

Bond Lengths in Carbon Dioxide, Carbon Monoxide and Carbonic Acid as Sums of the Atomic, Ionic and Bohr Radii

Raji Heyrovska¹ 

¹Na Stahlavce 6, 160 00 Praha 6, Czech Republic.

*Dedicated to Joseph Black (April 1728 - December 1799)

Abstract: Joseph Black is known for his pioneering work on "fixed air" which we know as carbon dioxide. This paper accounts for the different carbon to oxygen distances in carbon dioxide, carbon monoxide and carbonic acid in terms of the atomic, ionic and Bohr radii of the atoms, which are all related by the Golden ratio. The results confirm the author's work on the additivity of the appropriate radii of adjacent atoms or ions in the structures of small as well as big molecules.

Keywords: CO bond lengths, Atomic radii, Bohr radii, Golden ratio, Additivity of radii in bond lengths, Carbon dioxide, Carbon monoxide, Carbonic acid.

1. Introduction

1.1. General

Joseph Black¹ (16 April 1728 – 6 December 1799), a Scottish physician chemist and a fascinating personality, is known for his pioneering work on "fixed air" or carbon-dioxide. He was one of the founding pillars of the School of Chemistry of the University of Edinburgh, which is celebrating the tercentenary this year.

His predecessor, Jan Baptist van Helmont² (12 January 1580 – 30 December 1644) named the gas given off by burning charcoal as "gas sylvestre" (wood gas). Joseph Black made more fundamental studies of this gas by incinerating chalk and called it "fixed air". Antoine-Laurent de Lavoisier³ (26 August 1743 – 8 May 1794) investigated further the "fixed air" and discovered the importance of oxygen in combustion, and the gas has since been known as an oxide of carbon.

Carbon dioxide⁴ is an important respiratory gas and a fire extinguisher since it does not support fire. Its presence in the atmosphere keeps the Earth warm, but in larger concentrations it contributes to global warming along with other green house gases^{5,6}.

Here, the carbon to oxygen bond lengths and structures of carbon dioxide, carbon monoxide and carbonic acid are shown to be sums of the appropriate covalent atomic radii⁷, Golden ratio based ionic radii^{8,9} and Bohr radii^{10,11} from first ionization potentials.

1.2. Bohr radius and its Golden sections

The ground state Bohr radius ($a_{B,A}$) of atom A was calculated⁸⁻¹¹ from its first ionization potential ($I_{1,A}$) as in the case of hydrogen^{8,9},

$$a_{B,A} = (e/2\kappa I_{1,A}) = a_{B,e} + a_{B,n+}; a_{B,n+} = a_{B,A}/\phi^2 < a_{B,e} = a_{B,A}/\phi \quad (1)$$

where e is the charge, κ is the electrical permittivity of vacuum, $e/2\kappa = 7.1998 \text{ \AA.eV}$, $\phi = (1+5^{1/2})/2 = 1.618$ is the Golden ratio, also known as The Divine Ratio¹², $a_{B,e}$ and $a_{B,n+}$ are the two Golden sections of the Bohr radius pertaining to the electron and the nucleus, respectively⁸⁻¹¹. This gives the nucleus and the outer electron their own apportioned distances in the ground state Bohr radius of every atom.

1.3. Covalent bond length and its Golden sections

It was also shown in^{8,9} that the covalent bond length $d(AA)$ between two atoms (A) of the same kind are the sums of the cationic (R_{A+}) and anionic (R_{A-}) radii of the atom, which are the two Golden sections of the bond length, $d(AA)$,

$$d(AA) = 2R_A = R_{A+} + R_{A-}; R_{A+} = d(AA)/\phi^2 < R_A < R_{A-} = d(AA)/\phi \quad (2)$$

where, $R_A = d(A) = d(AA)/2$, the covalent radius⁷ is half the bond length, $d(AA)$.

1.4. Covalent and Bohr radii of atoms and structures of molecules

In another paper¹³, many radii of atoms, like van der Waals radii, valence shell radii and covalent radii were all shown to be linearly dependent on their Bohr radii, $a_{B,A}$ obtained from the first ionization potentials



Raji Heyrovska (Correspondence)



rheyrovs@hotmail.com



+

($I_{1,A}$). Thus, the ground state Bohr radius can be considered as a yard stick for the different radii of atoms. Further, it has been shown^{10, 11} that the covalent radii of all atoms are proportional to their respective Bohr radii, with the constant of proportionality (K_ϕ) as simple functions of the Golden ratio,

$$d(A) = R_A = K_\phi a_{B,A} \quad (3)$$

where $a_{B,A} = a_{B,e^-} + a_{B,n^+}$ (see Eq. 1) and $2d(A) = (R_{A^+} + R_A)/2$ (see Eq. 2).

