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Theory of the Chemical Bond. Bond Ionicities and Bond Energies of Diatomic Molecules

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A revised simple method is proposed to calculated the ionicities and bond energies of diatomic molecules including hydrogen halides, interhalogen compounds, alkali hydrides, and alkali halides. The relative nuclear quadrupole coupling constants are evaluated to check the further validity of this method. It is shown that calculated values are consistent with available experimental values.

Introduction

Several attempts have been made to calculate the bond properties of diatomic molecules. Each method has been proposed to calculate a particular property of the bonds, which includes bond energy, dipole moment, or nuclear quadrupole coupling constant. Although most of the results are in good agreement with experiment, some systematic discrepancies are observed and a simple general treatment has not nearly developed.

The principle of electrongeativity equalization provided by Sanderson[1,2] has been used to calculate bond distances and energies of diatomic systems. However, as a result the charge distribution calculated from this principle is invariant with respect to bond distance, obviously an absurd result. Pauling[3] assigned electronegativity values to the elements in such a way that electronegativity difference could be used to predict the ionic character and the strength of a polar bond. But his method did not give a quantitatively good result. Rittner[4] proposed the polarizable spherical charge distribution method to describe the bond energies and dipole moments of alkali halide molecules, but nearly all the calculated values are slightly too low compared to available experimental data.

Klopman[5] has proposed that a molecule will reach its maximum stability when the potentials around each atom in each orbital are equalized; it is the total energy of the molecule which must be at a minimum for the equilibrium charge distribution. Ferreira[6] calculated the ionicities and bond energies of diatomic molecules by utilizing the idea of Klopman's, and partitioned the bond energy into a sum of a homopolar term and a heteropolar term. Later, Evans and Huheey[7] reexamined this method to describe the reactivity of hard and soft acid-base interactions in predominantly ionic compounds. However, these approaches do not give a quantitatively good result.

Also, the quantum mechanical techniques such as exchange perturbation theory[8] and implicit perturbation theory[9] have been used to analyze the dipole moments and bond energies of alkali halides. Recently, Parr *et al.*[10] have applied the Hohenberg-Kohn density functional theory[11] to describe the bond properties of diatomics, but many further studies are called for by this analysis.

In the present work, we have utilized the method of Evans and Huheey's[7] to a conceptually simple model of bonding and calculated the bond properties such as bond energies, dipole moments and nuclear quadrupole coupling constants of various diatomics. One of the primary purposes of the present work is to evaluate the effective net charges of atoms in diatomic molecules and to extend this method to the calculation of those in polyatomic molecules.

Methods

Total Bond Energy. The total bond energy E_{tot} is the sum of the covalent energy E_c, the electrostatic energy E_e, and the charge transfer energy E_x;[7]

$$E_{tot}=E_c+E_e+E_x \tag{1}$$

Covalent Energy. It is reasonable to assume the covalent bond formed between atoms of different sizes will overlap to an extent which is intermediate between those of the constituent atoms in homopolar bonds. This "overlap" factors (C) can be estimated from the square roots of the adjusted homopolar bond energies of the elements involved according to Pauling's assumption.[3] The contribution of nonbonding lone pairs to the destablization of the bonding, resulting from Pauli repulsion should be also considered in the calculation of the covalent bond energy. Thus, Evans and Huheey[7] have calculated the "repulsive" factors (R) from the difference between the extrapolated values and the experimental bond energies.

The contribution of covalent energy to a bond is inversely related to the ionicity of the bond. For a diatomic molecule AB the simple expression for the covalent energy can be written as

$$E_c = -f(\delta)\, E_h \tag{2}$$

where E_h is the homopolar bond energy. Following Pauling, the expected homopolar energy of the molecule AB is given by

$$E_h = C_A C_B - R_A R_B \tag{3}$$

In this work, we used the decreasing function of the ionicity, $f(\delta)$, as follows;

$$f(\delta) = 1 - \delta^2 \tag{4}$$

TABLE 1: Parameters[a]

Atom	C_i	R_i	a_i	b_i
H	10.21	0.00	7.18	6.43
Li	5.46	0.00	3.11	2.29
Na	4.12	0.00	2.81	2.34
K	3.88	0.00	2.90	1.44
Rb	3.22	0.00	2.68	1.48
Cs	3.20	0.00	2.36	1.77
F	10.70	8.83	12.18	8.68
Cl	9.56	5.78	9.38	5.65
Br	8.28	4.74	8.40	4.70
I	6.83	3.25	8.10	4.58

[a] Unit for C_i and R_i is (kcal/mol)$^{1/2}$, and units for a_i and b_i are kcal/mol. eu and kcal/mol. eu^2, respectively.

because the function is computationally much simpler than others and gives a good result.[6,7]

In Table 1, the revised overlap factors C_i's and repulsive factors R_i's are listed. The procedure of revision will be described later.

