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Bond dissociation energies and bond orders for diatomic alkali halides

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The bond dissociation energies for Alkali halides have been estimated based on the derived relations:

$$D_{AB} = \bar{D}_{AB} + 31.973\ e^{0.363\Delta x} \text{ and}$$

$$D_{AB} = \bar{D}_{AB}(1 - 0.2075\Delta x r_e) + 52.29\Delta x,$$

where $\bar{D}_{AB} = (D_{AA} \cdot D_{BB})^{1/2}$, Δx represents Pauling electronegativity differences $(x_A - x_B)$ and r_e is the internuclear distance. A simplified formula relating bond orders, q, to spectroscopic constants is suggested. The formula has the form $q = 1.5783 \times 10^{-3}\ (\omega_e^2 r_e / B_e)^{1/2}$. The ambiguity arising from the Parr and Borkman relation is discussed. The present study supports the view of Politzer that $q/(0.5r_e)^2$ is the correct definition of bond order. The estimated bond energies and bond orders are in reasonably good agreement with the literature values. The bond energies estimated with the relations we suggested, for alkali halides give an error of 4.5% and 5.3%, respectively. The corresponding error associated with Pauling's equation is 40.2%.

Key words: Bond dissociation energy—bond order—eletronegativity—internuclear distance

1. Introduction

The bond dissociation energy of diatomic molecules is of fundamental importance in the studies of thermochemistry and astrophysics [1]. Dealing with molecular orbital theory, the bond order which is referred to as the amount of charge located on a bond, is of great importance in the calculation of various molecular parameters, e.g. dipole moment and oscillator strength. It also gives an insight into the understanding of the chemical properties associated with the bond. The procedure for the computation of the total bond order in a molecule involves the linear combination of atomic orbitals of the two atoms joined by the bond with suitable coefficients. This makes the computation of the total bond order a tedious job. However, using the simple model of Parr and Borkman [2, 3], Politzer [4] has shown that it works well for N_2, F_2, O_2 and B_2. As the model has also been found quite suitable for those molecules in which the ionic and covalent contributions to the bond are almost comparable, it was thought to be worthwhile to test the validity of the model for those molecules in which the ionic contribution is predominant. In view of their importance, it is proposed to evaluate bond dissociation energies and bond orders using the simple formulae for alkali halides.

Bond dissociation energies: In course of our studies on bond dissociation energies [5] it is assumed that the following relations are suitable to evaluate bond dissociation energies for alkali halides. The relations are

$$D_{AB} = \bar{D}_{AB} + 31.973\ \mathrm{e}^{0.363\Delta x} \tag{1}$$

$$D_{AB} = \bar{D}_{AB}(1 - 0.2075\Delta x r_e) + 52.29\Delta x \tag{2}$$

where $\bar{D}_{AB} = (D_{AA} \cdot D_{BB})^{1/2}$, Δx represents Pauling electronegativity differences $(X_A - X_B)$ and r_e is the internuclear distance. The necessary constants for the present study are taken from Huber and Herzberg [6] and Pauling [7].

As it has been pointed out by Matcha [8], Pauling's empirical relation $D_{AB} = \bar{D}_{AB} + 30\Delta x^2$ works badly for ionic molecules. Estimated bond energies will have an error of 190%. Keeping the above point in view, it is desirable now to have an accurate relationship for ionic molecules. The present work deals with the estimation of bond dissociation energies for alkali halides using Eqs. (1) and (2). For comparison, bond energies are computed with Pauling's relation also.

Recently Matcha [8] proposed a relation $[D_{AB} = \bar{D}_{AB} + K\{1 - \exp(-\alpha\Delta x^2)\}$, where $K = 103$ and $\alpha = 0.29]$ to evaluate bond energies. He has not given the electronegativity values appropriate to his model so far. In order to test the reliability of the above relation for ionic molecules, we have used the above relation with Pauling's electronegativities, and estimated bond energies. Some conclusions have been drawn by using Pauling's electronegativities in Matcha's formula (P-M relation).

Bond order: Parr and Borkman [2, 3] suggested the following relation for bond order:

$$q = (4R_e^3 K_e / 7\mathrm{e}^2)^{1/2} \tag{3}$$

In the present investigation, the authors proposed a simplified relation for q as follows:

$$q = 1.5783 \times 10^{-3}(\omega_e^2 r_e / B_e)^{1/2}. \tag{4}$$

Here the experimental values of ω_e, r_e and B_e determine the bond order.

Parr and Borkman extensively studied [2, 3] the measure of bond charge in the bond region. The main aim of this study is to test the difference in statements given by Parr and Borkman and Politzer for bond order. The necessary constants for the present study are taken from Huber and Herzberg [6].

2. Results and discussion

The calculated bond dissociation energies for alkali halides from Eqs. (1) and (2) are presented in Table 1 along with the values obtained from P-M relation and Pauling's expression. The average percentage deviation

$$\frac{(D_0)_{\text{obs}}-(D_0)_{\text{cal}}}{(D_0)_{\text{obs}}}\times 100$$

is also given. The bond order values calculated from Eq. (4) are presented in Table 2.

