

Binding energy and dissociation energy of alkali halide and alkali hydride molecules

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Theoretical evaluation of molecular spectroscopic constants is of considerable importance for the understanding of the nature of chemical bonding in the molecules. Binding energy and dissociation energy are calculated for 20 alkali halides and 5 alkali hydrides using the modified Rittner model or T-Rittner model. Polarizability of the molecules and effect of van der Waals dispersive force are considered in this interaction potential model (IPM). Four forms of repulsive interactions suggested by Born-Mayer (BM), Hellmann (Hm), Varshni-Shukla (VS) and Ali-Hasan (AH) are used here. The aim of the present work is to show the relative merit of the IPM in predicting the spectroscopic constants of diatomic molecules (alkali halides and alkali hydrides) like binding energy and dissociation energy.

Keywords: Binding energy, dissociation energy of alkali halide, alkali hydride molecules.

Introduction

The present work shows that the interaction potential energy function is applicable to describe the binding energy and dissociation energy in the molecular or gaseous state. Short range repulsive interaction is essential of the interaction potential energy function. Here four forms of repulsive interactions are used.

The interaction potential model (IPM) was first developed by Rittner (R-2). This model is one of the simple models by which the spectroscopic constants of diatomic molecules can be determined. The IPM is based on the concept that the attractive and repulsive forces in the system balance each other so that the system remains in equilibrium and becomes stable.

The simple form of the model is

$$U(r) = -Z_1 Z_2 \frac{e^2}{r} + \Psi_R(r) \quad (1)$$

where the first term is the coulomb energy due to force of attraction operating between the positive ($+Z_1e$) and negative ($-Z_2e$) charges. The second term is the repulsive interaction arising from the mutual overlap of the electron clouds between two combining ions. This model is actually suitable for ionic molecules. Various workers have suggested various forms of the repulsive interactions for the evaluation of molecular constants and achieved limited success. This led

us to improve the theoretical results by suggesting certain modifications in the IPM.

The shortcoming in their results may be due to the omission of the polarizability of the molecules, covalent effect and effect of van der Waals dispersive force. Considering these effects in the interaction potential model is now be expressed as

$$U(r) = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{c}{r^6} + \Psi_R(r) \quad (2)$$

where e is the electronic charge, r is the inter nuclear separation, α_1 and α_2 are the electronic polarizabilities of cation and anion respectively and c is the van der Waals constant in the molecular state. This model is called Polarizable Ion Model (PIM). The first term is the electrostatic interaction energy, the second term is the polarization energy, third term is the van der Waals dipole-dipole energy and $\Psi_R(r)$ is the short-range repulsive interaction.

Method of analysis:

General form of repulsive interactions is $\Psi_R(r) = (S_i/r^m) \exp(-r^n/\rho_i)$, where S_i , ρ_i , m , n are potential parameter. S_i is the repulsive strength parameter and ρ_i is the repulsive softness parameter.

Four forms of overlap repulsive interactions which have been used in our calculation, suggested Born-Mayer (BM), Hellmann (Hm), Varshni-Shukla (VS) and Ali-Hassan (AH)

are expressed as

$$\text{Born-Mayer (BM): } \Psi_R(r) = S \exp\left(-\frac{r}{\rho}\right) \quad (3)$$

($m = 0, n = 1$)

$$\text{Hellmann (Hm): } \Psi_R(r) = \frac{S_1}{r} \exp\left(-\frac{r}{\rho_1}\right) \quad (4)$$

($m = 1, n = 1$)

$$\text{Varshni-Shukla (VS): } \Psi_R(r) = \frac{S_2}{r^2} \exp\left(-\frac{r}{\rho_2}\right) \quad (5)$$

($m = 2, n = 1$)

$$\text{Ali-Hassan (AH): } \Psi_R(r) = \frac{S_3}{r^2} \exp\left(-\frac{r^{\frac{3}{2}}}{\rho_3}\right) \quad (6)$$

$$m = 2, n = \frac{3}{2}$$

The PIM model (eq. (2)) depends on the electronic polarizabilities (α_1 and α_2) of the ions. From Pouling's analysis (R-1) for free ions and from other worker's (R3-R7) we know that the electronic polarizabilities of ions in a molecule are differ from the free state polarizabilities because of the existence of the coulomb potential. The polarizability of an anion is decreased at the cation site and that of a cation is increased at the anion site. Hence the coulomb potential is negative at the cation site and positive at the anion site.

The electronic polarizability of an ion in free state is (R-8)

$$\alpha_f = \frac{e^2 h^2 n}{4\pi^2 m E_f^2} \quad (7)$$

where e and m are the charge and mass of electron respectively, n is the total number of electrons in the ion, h is Planck's constant and E_f is an energy parameter, pertaining to the free ionic state.