Electrostatic Energy. The electrostatic energy is calculated by using the Born-Landé equation;

$$E_e = \frac{A\,\delta_A \delta_B}{r_{AB}}\left(1 - \frac{1}{n}\right) \tag{5}$$

where A is the Madelung constant ($A = 1$ for the diatomics), δ_A and δ_B are the net charges of the atom A and B, and r_{AB} is the interatomic distance of the bond. The Born exponent n is taken as a constant value 8.

Charge Transfer Energy. The charge transfer energy associated with the transfer of electron density from one atom to another has followed the equation proposed by Jaffé *et al.*[12];

$$E_x = a_A\delta_A + b_A\delta_A^2 + a_B\delta_B + b_B\delta_B^2 \tag{6}$$

where the values of parameter a_i and b_i are adopted from the work of Jaffé's except those of Cs being newly estimated due to insufficient experimental data of ionization potential and electron affinity. In Table 1, we listed these values.

Bond Ionicities. As the charge is transferred from one atom to another, we must also take into account the simultaneous decrease in the covalent energy and increase in electrostatic and charge transfer energies.[6] Thus, to find the minimum total

TABLE 2: Ionicity and Dipole Moments of Hydrogen Halides and Interhalogen Compounds

Molecule	Bond Distance r_e (Å)	Ionicity δ (e.u.)	Dipole Moment μ(D)				
			This Work	K[a]	F[b]	EH[c]	Expl.[d]
HF	0.917	0.410	1.81	2.62	2.71	1.52	1.74 1.91
HCl	1.275	0.171	1.05	1.72	1.53	1.05	1.07
HBr	1.414	0.104	0.71	1.19	1.02	0.73	0.79
HI	1.604	0.075	0.57	0.43	0.53	0.57	0.38
ClF	1.628	0.159	1.24	2.23	1.44	1.23	0.88
BrF	1.756	0.230	1.94	3.03	2.02	1.97	1.29
IF	1.985	0.231	2.20	4.07		2.27	
BrCl	2.138	0.073	0.75	0.95	0.69	0.82	0.57
ICl	2.321	0.094	1.05	2.23	1.43	1.11	0.65
IBr	2.485	0.025	0.30	1.32		0.36	

[a] Ref 5 [b] Ref 6 [c] Ref 7 [d] Ref 15.

TABLE 3: Calculated and Experimental Bond Energies of Hydrogen Halides and Interhalogen Compounds[a]

Molecule	This Work	K[b]	P[c]	F[d]	EH[e]	P[f]	Expl.[g]
HF	132.8	135.4		111.4	119.1	153.4	134.0
HCl	101.9	100.4	97.0	90.2	89.5	99.7	102.2
HBr	86.0	85.2		80.2	82.4	86.5	86.5
HI	70.5	70.6		72.7	75.1	73.9	70.5
ClF	56.4	56.5		53.7	60.4	70.3	60.5
BrF	56.7	53.4		51.9	56.3	74.5	55.0
IF	55.2	48.3		50.6	50.8	88.1	46.0
BrCl	52.6	51.3	53	52.5	52.9	53.0	52.1
ICl	47.9	47.5	59	49.0	48.0	52.9	49.6
IBr	41.2	40.6	49	41.4	41.3	43.2	41.9

[a] Units in kcal/mol, [b] Ref 5, [c] Ref 16, [d] Ref 6, [e] Ref 7, [f] Ref 3, [g] Ref 17.