The values of the Bohr radii, covalent radii, their Golden sections and the constant, K_ϕ in terms of the Golden ratio have all been tabulated in¹¹ for all the elements of the Periodic Table. Here, the data from¹¹ for the various radii of hydrogen, carbon, oxygen are given in **Table 1**. For carbon and oxygen, $K_\phi = (\phi^2 + 1)/2\phi = 1.118$

The bond lengths, bond angles and structures of some simple molecules like H_2^+ , O_2 , O_3 , H_2O , SO_2 , NO_2 and CO_2 have been explained in terms of the appropriate Bohr radii, covalent and ionic radii in¹⁴.

2.1. Bond length and structure of carbon dioxide

The molecule of carbon dioxide is known to be linear^{4,7} with both carbon to oxygen bonds of lengths of 1.16 Å. The covalent atomic radius of carbon obtained as half the interatomic distance, $d(CC)/2 = R_C$, has the following values⁷ for the single bond (sb), and double bond (db):

$$\begin{aligned} d(CC)_{sb}/2 &= R_{C,sb} = 0.77 \text{ \AA} & (4a) \\ d(CC)_{db}/2 &= R_{C,db} = 0.67 \text{ \AA} = (3^{1/2}/2) R_{C,sb} & (4b) \end{aligned}$$

It was shown in¹⁵ that these radii correspond to different distances in a tetrahedron. The graphitic/graphene radius¹⁵ (0.71 Å) of carbon, C_{gr} is nearly the mean of the single and double radii, which Pauling⁷ notes as 1.5 bond character. All the above different radii of the atom are demonstrated in Fig. 1 for C_{gr} as an example. The covalent single and double bond atomic radii of oxygen are $d(OO)_{sb}/2 = R_{O,sb} = 0.67 \text{ \AA}$ and $d(OO)_{db}/2 = R_{O,db} = 0.60 \text{ \AA}$.

It can be seen from the above radii that the bond length $d(CO)_{db} = 1.16 \text{ \AA}$ in carbon dioxide is not a sum of the double bond atomic radii of carbon and oxygen, $0.67 + 0.60 = 1.27 \text{ \AA}$.

The Bohr radii of C and O, using the first ionization potentials for C (11.260 eV) and O (13.618 eV) from¹⁶ and their sum have the values,

$$a_{B,C} = (e/2kI_{1,C}) = 0.639 \text{ \AA} \quad (5)$$

$$a_{B,O} = (e/2kI_{1,O}) = 0.529 \text{ \AA} \quad (6)$$

$$a_{B,C} + a_{B,O} = 1.168 \text{ \AA} = d(CO) \quad (7)$$

Eq. (7) accounts for the CO bond length in carbon dioxide, as shown in¹⁴. Fig. 2 a) shows the linear molecule drawn to scale.

2.2. Bond length and structure of carbon monoxide

For CO, the bond length has been found^{7,17} to be $d(CO) = 1.13 \text{ \AA}$. In this case, the radii of carbon and oxygen and their sum are given by,

$$\begin{aligned} R_{C,db} &= 0.67 \text{ \AA} & (8) \\ R_{O^+} &= 0.46 \text{ \AA} & (9) \\ R_{C,db} + R_{O^+} &= 1.13 \text{ \AA} = d(CO) & (10) \end{aligned}$$

This explains the partial ionic character of the CO bond⁷ as due to O^+ . This molecule is shown in Fig. 2 b).

2.3. Bond length and structure of carbonic acid

In carbonic acid^{7,18}, H_2CO_3 , all three CO bonds are of equal length⁷, 1.30 Å. This is accounted for by the radii sum,

$$\begin{aligned} R_{C,sb} &= 0.77 \text{ \AA} & (11) \\ a_{B,O} &= 0.53 \text{ \AA} & (12) \\ R_{C,sb} + a_{B,O} &= 1.30 \text{ \AA} = d(CO) & (13) \end{aligned}$$

Fig. 2 c) shows the structure and bond lengths in this molecule.

Thus, the bond lengths in all the three compounds have been accounted for by the sums of the appropriate radii of the adjacent atoms.

