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Study of Repulsive Interaction in Ionic Crystals

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The repulsive interaction in an interaction potential of ion-ion interaction in alkali halides in molecular and crystalline states has been presented. The different contributions arising from the polarization forces and van der Waals interactions are investigated for these molecules. In crystal binding, the contributions arising from the van der Waals dispersion forces and the repulsive interaction between nearest neighbours and next nearest neighbours have also been taken into account. The result of various spectroscopic constants, cohesive energy and bulk modulus for a number of alkali halides are in excellent agreement with corresponding experimental results.

INTRODUCTION

To study the crystalline state propoerties of ionic crystals the interaction potential energy function is often used. Recently it has also been shown that it can be applied to study the binding in crystal state.

In this article the author applied a short-range repulsive interaction in the expression for the interaction potential and investigate its validity for crystalline states. All types of ion pair interactions are taken into consideration for crystal binding in alkali halides. The agreement between theoretical and experimental results is satisfactory.

Theoretical Consideration

The potential energy for alkali halide molecules[1] is given by

$$U(r) = \frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{C}{r^6} + \psi(r) \tag{1}$$

where the first to 4th terms are the electrostatic interaction energy, the polarization energy, the van der waals dipole-dipole energy and $\psi(r)$ is the short-range repulsive interaction energy respectively and α_1 and α_2 are the electronic polarizabilities of cation and anion respectively[2] given by

$$\alpha_1 = \frac{e^2h^2n}{4\pi^2m(E_r - e_\phi)^2} \tag{2}$$

$$\alpha_2 = \frac{e^2h^2n^2}{4\pi^2m(E_r - e_\phi)^2} \tag{3}$$

where $\phi = e^2/r$.

The values of E_r are calculated from free-ion polarizabilities[3] α_1 by Ruffa's theory are the electronic polarizabilities[4] as

$$E_r = \frac{e^2h^2n}{4\pi^2m\alpha_1} \tag{4}$$

where e, m, n and h are electronic charge, electronic mass, the total number of electrons in the ion and h is Planck's constant respectively.

Knowing the value of α_1 and α_2, the van der Waal's dipole-dipole (w_{d-d}) energy can be evaluated[5] by the following equation.

$$w_{d-d} = \frac{3eh}{2m^{1/2}r^6}\frac{\alpha_1\alpha_2}{[(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}]} \tag{5}$$

where N_1 and N_2 are effective numbers of electrons in the ions[6].

It has been suggested that method[6] is superior to other methods when evaluating the W_{d-d} energy in ionic molecules. In this study the author has applied short-range repulsive interaction suggested by Ali *et al.*[7, 8] as:

$$\psi(r) = (P'r^m) \exp(-b'r^N) \tag{6}$$

where m = 2, and P′, b′ and N are the potential parameters.

The crystal lattice energy of an ionic crystal is usually expressed as

$$W = Ae^2/r - C/r^6 - D/r^8 + \psi(r) \tag{7}$$

where A is Madelung constant, the first term is the Coulomb energy arising from the electrostatic interaction between unlike point ions, the second and third terms represent the van der Waal's dipole-dipole and dipole-quadrupole interaction respectively. Values of C and D are taken from the work of Ali *et al.*[6] $\Psi(r)$ is the short-range repulsive interaction arising from the overlap of two combining ions. The short-range repulsive potential equation (6) is investigated by taking into account:

(i) The effect of nearest neighbour (NN) and

(ii) The effect of next nearest neighbour (NNN) interactions.

The repulsive potential of second neighbour interaction is given by

$$\Psi(r) - M\Psi_{+-} + \frac{1}{2}M'(\Psi_{++} + \Psi_{--}) \tag{8}$$

where M and M′ are the numbers of nearest neighbours of unlike ions and next nearet neighbours of like ions respectively.

Ψ_{+-}, Ψ_{++} and Ψ_{--} are the replusive potentials for cation-anion, cation-cation and anion-anion pair interaction respectively. Equation (8) reduces to the equation which considers only the NN interactions if the effects of Ψ_{++} and Ψ_{--} are taken to be zero.

The generalized form of replusive potential of all types of ion pair interactions can be expressed as

$$\Psi_{ij}(r) = \frac{\beta_{ij}P}{r_{ij}^m} \exp(-b_{ij}r_{ij}^N) \tag{9}$$

where P is the repulsive strength parameter. For NaCl structure $r_{ii} = r_{jj} = 1.4142r$ and for CsCl structure $r_{ii} = r_{jj} = 1.1547r$. β_{ij} are the Pauling coefficients introduced in order to provide the appropriate weight for various ion pair interactions expressed by eqn. (7) as

$$\beta_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \tag{10}$$

where z_i and z_j are the valencies and n_i and n_j are the numbers of the outermost electrons of ions i and j.