The results obtained from Eq. (2) reveal that the bond energy values for fluoride molecules deviate from the general trend. The predicted bond energies for fluorides have higher values than the experimental value by 24 kcal/mole. This value is deducted from the dissociation energy values obtained from Eq. (2) and are presented in Table 1. It is in excellent agreement with the view of Kushawaha

Table 1. Comparison of experimental and predicted bond energies for alkali halides

		predicted Bond energies from			
Molecule	D_{AB} (Exptl.)	Eq. (1)	Eq. (2)	P-M relation	Pauling
LiF	136.28	125.72	136.81	126.20	300.77
LiCl	111.67	104.58	106.21	109.24	158.33
LiBr	99.84	95.54	96.46	96.86	131.31
LiI	84.60	85.26	84.79	79.54	97.67
NaF	122.90	123.76	124.95	121.95	313.60
NaCl	97.54	100.18	104.08	106.00	163.98
NaBr	86.24	91.74	95.38	94.89	136.34
NaI	77.70	81.93	82.47	78.78	101.60
KF	116.91	122.99	126.79	118.65	328.09
KCl	100.08	97.19	104.31	103.65	171.36
KBr	90.16	89.21	96.04	93.78	143.16
KI	77.30	79.72	83.46	78.93	107.18
RbF	115.30	122.09	125.85	117.71	327.19
RbCl	100.08	96.06	103.18	102.72	170.23
RbBr	89.93	88.21	95.07	92.87	142.16
RbI	76.09	78.83	82.63	78.04	106.29
CsF	118.76	125.49	129.11	118.24	346.32
CsCl	105.61	98.21	105.35	105.34	183.26
CsBr	96.16	90.24	97.64	96.07	154.04
CsI	82.23	80.66	85.42	81.99	116.43
Average % deviation		4.5	5.3	3.4	40.2

Energies in kcal/mole

Table 2. Parameters q and $q/(0.5r_e)^2$ for alkali halides

Molecule	q (present work)	$q/(0.5r_e)^2$ (present work)	$q/(0.5r_e)^2$ (Pande et al. [16])
LiF	1.549	2.533	2.256
LiCl	1.717	1.682	1.674
LiBr	1.757	1.491	1.484
LiI	1.826	1.277	1.248
NaF	1.776	1.915	1.671
NaCl	1.900	1.364	1.273
NaBr	1.939	1.239	1.224
NaI	1.953	1.062	1.077
KF	1.881	1.596	1.588
KCl	2.091	1.135	1.135
KBr	1.981	0.995	1.027
KI	2.083	0.896	0.897
RbF	1.948	1.511	1.501
RbCl	2.029	1.045	1.073
RbBr	2.105	0.971	0.975
RbI	2.150	0.852	0.852
CsF	1.984	1.443	1.441
CsCl	2.146	1.016	1.021
CsBr	2.179	0.923	0.920
CsI	2.228	0.810	0.810

[9]. Several explanations [10–13] have been given for the deviation of fluoride from other halides. Normally the first member of a periodic group differs from the remaining members of the group. In the case of fluorine it is more pronounced. Politzer [14, 15] has exposed this odd behaviour by observing the weakening of bonding by fluorine to other elements compared with that expected on the basis of extrapolations from the heavier halogens. As a result of lower electron affinity, ionic compounds of fluorine have bond energies which are about 25.81 kcal/mole lower than values extrapolated from the other halides. This destabilization can be attributed to forcing a full electronic charge (or nearly one) on to the small fluorine atom. The same fact has been observed in some organic halides [9]. The estimated bond energy values obtained from Eq. (1) and P–M relation are in good agreement with the experimental values. This suggests that Matcha's electronegativities (still to be estimated) and Pauling's electronegativities for the atoms Li, Na, K, Rb, Cs, F, Cl, Br, and I are in the same order.

Parr and Borkman suggested that q is a measure of the charge located in the bond region and called this quantity bond order. Taking a few examples, Politzer [4] proved that the interpretation of q as bond order is not satisfactory. Politzer's relation for a realistic representation of bond order is $q/(0.5r_e)^2$.

The values of q are computed for alkali halides using Eq. (4). The values obtained are in good agreement with the values obtained from Eq. (3), i.e., the simplified Eq. (4) gives equally good values as the Borkman and Parr relation [3].

It is obvious from Table 2 that if q (from Eq. (3)) is taken as bond order, it leads to ambiguity. Proceeding from F to I, the value of q increases while the binding energy decreases. According to Parr and Borkman, KBr and CsF; RbI and CsCl have approximately the same values for q, 1.98 and 2.15, respectively (Table 2). It has no meaning to have the same bond order for all these molecules. The descrepancy may be removed by taking the relation $q/(0.5r_e)^2$ as bond order, given by Politzer. According to his definition the bond order values for the above molecules are different (Table 2). In order to calculate $q/(0.5r_e)^2$ for alkali halides in the present study the authors have used the q values obtained from Eq. (4). The present investigation supports the Politzer view that $q/(0.5r_e)^2$ is the correct definition for the bond order. The bond order values obtained for alkali halides are well comparable with the literature values [16].

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