TABLE 4: Components of Bond Energies of Hydrogen Halides and Interhalogen Compounds[a]

Molecule	E_c	E_e	E_x	E_{tot}
HF	−90.9	−53.1	11.2	−132.8
HCl	−94.7	−6.7	−0.5	−101.9
HBr	−83.6	−2.2	−0.2	−86.0
HI	−69.3	−1.0	−0.2	−70.5
ClF	−50.0	−4.5	−1.9	−56.4
BrF	−44.3	−8.7	−3.7	−56.7
IF	−42.0	−7.8	−5.4	−55.2
BrCl	−51.5	−0.7	−0.4	−52.6
ICl	−46.1	−1.1	−0.7	−47.9
IBr	−41.1	−0.1	0.0	−41.2

[a] Units in kcal/mol.

energy of the diatomic molecule AB, the total bond energy is differentiated with respect to the ionicity of the bond AB, that is

$$dE_{tot}/d\delta = 2\delta\,(C_A C_B - R_A R_B) - \frac{2\delta A}{r_{AB}}\left(1-\frac{1}{n}\right) + (a_A - a_B) + 2\,(b_A + b_B)\,\delta = 0 \tag{7}$$

where $\delta = \delta_A - \delta_B$.

From eq 7, we can calculate the ionicity of the bond AB.

In present work, the values of parameters C_i and R_i are revised from fitting the calculated dipole moments and bond energies of hydrogen halides and interhalogen compounds to the experimental data (shown in Table 1). The dipole moment μ is calculated with the product of the ionicity δ and the experimental interatomic distance r_{AB}.

Results and Discussion

We have calculated the dipole moments and bond energies of hydrogen halides (HF, HCl, HBr and HI), interhalogen compounds (ClF, BrF, IF, BrCl, ICl and IBr), alkali hydrides (LiH, NaH, KH, RbH and CsH), and alkali halides (LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr and CsI). All the interatomic distances are taken from the experimental values.[14]

Hydrogen Halides and Interhalogen Compounds. In Table 2, the calculated ionicities of hydrogen halides and interhalogen compounds have been shown. The dipole mement is simply calculated by the product of the ionicity and the experimental interatomic distance. Although the total electric moment is given by the vector sum of the primary, overlap, and lone pair electron moments,[13] only the primary moment is considered because one of the important purposes of this work is to calculate the effective charges of atoms involved in diatomic molecules and the resultant net charges give quantitatively good bond energies. The calculated dipole moments show the good agreement with experimental data.

Table 3 shows the calculated bond energies of hydrogen

TABLE 5: Ionicities and Dipole Moments of Alkali Hydrides and Halides

Molecule	Bond Distance[a] r_e (Å)	Ionicity δ (e.u.)	This Work	Dipole Moment $\mu(D)$						
				K[b]	F[c]	MK[d]	DW[e]	T-Ritt[f]	Ritt[f]	Expl[g]
LiH	1.595	0.628	4.816	4.51						
LiF	1.564	0.833	6.257	6.63	6.83	6.153	6.04	5.392	5.311	6.284
LiCl	2.021	0.790	7.671	8.30	8.26	7.128	6.75	5.331	5.241	7.085
LiBr	2.170	0.841	8.771	8.67	8.88	7.210	7.10	5.491	5.408	7.226
LiI	2.392	0.775	8.907	9.33	9.39	7.361	7.44	5.453	5.375	7.429
NaH	1.887	0.558	5.058	5.40						
NaF	1.926	0.733	6.786	8.14	7.73	8.129	8.02	7.656	7.492	8.123
NaCl	2.361	0.753	8.545	9.72	9.07	8.917	8.94	8.004	7.773	8.972
NaBr	2.502	0.802	9.647	10.17	9.63	9.073	—	8.188	7.960	9.092
NaI	2.712	0.757	9.865	10.69	10.02	9.247	—	8.227	7.992	9.210
KH	2.244	0.539	5.808	7.00						
KF	2.172	0.758	7.914	9.41	9.18	8.555	8.61	8.504	8.074	8.558
KCl	2.667	0.815	10.448	11.37	10.60	10.217	10.25	9.749	9.181	10.238
KBr	2.821	0.897	12.156	11.94	11.40	10.601	10.79	10.137	9.575	10.603
KI	3.048	0.857	12.546	12.66	12.00	11.070	11.41	10.502	9.921	11.05
RbH	2.367	0.561	6.378	7.51						
RbF	2.270	0.778	8.489	9.84		8.530		8.603	8.001	8.513
RbCl	2.787	0.849	11.375	11.93		10.450		10.225	9.449	10.483
RbBr	2.945	0.935	13.237	12.53		10.956				
RbI	3.177	0.889	13.575	13.28		11.638				
CsH	2.494	0.528	6.327	8.14						
CsF	2.345	0.748	8.432	10.27		7.831	7.96	8.217	7.278	7.849
CsCl	2.906	0.796	11.112	12.56		10.417	10.51	10.474	9.364	10.358
CsBr	3.072	0.859	12.674	13.21		11.294				
CsI	3.315	0.821	13.073	14.04		12.436	12.12	11.727	10.610	1

