden ratio based ionic radii, [6].

1.2 The Golden ratio (ϕ)

The Golden ratio, also called the Divine ratio, has been known since Euclid (~300 BC) and is

denoted by the symbol, ϕ, after the Greek sculptor Phidias (~ 480 – 430 BC), [8]. It is found in

the geometry of the microscopic and macroscopic spontaneous creations of Nature, [8, 9]. It is

the ratio a/b of two parts a and b of a quantity d (= a + b), which are such that,

$$a/b = d/a = (a + b)/a = 1 + b/a \qquad (3)$$

On multiplying the first and last terms by a/b, one gets the Golden quadratic equation,

$$(a/b)^2 = (a/b) + 1 \qquad (4)$$

The +ve root of Eq. (4) is the Golden ratio ϕ of the two Golden sections, a and b,

$$a/b = (1 + 5^{1/2})/2 = 1.618... = \phi \qquad (5)$$

$$a = b\phi = d/\phi \text{ and } b = a/\phi = d/\phi^2 \qquad (6)$$

1.3 <u>Golden ratio in the Bohr radius ($a_{B,H}$) of the hydrogen atom (H):</u>

It was shown in [6], by considering the ionization potential of hydrogen (H) as the difference between those of the electron (e^-) and proton (p^+), that the Bohr radius, $a_{B,H}$ (which is the distance between the two particles, e^- and p^+), is divided at the point of electric neutrality into two Golden sections, a_{B,e^-} and a_{B,p^+} pertaining to the electron and proton, respectively. Thus, the following relations were established:

$$a_{B,H} = a_{B,e^-} + a_{B,p^+}; \quad a_{B,e^-} = a_{B,p^+}\phi = a_{B,H}/\phi \text{ and } a_{B,p^+} = a_{B,e^-}/\phi = a_{B,H}/\phi^2 \qquad (7a,b,c)$$

1.4 <u>The Golden sections of the bond length d(HH) in the hydrogen molecule (H_2):</u>

In the case of the hydrogen molecule (H_2), it was shown [6] that the observed bond length, $d(HH)_{obs}$ is the diagonal of a square with the Bohr radius ($a_{B,H}$) as a side. Therefore, $d(HH)_{obs}$ is also divided into two Golden sections, which give the radii of the cation (H^+) and anion (H^-),

$$d(HH)_{obs} = 2^{1/2}a_{B,H} = 2^{1/2}(a_{B,H}/\phi + a_{B,H}/\phi^2) \qquad (8)$$

$$= 2R(H) = d(H^-H^+) = R(H^-) + R(H^+) \qquad (9)$$

where, $R(H) = d(HH)/2$ is [4] the covalent radius, $R(H^-) = 2^{1/2}a_{B,H}/\phi = d(HH)/\phi = 0.618d(HH)$ and $R(H^+) = 2^{1/2}a_{B,H}/\phi^2 = d(HH)/\phi^2 = 0.382d(HH)_{obs}$ are the anionic and cationic radii, respectively. Therefore, $R(H^-) : R(H) : R(H^+) = (1//\phi) : 1/2 : (1/\phi^2) = 0.618 : 0.5 : 0.382$. For the value [4], $d(HH)_{obs} = 0.74$ Å, $R(H) = 0.37$ Å, $R(H^-) = 0.46$ Å and $R(H^+) = 0.28$Å.

Note: The ionic form, H^-, H^+ corresponds to the resonance structures [4] for the hydrogen molecule (HH) at the same equilibrium distance, d(HH).

1.5. Golden ratio based radius $R(H^+)$ explains the bond lengths of hydrogen halides (HX) and shows the additivity of ionic and atomic radii:

It was a great surprise to find that the radius, $R(H^+) = 0.28\text{Å}$ is exactly the value which Pauling [4] suggested (empirically) as the radius of H in hydrogen halides (HX), where X is the halogen. On subtracting $R(H^+)$ from the observed [4] bond lengths $d(HX)_{obs}$ in hydrogen halides, another surprising result was found [6],

$$d(HX)_{obs} - R(H^+) = R(X) = d(XX)/2 \tag{10}$$

where $R(X) = d(XX)/2$ is the covalent radius of X. This showed that the partial ionic character [4] of HX bonds is due to H^+ and that the Golden ratio based ionic radii and covalent atomic radii are additive.