α_1 and α_2 are calculated by the expression for the molecular state polarizabilities according to the energy level analysis of (R-8)

$$\alpha_1 = \frac{e^2 h^2 n}{4\pi^2 m (E_f - e\phi_c)^2} \quad (8)$$

$$\alpha_2 = \frac{e^2 h^2 n}{4\pi^2 m (E_f + e\phi_c)^2} \quad (9)$$

where $\phi_c = \frac{e}{r}$, E_f is calculated from the expression of eq. (7).

Calculating the values of α_1 and α_2 from eqs. (8) and (9) van der Walls dipole-dipole energies (W_{d-d} or $\frac{c}{r^6}$) are calculated from the Slater-Kirkwood vibrational approach (R-9)

$$\frac{c}{r^6} = W_{d-d} = -\frac{3e\hbar}{2m^{1/2}r^6} \frac{\alpha_1\alpha_2}{\left[\left(\frac{\alpha_1}{N_1}\right)^{1/2} + \left(\frac{\alpha_2}{N_2}\right)^{1/2}\right]} \quad (10)$$

where N_1 and N_2 are the effective numbers of electrons in the ions (R-9, -10). This method is one of the best method to evaluate the van der Walls dipole-dipole energy in ionic diatomic molecules.

The various contributions except the last term $\Psi_R(r)$ to the binding energy of the alkali halide or alkali hydride molecule as expressed in eq. (2) are calculated from the data on polarizabilities and inter nuclear distances.

The last term $\Psi_R(r)$ is the short range repulsive interactions can be known by a potential with an exponential dependence on inter ionic distance. Various workers are used an exponential form for the repulsion between ions in an alkali halide or alkali hydride molecule.

Here four potential forms which are used in calculation are suggested by Born-Mayer (BM), Hellmann (Hm), Varshni-Shukla (VS) and Ali-Hasan (AH). The parameters which are contained in each potential forms are calculated by molecular equilibrium criteria and molecular force constant condition:

$$\left(\frac{dU(r)}{dr}\right)_{r=r_e} = 0 \quad (11)$$

$$\left(\frac{d^2U(r)}{dr^2}\right)_{r=r_e} = k_e \quad (12)$$

where k_e is the force constant related to vibrational frequencies. The potential parameters S_i and ρ_i are calculated from eqs. (2), (3), (4), (5), (6), (11) and (12) using the experimental data (R-11) on r_e and k_e . By the values of these parameters we can determined the molecular state properties like the binding energy (D_i) and dissociation energy (D_e) to test the suitability of the four potential form and to investigate the

effect of calculated polarizabilities and van der Waals energies.

The relations for the expression of binding energy (D_i) and dissociation energy (D_e) are (R-14)

$$D_i = -N U(r_e) \quad (13)$$

$$D_e = D_i + E - I \quad (14)$$

where N is the Avogadro number and r_e is the equilibrium inter-nuclear separation, E is the electron affinity and I is the ionization potential.

The value of E and I are taken from R-21.

The results of D_i and D_e for 20 alkali halides and 5 alkali hydrides are compared with the experimental value (R-3) (R-17) in Tables 1, 2, 3 and 4.

Results and discussion

The aim of the present investigation is to study relative superiority of four form of repulsive interaction within the frame work of PIM for predicting the binding energy and dissociation energy of diatomic molecules like alkali halides and alkali hydrides.

The present work gives better understanding of the nature of inter-atomic forces.

It is clear that the inclusion of the van der Waal's terms in the potential energy functions improves the theoretical results on binding energy (D_i) and dissociation energy (D_e) values. The theoretical value of D_i and D_e also better agreement with the experimental values for the consideration of electronic polarizabilities in the potential energy function.

It is clear from the study of Table 1 that the theoretical values of binding energy (D_i) of 20 alkali halide molecules calculated with VS model show the least average percentage deviation from the experimental results compared to other three potential models.

Table 2 clearly depict that the theoretical values of dissociation energy (D_e) of 20 alkali halide molecules calculated with AH model show the least average percentage deviation from the experimental results as are evident from the deviations in case of BM, Hm and VS potential models.

The theoretical values of binding energy (D_i) of 5 alkali hydride molecules calculated with BM model show the least average percentage deviation from the experimental results as Table 3 clearly shows.