RESULTS AND DISCUSSION

The author has calculated the molecular state polarizabilities of alkali and halogen ions[5] in light of reference[3]. The choice of these free-ion state polarizabilities is based on the fact that no attempts have been made to utilizes them in the analysis of the molecular binding in alkali halide molecules. The recent calculated values of molecular state polarizability are employed to evaluate the van der Waal's dipole-dipole energies. The values come to yield D_e, α_e and $w_e x_e$ for several alkali halide molecules in fair agreement with their corresponding experimental values[9]. From Table-1 it is evident that the calculated values of dissociation energy (D_e), α_e and $w_e x_e$ for LiCl, NaF, NaCl and KF molecules agree will with available quantum mechanical results[10]. The author has calculated the values of cohesive energy and bulk modules of several alkali halide crystals taking into account the interaction potential model consisting of various interionic forces of interest. The calculated values of cohesive energy with and without NNN interactions are in appreciable agreement with the experimental values[1] with the inclusion of NNN interactions that arise from the contributions of cation-anion, cation-cation and anion-anion ion pair interactions in the short-ranged repulsive potential. The values of the bulk modulus have been improved significantly and the average % deviation reduces from 12.1 to 3.2 as shown in Table-2.

TABLE-1
COMPARISON OF PRESENT CALCULATED RESULTS WITH OTHER CALCULATIONS

Molecule	Dissociation energy (kcal/mol)				Rotational constant (10^{-4} cm^{-1})			Vibrational constant (cm^{-1})		
	(a)	(b)		(c)	(a)	(b)	(c)	(a)	(b)	(c)
		$De^{H.F.}$	De							
LiCl	106.41	88.20	109.21	112.04	78.23	75.99	80.04	4.68	4.67	4.50
NaF	111.82	70.32	111.71	115.80	40.45	46.81	45.56	3.34	4.39	3.83
NaCl	93.61	73.41	91.60	98.23	15.93	17.95	16.24	1.86	2.59	1.76
KF	118.81	70.30	110.41	119.61	20.57	21.41	23.33	2.19	2.48	2.43

(a) Present study; (b) Other calculations; (c) Experimental values[9].

TABLE-2

CALCULATED VALUES OF REPULSIVE HARDNESS PARAMETERS, b_{+-} (10^{12} cm^{-1}), COHESIVE ENERGY W (kcal/mol) AND BULK MODULUS B_T (10^{12} $dyne/cm^2$)

Crystal	b_{+-}	W			B_T		
		experimental	present study		experimental	present study	
			wihtout NNN	with NNN		without NNN	with NNN
LiF	1.352	−246.7	−253.0	−250.0	0.674	0.787	0.719
LiCl	1.049	−203.3	−203.2	−200.4	0.300	0.349	0.313
LiBr	0.954	−194.2	−191.0	−188.3	0.238	0.273	0.243
LiI	0.857	−180.5	−177.2	−174.3	0.175	0.205	0.181
NaF	1.296	−219.5	−225.6	−223.5	0.471	0.553	0.512
NaCl	1.025	−187.1	−188.6	−186.6	0.240	0.282	0.258
NaBr	0.946	−178.5	−179.1	−177.1	0.197	0.230	0.210
NaI	0.828	−167.0	−164.4	−164.4	0.151	0.169	0.154
KF	1.086	−194.3	−198.3	−196.1	0.306	0.338	0.310
KCl	0.902	−170.2	−171.6	−169.6	0.176	0.198	0.180
KBr	0.798	−163.2	−163.2	−161.2	0.148	0.156	0.142
KI	0.759	−153.6	−154.7	−152.7	0.117	0.131	0.118
RbF	1.049	−185.8	−189.5	−187.4	0.271	0.293	0.268
RbCl	0.844	−163.6	−164.6	−162.7	0.158	0.168	0.153
RbBr	0.815	−157.2	−158.9	−156.9	0.134	0.150	0.135
RbI	0.746	−148.5	−148.1	−146.3	0.106	0.113	0.103
CsF	0.968	−177.0	−180.1	−177.9	0.235	0.241	0.219
CsCl	0.830	−159.8	−158.9	−156.5	0.180	0.201	0.178
CsBr	0.781	−154.1	−154.7	−152.2	0.159	0.180	0.159
CsI	0.720	−146.1	−146.2	−143.8	0.128	0.145	0.128
	Average deviation (%)		1.09	1.24		12.11	3.27

Conclusion

The merit of these fitting schemes is judged by the success of the critical results that are found to be reasonably satisfactory in alkali halide crystals. The agreement between the theoretical as well as experimental values obtained from the present interaction potential model is good for the whole family of alkali halides both in molecular and crystalline states.

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