1.6 Golden ratio based radius $R(H^+)$ explains the bond length in alkali metal hydrides (MH) and shows the additivity of ionic radii:

Yet greater surprise was found [6] on subtracting $R(H^+) = 0.28\text{Å}$ from the observed [4] bond lengths $d(MH)_{obs}$ in alkali metal (M) hydrides (MH) that,

$$d(MH)_{obs} - R(H^+) = d(MM)/\phi^2 = R(M^+) \tag{11}$$

where $d(MM)$ is the inter-atomic distance [10] in the metal lattice and $R(M^+)$, is the Golden ratio based radius of the alkali metal cation (M^+). Pauling [4] suggested (empirically) 0.03 Å as the radius of H in alkali metal hydrides. Therefore, the ionic character [4] of the MH bond is due to H^+ and M^+.

1.7. Golden ratio based ionic radius, R(M$^+$) explains the interionic distance in alkali halides (MX) and shows the additivity of ionic radii:

On subtracting the alkali metal ion radius, R(M$^+$) from the observed [4, 10] crystal ionic distance d(MX)$_{obs}$ in alkali halides (MX), it was astonishing to obtain [6],

$$d(MX)_{obs} - R(M^+) = R(X^-) = d(XX)/\phi \tag{12}$$

where R(X$^-$) is the Golden ratio based anionic radii of halogens. For full details and additivity of radii in bond lengths, see [6]. It was thus shown [6] that Pauling's radius ratio corrections [4] are not necessary to account for the crystal ionic distances in MX.

Since chemical processes, in general, involve transfer or sharing of electrons, 'Chemistry is electric' [11] and hence, the Golden ratio prevails in chemistry. The two sections below show the involvement of the Golden ratio in the formation and structure of ozone.

2.1. Bond length in O$_3$ in terms of the atomic and Golden ratio based ionic radii of oxygen

Ozone is formed from an oxygen molecule (O$_2$) and an oxygen atom (O) as per Eq. (1).

In the molecule of oxygen (O$_2$), the O=O double bond length d(OO)$_{d.b.}$ = 1.21 Å. Its Golden sections, R(O$^-$)$_{d.b.}$ and R(O$^+$)$_{d.b.}$ are given by (see Fig. 2a),

$$d(OO)_{d.b.} = R(O^-)_{d.b.} + R(O^+)_{d.b.} \tag{13}$$

$$R(O^-)_{d.b.} = d(OO)_{d.b.}/\phi = 1.21/\phi = 0.75 \text{ Å} \tag{14}$$

$$R(O^+)_{d.b.} = d(OO)_{d.b.}/\phi^2 = 1.21/\phi^2 = 0.46 \text{ Å} \tag{15}$$

In ozone, O$_3$ = O$^-$OO$^-$, the central oxygen atom (O) (see Fig. 2b) has a radius, a$_{B,O}$ = 0.53 Å as obtained [7] from its 1st ionization potential (which is close to that of H). The end anions (O$^-$)

have radii, $R(O^-)_{d.b.} = 0.75$ Å (see Eq. 14). The observed bond length, $d(OO^-)_{obs} = 1.28$ Å in ozone is simply the exact sum given by,

$$d(OO^-)_{obs} = R(O^-)_{d.b.} + a_{B,O} = 0.75 + 0.53 = 1.28 \text{ Å} \tag{16}$$

which in turn is also equal to the sum of the covalent radii in Eq. (2). However, Eq. (2) does not explain the negative charges on the two end oxygens in ozone, whereas Eq. (16) does. Fig. 2c shows the fusion of the oxygen molecule with the oxygen atom which results in the formation of ozone shown in Fig. 2d.

2.2. The bond angle in ozone

Turning now to the bond angle, $\theta_{obs} = 116.78^o$, the ratio of the sides, $x/d(OO^-)_{obs} = \cos(\theta/2)$, where $d(OO^-)_{obs} = 1.278$ Å and x is the perpendicular distance (shown by the dotted line in Fig. 2c,d) from the centre of the O atom to the line ($O^-..O^-$) joining the two end $\mathbf{O^-}$. Thus,

$$\cos(\theta/2)_{obs} = 0.524 = x/d(OO^-)_{obs} \tag{17}$$
$$x = 0.524 d(OO^-)_{obs} = 0.67 \text{ Å} = R(O)_{s.b} \tag{18}$$
$$\cos(\theta/2)_{obs} = R(O)_{s.b}/d(OO^-)_{obs} \tag{19}$$

Eq. (18) shows that $x = R(O)_{s.b}$, is the single bond covalent radius of oxygen. Therefore, the observed angle ($\theta/2$) is determined by the ratio, $R(O)_{s.b}/d(OO^-)_{obs}$ as shown in Eq. (19).