In Table 4 the theoretical values of dissociation energy

Table 1. Calculated values of binding energy (D_i) (kcal/mol)

	Expt.	BM	Hm	VS	AH
LiF	184.1	179.72	178.25	176.56	179.57
LiCl	153.3	145.3	144.3	143.19	145.48
LiBr	147.4	137.87	136.96	135.95	138.12
LiI	138.7	127.31	126.5	128.34	127.6
NaF	153.9	151.70	151.09	150.42	152.05
NaCl	132.9	127.31	126.83	126.31	127.67
NaBr	127.7	121.48	121.0	120.49	121.84
NaI	120.3	113.45	112.57	112.06	113.39
KF	139.2	140.25	139.51	138.7	140.68
KCl	118.0	115.81	115.35	114.86	116.22
KBr	113.6	109.28	108.79	108.27	109.66
KI	106.1	102.69	102.3	101.88	103.07
RbF	133.6	136.18	135.49	134.73	136.64
RbCl	133.4	111.27	110.83	110.33	111.67
RbBr	109.0	106.48	106.08	105.66	106.88
RbI	101.9	99.38	99.03	98.66	99.76
CsF	130.5	135.13	134.31	133.33	135.52
CsCl	112.3	109.35	108.92	108.46	109.8
CsBr	108.6	103.87	103.47	103.05	104.3
CsI	101.1	96.72	96.39	96.03	97.12
Av. dev. (%)		4.3	4.6	2.0	4.1

Table 2. Calculated values of dissociation energy (D_e) (kcal/mol)

	Expt.	BM	Hm	VS	AH
LiF	137	133.62	132.15	130.46	133.47
LiCl	115	105.41	104.41	103.3	105.59
LiBr	100	84.14	83.23	82.22	84.39
LiI	81	77.05	76.24	73.08	77.34
NaF	107	111.38	110.37	110.10	111.73
NaCl	90.3	93.2	92.72	92.2	93.56
NaBr	87.5	73.53	73.05	72.54	73.89
NaI	70.6	68.97	68.09	67.58	68.91
KF	115	118.36	117.62	116.81	118.79
KCl	101.4	100.13	99.67	99.18	100.54
KBr	90.6	79.76	79.27	78.75	80.14
KI	76.4	76.64	76.25	75.83	77.02
RbF	123	118.06	117.37	116.61	118.52
RbCl	103	99.36	98.92	98.42	99.76
RbBr	92	80.73	80.33	79.91	81.13
RbI	77	77.1	76.75	76.38	77.48
CsF	127	123.56	122.74	121.76	124.05
CsCl	106	103.99	103.56	103.1	104.44
CsBr	95	84.67	84.27	83.85	85.1
CsI	78	80.99	80.66	80.30	81.39
Av. dev. (%)		6.9	6.0	6.2	5.5

(D_e) of 5 alkali hydride molecules calculated with AH model show the minimum deviation from the experimental results.

From Table 5 we can easily distinguish the relative supe-

Table 3. Calculated values of binding energy (D_i) (kcal/mol)

	Expt.	BM	Hm	VS	AH
LiH	165.11	158.11	153.76	151.92	153.48
NaH	150.26	137.97	135.28	131.87	134.81
KH	127.20	121.69	119.65	117.2	120.66
RbH	119.62	117.05	115.18	112.96	116.24
CsH	115.39	113.37	111.49	109.27	112.66
Av. dev. (%)		4.1	5.1	6.9	4.6

Table 4. Calculated values of dissociation energy (D_e) (kcal/mol)

	Expt.	BM	Hm	VS	AH
LiH	58	51.63	47.28	45.49	47.00
NaH	47	37.27	34.58	31.17	33.11
KH	42	39.42	37.38	34.93	38.39
RbH	39	38.55	36.68	34.46	37.74
CsH	41	41.42	39.54	37.32	40.70
Av. dev. (%)		8.0	13	18	12

Table 5. Comparison of percentage average deviation for four model

		BM	Hm	VS	AH
D_i	Alkali halides	4.3	4.6	2.0	4.1
D_e	Do	6.9	6.0	6.2	5.5
D_i	Alkali hydrides	4.1	5.1	6.9	4.6
D_e	Do	8.0	13.0	18.0	12.0

riority of four forms (BM, Hm, VS, AH model) for binding energy and dissociation energy of 20 alkali halide and 5 alkali hydride molecules.

Calculated values of binding energy (D_i) for the 20 alkali halide molecules with the VS model are in best agreement with experimental results where as calculated values of binding energy (D_i) for the 5 alkali hydride molecules for BM model are in better agreement with experimental results.

On other side calculated values of dissociation energy (D_e) for the 20 alkali halide molecules and 5 alkali hydride molecules both with AH model are in best agreement with experimental results.

When our works are compared with the works of other workers we observed that the inclusion of the van der Waals term in the potential energy function improves the theoretical results of D_i and D_e as per observed values. Further improvement in agreement between the theoretical and experimental values has been observed on the inclusion of polarizability terms in the potential function. The four forms of

potential energy functions give values of D_i and D_e closer to the alkali halides than alkali hydrides. The deviations in the case of hydrides are large.

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