[a] Ref 14; [b] Ref 5; [c] Ref 6; [d] Ref 9; [e] Ref 18; [f] As calculated by Brumer and Karplus, ref 8; [g] Taken from references in ref 8.

halides and interhalogen compounds. The results show the good agreement between theory and experiment. The components of bond energies of hydrogen halides and interhalogen compounds are listed in Table 4. It is found that the contribution of the covalent term to the total bond energy is dominant and that the contribution of the electrostatic term to the bond energy increases as the bond ionicity increases. There is an interesting fact for HF that the charge transfer energy is a large positive value due to the larger ionicity of the molecule.

Alkali Hydrides and Halides. Table 5 shows the calculated ionicities and primary dipole moments of alakli hydrides and halides. The results show the good agreement between theory and experiment. In Table 6, the calculated bond energies of alkali hydrides and halides are shown and show satisfactory agreement with experimental values. The components of bond energies are also listed in Table 7. It is found that the contribution of the electrostatic energy term to the total bond energy is dominant and the second significant term to the bond energy is the covalent energy term. Also the charge transfer energy is significant for the cases of alkali fluorides and chlorides.

Nuclear Quadrupole Coupling Constants. Nuclear quadrupole coupling constants in molecules have been shown to be closely correlated with molecular electronic structure and in favorable cases to give fairly clear evidence about the nature of chemical bonds, particularly in the case of halogen compounds.[20]

We find a satisfactory correlation between experimental values of quadrupole coupling constants and calculated net charges (*i.e.*, ionicities) by using the following equation;

$$eQq/eQq_0 = 1 + \alpha\beta + \beta\delta^2 \tag{8}$$

where eQq_0 and eQq are the experimental nuclear quadrupole coupling constants of halogens in the homo-and hetero-nuclear diatomics, respectively. The constant α and β have been estimated from fitting the experimental data[20] to the equation. In order to consider a contribution to the electric-field gradient from dipolar polarization, the second-order equation is adopted. We obtained the best fit values of 2.191 and 1.187 for α and β, respectively. The results are shown in Figure 1, and the agreement between calculated and experimental values shows a validity of this work.

Conclusion

The revised attempt is proposed to evaluate the ionicities and bond energies of diatomic molecules such as hydrogen halides, interhalogen compounds, alkali hydrides, and alkali halides. To check the further validity of this work, the relative nuclear quadrupole coupling constants are calculated. The results show the good agreement between theory and experiment. It is to be

TABLE 6: Calculated and Experimental Bond Energies of Alkali Hydrides and Halides[a]

Molecule	This Work	K^b	F^c	EH[d]	P^e	Expl.[f]	
LiH	85.2	62.3		74.6	88.8	58	
LiF	145.5	125.1	140.0	115.5	301.1	137	137.5[g]
LiCl	109.3	109.6	113.7	93.4	159.2	115	111.9
LiBr	96.5	99.0	96.7	83.8	132.2	101	100.2
LiI	81.9	84.9	80.3	75.9	98.4	81	84.6
NaH	70.2	50.5		68.2	86.5	47	
NaF	123.3	106.7	113.5	112.3	314.0	107	114.0
NaCl	96.4	96.7	103.1	90.5	164.6	98	97.5
NaBr	85.9	87.3	88.9	82.0	137.1		86.7
NaI	74.3	75.2	74.3	74.0	102.3	71	72.7
KH	66.2	46.5		61.1	86.4	43	
KF	122.7	105.2	111.0	107.2	328.3	118	117.6
KCl	97.9	97.1	106.5	89.3	171.8	101	101.3
KBr	89.1	88.5	92.8	83.0	143.7	91	90.9
KI	77.9	77.1	78.4	75.3	107.7	77	76.8
RbH	61.9	46.0		63.4	85.2	39	
RbF	119.7	105.0		109.1	327.6	119	
RbCl	96.4	97.0		91.3	170.9	102	
RbBr	88.4	88.4		84.5	142.9	90	
RbI	77.5	77.3		77.4	107.0	77	
CsH	62.1	46.3			92.2	42	
CsF	119.0	106.1			346.5	121	
CsCl	95.0	98.4			183.6	101	
CsBr	86.3	90.0			154.5	91	
CsI	76.1	79.0			116.9	75	