It is interesting to note the following: $R(O)_{s.b.}/R(O)_{d.b.} = 0.67/0.61 = 1.10 \sim 5^{1/2}/2 = 1.12 = \phi - 1/2$. The centers of the two dotted circles for $(OO)_{s.b.}$ and those of the two O^- make a rhombus (see Fig. 2c) with equal sides of length, 1.28 Å shown by the dotted lines, and with the

diagonals perpendicular to each other. The distance $d(O^- .. O^-)$ and angle θ_{obs} of the rhombus are related to ϕ as shown,

$$d(O^- .. O^-) = \tan(\theta_{obs}/2)d(OO)_{s.b.} = 2.18 \sim \phi d(OO)_{s.b.} = 2.17 \qquad (20)$$

$$(\theta_{obs}/2) = 58.39^o \sim \tan^{-1} \phi = 58.28^o \qquad (21)$$

where $\tan(\theta_{obs}/2) = 1.624 \sim \phi (= 1.62)$. For recent observations of association of oxygen molecules into rhomohedral units, see [12]. (*Note:* A water molecule has a similar rhombus with the HOH angle $\theta = 104.5^o$ and $\cos(\theta/2) = R(O)_{d.b.}/d(OH) \sim 1/\phi$, see [7]).

Thus Fig. 2 gives a neat, precise and simple explanation of the structures at the atomic level of the formation of ozone from oxygen molecule and atomic oxygen and accounts for the observed bond length (Eq. 16) and angle (Eq. 19) in O_3.

The ClO bond lengths in chlorine monoxide and peroxide [2], which decompose ozone were accounted for [6] similarly as the sums of the Golden ratio based ionic radii of Cl and O. The details of this will form the topic of the next paper on environmentally noxious molecules.

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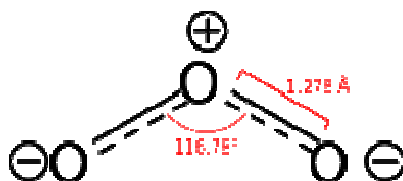
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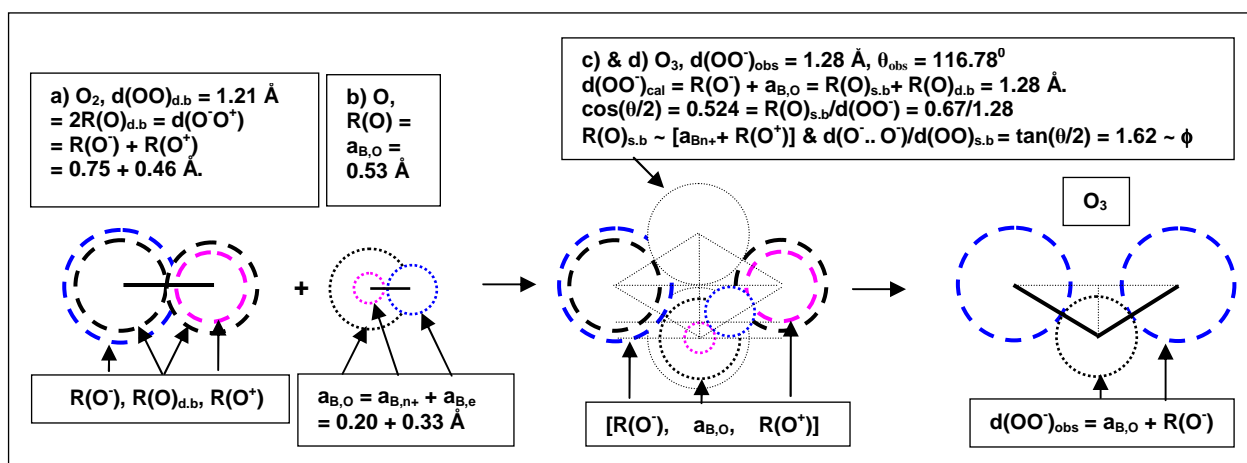

Fig. 1. Structural formula for Ozone from [1]

Fig 2. Details at the atomic level of the structure and formation of ozone from molecular and atomic oxygen.