References

- [1] a) Ramsay, W., *The Life and Letters of Joseph Black, M.D.*, Constable and Company Ltd., London, 1918.
<http://archive.org/stream/cu31924012362806#page/n25/mode/2up>
 b) http://en.wikipedia.org/wiki/Joseph_Black
- [2] a) http://en.wikipedia.org/wiki/Jan_Baptist_van_Helmont
 b) http://people.mech.kuleuven.be/~erik/local_heroes.html
- [3] <http://en.wikipedia.org/wiki/Lavoisier>
- [4] http://en.wikipedia.org/wiki/Carbon_dioxide
- [5] Crawford, E., *ARRHENIUS: From Ionic Theory to the Greenhouse Effect*, Science History Publications, USA, 1966.
- [6] http://en.wikipedia.org/wiki/Greenhouse_gas
- [7] Pauling, L., *The Nature of the Chemical Bond*, Cornell Univ. Press, NY, (1960).
- [8] Heyrovská, R., *Molecular Physics*, **103**, 877 - 822, 2005.
- [9] Heyrovská, R., Chapter 12 in: *Innovations in Chemical Biology*, Editor: Bilge Sener, Springer.com, January 2009; (Proceedings of the 9th Eurasia Conference on Chemical Sciences, Antalya, Turkey, September 2006, invited talk)
- [10] Heyrovská, R., *International J. Sciences.*, Vol 2, 82-92, Issue-Mar-2013. <http://www.ijsciences.com/pub/pdf/V2-201303-19.pdf>
- [11] Heyrovská, R., *International J. Sciences.*, Vol 2, 63-68, Issue-Apr-2013, <http://www.ijsciences.com/pub/pdf/V2-201304-18.pdf>
- [12] Livio, M., *The Golden Ratio: The Story of PHI, the World's Most Astonishing Number*, Broadway Books, NY, (2002).
- [13] Heyrovská, R., *Philippine Journal of Science*, 137 (2): 133-139, 2008. Full text also in: <http://arxiv.org/ftp/arxiv/papers/0708/0708.1108.pdf> v(2).
- [14] Heyrovská, R., *International J. Sciences.*, Vol 2, 1-4, Issue-

Apr-2013, <http://www.ijsciences.com/pub/pdf/V2-201304-08.pdf>
 [15] Heyrovská, R., arXiv:0809.1957 [pdf]
 [16] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2013). NIST Atomic Spectra Database (ver. 5.1), [Online]. Available: <http://physics.nist.gov/asd> [2013, December 7]; <http://physics.nist.gov/cgi-bin/ASD/ie.pl?spectra=H->

DS+i&units=1&at_num_out=on&el_name_out=on&seg_out=on&shells_out=on&level_out=on&e_out=0&biblio=on
 [17] a) http://en.wikipedia.org/wiki/Carbon_monoxide
 b) Gero, L., Herzberg, G., Schmid, R., *Phys. Rev.*, **52**, 467, 1937.
 c) Glockler, G., *J. Phys. Chem.*, **62**(9), 1049-1054, 1958.
 [18] http://en.wikipedia.org/wiki/Carbonic_acid

Table 1. Ionization potential (I_1 in eV), Bohr radius ($a_{B,A}$) and its sections, a_{B,e^-} and a_{B,n^+} , covalent radius, $d(A)$, ionic radii, $d(A^-)$ and $d(A^+)$, the constant K_ϕ and $d(A)_{cal}$; (in Å)

Gp.	Atom	I_1	$a_{B,A}$	a_{e^-}	a_{n^+}	$d(A)$	$d(A^-)$	$d(A^+)$	K_ϕ	$K_\phi =$ (value)	$d(A)_{cal} =$ $K_\phi a_{B,A}$
1A	H	13.598	0.53	0.33	0.20	0.37	0.46	0.28	$1/2^{1/2}$	0.707	0.37
4A	C	11.260	0.64	0.40	0.24	0.71	0.88	0.54	$(\phi^2+1)/2\phi$	1.118	0.71
6A	O	13.618	0.53	0.33	0.20	0.60	0.75	0.46	$(\phi^2+1)/2\phi$	1.118	0.59

Figure legends.

Figure 1. Atomic, ionic and Bohr radii of C_{gr} (drawn to scale), see¹⁴.

Figure 2. Structures at the atomic level of a) carbon dioxide¹⁴, b) carbon monoxide and c) carbonic acid, with bond lengths based on additivity of the appropriate radii of atoms.

Figure 1

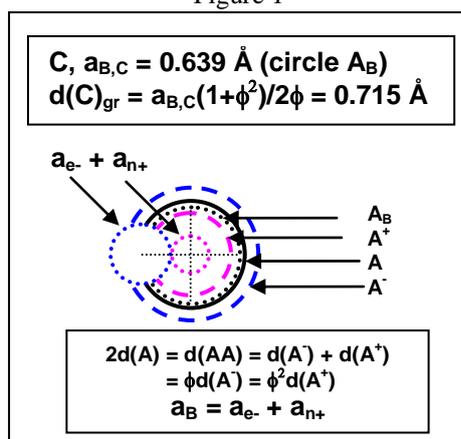


Figure 2

