Bond Lengths in Gaseous Alkali Metal Chlorides as Sums of the Golden Ratio Based Cationic Radii and Covalent Radius of Chlorine.

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Abstract: Alkali metal halides are known to have shorter bond lengths in the gaseous state than in their crystalline state. It is also known that the bonds are polar covalent. However, an exact interpretation of these bond lengths has remained an open question for the last 85 years. The present author has shown for the first time in 2004 that the crystal ionic distances in alkali halides are exact sums of the Golden ratio based radii of the alkali metal cations and halide anions. In this short report, it is shown that in gaseous alkali metal chlorides, alkali metal cations are bound to covalent chlorine as in the partially ionic bond in HCl.

Introduction

Experimental results by electron diffraction [1] showed that gaseous alkali halides have shorter bond lengths than in their crystalline forms. This result has intrigued many minds ever since and various explanations have been suggested. It was recognized that the bonds are polar covalent and an account of these can be found in [2]. The present author established [3, 4] that the crystal ionic distances, d(MX) in alkali halides ($M^+ X^-$, where M^+ is metal cation and X^- is the halogen anion) are exact sums of the Golden ratio (ϕ) based ionic radii of the metal and halogen ions. In general, it was also established over the years that interatomic bonding distances in all molecules including hydrogen bonds, are sums of the covalent atomic and or the Golden ratio based ionic radii of the adjacent atoms or ions, whether the bond is fully or partially covalent or ionic. For the collected work and a meeting presentation, see [5, 6]. Here, it shown that the additivity of Golden ratio based ionic radii of alkali metals and covalent radii of halogens holds even for the gaseous molecules.

Bond lengths in alkali metal chlorides.

It is found here that the bond lengths in gaseous alkali metal chlorides are given by,

$d(M^+X)_{gas} = R(M^+) + R(X)$

where the Golden ratio based ionic radius [3, 4], $R(M^+)_{ion} = d(MM)/\phi^2$ and $R(X)_{cov} = d(XX)/2$.

The bond length d(MM) is the distance between center to corner atoms of the body centered cubic alkali metals (which is shorter by a factor of 0.866 than the edge length which is involved in the crystalline alkali halides).

The experimental bond lengths $d(MX)_{gas}$ for MCl, where M = Na, K, Rb and Cs, from [1] reported in [2] are given in column 2 below (in Angstroms).

Table 1 Bond lengths of gaseous alkali chlorides and their correlation with the sum of Golden ratio-based metal ion radius and chlorine covalent radius.

MX	$d(MX)_{obs}$	d(MM)	$R(M^+)$	R(X)	$d(M^+X)_{sum}$
NaCl	2.51	3.66	1.40	0.99	2.39
KCl	2.79	4.52	1.73	0.99	2.72
RbCl	2.89	4.74	1.81	0.99	2.80
CsCl	3.06	5.00	1.91	0.99	2.90

It can be seen that the calculated sum in the last column is slightly less than the observed value in the column 2 by about 0.1 A. It is interesting to point out that in [1], the covalent radii of halogens are used as ionic radii to interpret the bond lengths. For values calculated by other methods, see [2].

NaCl bond lengths (< 2.51 A, [1]), for example 2.36 A for d(NaCl) have been reported [7 - 9], using spectroscopic methods. This value is close to the sum $a_{B,Na}$ (= 1.40 A) and R(Cl) (= 0.99 A), which is 2.39 A, where $a_{B,Na}$ is the atomic Bohr radius of Na and R(Cl) is the covalent radius of Cl. Since the Golden sections of the Bohr radius of Na give the radii of the positive nucleus and that of the outer electron (see [10] for the diagrams of each atom), the latter electron is shared by the Na and Cl atoms. It is interesting to note that $a_{B,Na} = R(M^+)$ (see the Table above).

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