[a] Units in kcal/mol; [b] Ref 5; [c] Ref 6; [d] Ref 7; [e] Computed with the formular $D_{AB} = \overline{D}_{AB} + 30\Delta X^2$ and Pauling's electronegativity values, $\overline{D}_{AB} = (D_{AA}D_{BB})^{1/2}$: Ref 9; [f] Ref 17; [g] Ref 19.

TABLE 7: Components of Bond Energies of Alkali Hydrides and Halides[a]

Molecule	E_c	E_e	E_x	E_{tot}
LiH	−33.7	−71.9	20.4	−85.2
LiF	−17.9	−128.8	1.2	−145.5
LiCl	−19.6	−89.8	0.1	−109.3
LiBr	−13.2	−94.7	11.4	−96.5
LiI	−14.9	−73.0	6.0	−81.9
NaH	−29.0	−47.9	6.7	−70.2
NaF	−20.4	−81.1	−21.8	−123.3
NaCl	−17.0	−69.8	−9.6	−96.4
NaBr	−12.2	−74.8	1.1	−85.9
NaI	−12.0	−61.4	−0.9	−74.3
KH	−28.1	−37.6	−0.5	−66.2
KF	−17.6	−77.0	−28.1	−122.7
KCl	−12.4	−72.4	−13.1	−97.9
KBr	−6.3	−82.9	0.1	−89.1
KI	−7.1	−70.0	−0.8	−77.9
RbH	−22.5	−38.6	−0.8	−61.9
RbF	−13.6	−77.5	−28.6	−119.7
RbCl	−8.6	−75.2	−12.6	−96.4
RbBr	−3.3	−86.4	1.3	−88.4
RbI	−4.6	−72.3	−0.6	−77.5
CsH	−23.6	−32.5	−6.0	−62.1
CsF	−15.1	−69.4	−34.5	−119.0
CsCl	−11.2	−63.3	−20.5	−95.0
CsBr	−7.0	−69.7	−9.6	−86.3
CsI	−7.1	−59.0	−10.0	−76.1

[a] Units in kcal/mol.

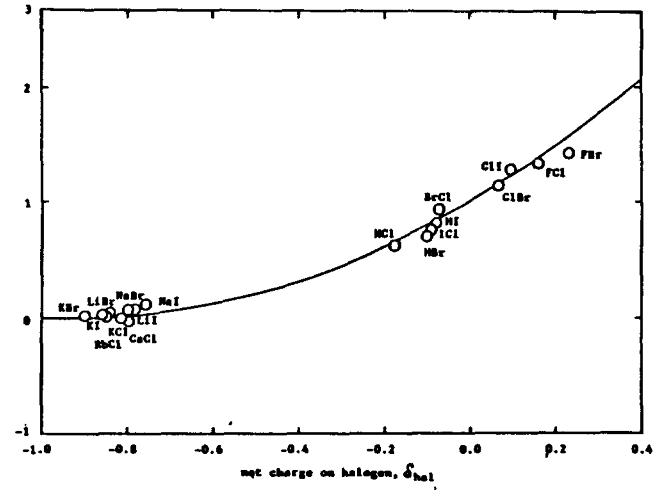

Figure 1. Plot of the relative nuclear quadrupole coupling constant eQq/eQq_0 of halogens in diatomic molecules vs. net charge (ionicity) on halogens δ_{hal}. The solid line and the open circles represent the calculated values and the available experimental data,[20] respectively. net charge on halogen, δ_{hal}

expected that this simple method might give a good result of bond ionicities and bond energies for polyatomic molecules, which we are currently investicgating.

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