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Bond Properties of Metal—Ligand Bonds

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An empirical relation has been developed to compute the bond order of ionic systems. The computed values have been compared with those calculated by using the experimental values of bond polarizability derivatives and are found to be in fair agreement. This shows that the proposed empirical relation for computing bond orders is quite suitable for ions.

(Keywords: Bond orders; Ionic systems, bond orders; Molecular orbitals)

Bindungseigenschaften von Metall—Ligand-Bindungen

Es wurde eine empirische Beziehung entwickelt, die die Berechnung von Bindungsordnungen für ionische Systeme erlaubt. Ein Vergleich der berechneten Werte mit solchen, die aus experimentellen Daten für Differentiale von Bindungspolarisierbarkeiten erhalten wurden, zeigte die Brauchbarkeit der Methode für Ionen.

Introduction

Bond order and bond polarizability derivatives are the important bond properties which provide direct information about the bonding electrons. With the advent of laser and its use as a source of light excitation in *Raman* spectroscopy, a great deal of research has been directed towards the measurement of the intensity of *Raman* active fundamentals. Such measurements permit the calculation of bond polarizability derivatives. Due to the fact that the bond order and bond polarizability derivative of a bond are closely related, it follows that bond order can now be properly estimated and various empirical relations verified. The present study has the objective of widening the scope of the earlier investigations on the bond properties so as to arrive at a reasonable conclusion in establishing the bond properties. For this purpose we have selected the ionic systems of the type $(A^{z+}B_n)^{z-nc}$, where z is the oxidation number, n is the ligancy and c is the valency of B.

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Theoretical Considerations

In the molecular orbital approach the bond order determines the number of electron pairs involved in bonding and provides information on the number of σ- and π-bonds between two atoms in a directional valence study. The quantum mechanical computation[1–5] (LCAO-MO) of bond order requires the knowledge of atomic orbitals, overlap integrals and electronic configurations which are rarely available for most of the compounds. Therefore, empirical formulae for estimating the bond order have been developed in literature[6–9]. But in case of ions, these empirical relations do not give satisfactory values of bond order as they are not in close agreement with the values estimated from *Raman* intensity measurements. However, for fractional bonds, an empirical relation proposed by *Pauling*[9] to determine the bond number is:

$$R = R(\text{A-B}) - 0.6 \log m \tag{1}$$

R and $R(\text{A-B})$ are the interatomic distances for a bond of fractional bond number and a single bond respectively, and m is the bond number. For a single bond the following formula was proposed:

$$R(\text{A-B}) = r_\text{A} + r_\text{B} - C\,|\chi_\text{A} - \chi_\text{B}| \tag{2}$$

r_A and r_B are the radii, χ_A and χ_B are *Pauling*'s electronegativities of atoms A and B, and C is the *Schomaker-Stevenson* coefficient[9].

Empirical Relation for Bond Order

The bond number, m, calculated from eqn. (1) is not equivalent to the bond order. We, therefore, directed our attention to seek some other properties which influence the bond order. Since the bond order and the corresponding stretching force constant are linearly related and also the effect of the oxidation state on the stretching force constant has been recognised, we are led to propose a relation of the form

$$N = m\frac{z}{n}, \tag{3}$$

where N is the bond order, z is the oxidation number and n is the number of ligands. Relation (1) can, therefore, be modified as to include the bond order, N, instead of bond number, m, and is given as

$$R = R(\text{A-B}) - 0.6 \log N - 0.6 \log\left(\frac{n}{z}\right). \tag{4}$$

Using the values 0.08 and 0.06 of C for systems involving oxygen and chlorine ligands respectively and zero for others in eqn. (2) for $R(\text{A-B})$, we calculated the value of bond order, N. Experimental values of bond polarizability derivatives[10, 11, 14, 15] have been used to estimate the values of bond order employing the relation of *Lippincott* and *Nagarajan*[12], viz.

$$\delta \bar{\alpha} \delta R = 13 \left(\frac{\sigma}{a_0} \right) A_{AB} N R^3 \qquad (5)$$

where $(\delta \bar{\alpha} / \delta R)$ is the bond polarizability derivative. R, N and a_0 are the

Table 1. *Comparsion of estimated* and calculated bond orders*

Ion	Bond Order Calc.	Bond Order Estim.	Ref.	Ion	Bond Order Calc.	Bond Order Estim.	Ref.
VO_4^{3-}	2.77	3.56	15	$CdBr_4^{2-}$	0.50	0.64	14
CrO_4^{2-}	3.08	4.12	15	$PtBr_4^{2-}$	0.44	0.41	10
MoO_4^{2-}	2.72	2.51	15	$AuBr_4^-$	0.94	1.08	10
WO_4^{2-}	2.16	2.44	15	$HgBr_4^{2-}$	0.68	1.04	14
ReO_4^-	2.76	2.29	15				
				SnF_6^{2-}	0.56	0.79	11
$ZnCl_4^{2-}$	0.34	0.27	14	$RhCl_6^{2-}$	0.51	0.53	11
$GaCl_4^-$	0.65	0.48	14	$PdCl_6^{2-}$	0.46	0.57, 0.51	11
$PdCl_4^{2-}$	0.37	0.39	10	$SnCl_6^{2-}$	0.45	0.62	11
$CdCl_4^{2-}$	0.30	0.31	14	$ReCl_6^{2-}$	0.54	0.41	11
$PtCl_4^{2-}$	0.35	0.33	10	$OsCl_6^{2-}$	0.38	0.43	11
$AuCl_4^-$	0.75	0.64	10	$IrCl_6^{3-}$	0.41	0.36	11
$HgCl_4^{2-}$	0.47	0.51	14	$PtCl_6^{2-}$	0.44	0.70, 0.67	11
ICl_4^-	0.61	0.54	10	$SnBr_6^{2-}$	0.47	0.79	11
$ZnBr_4^{2-}$	0.50	0.59	14	$OsBr_6^{2-}$	0.61	0.77	11
$GaBr_4^-$	1.06	1.07	14	$PtBr_6^{2-}$	0.55	0.84, 0.77	11
$PdBr_4^{2-}$	0.46	0.50	10	SnI_6^{2-}	0.84	0.89	11

* Bond polarizability derivatives are taken from corresponding references to estimate bond orders.

internuclear distance, bond order and first *Bohr* radius respectively. σ is the *Pauling* covalent character. A_{AB} is the root-mean-square delta function strength for a heteronuclear bond determined by the relation

$$A_{AB} = \sqrt{A_A A_B} \qquad (6)$$

where A_A and A_B (Ref.[13]) are the delta function strengths, respectively, for atoms A and B, constituting the bond.

Results and Discussion

The bond order for ions have been estimated from relation (5) using the experimental values of bond polarizability derivatives. These estimated values of bond order from the empirical relation (4) are compared in Tab. 1. It is obvious from the values quoted in the table that the calculated values are well comparable with the experimental ones. This agreement supports the suitability of the modified relation (4).

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