

할로겐화 알칼리 화합물의 해리에너지 및 이중극자 모멘트 계산

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Dissociation Energies and Dipole Moments of Alkali Halides

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요 약. 알칼리 할로겐 분자내의 이온의 편극률을 Seitz와 Ruffa의 에너지 분석 관계식을 이용하여 계산하였다. Slater-Kirkwood 식에서 이용되는 유효전자수(N_{eff}) 값을 등전자 구조를 갖는 화학종에 사용하였다. 유효 분산계수(C_6^{eff})는 원자-원자(혹은 분자)의 상호작용을 실험적으로 재현할 수 있도록 유효전자수를 예측하는 실험식(J. Chem. Phys., 1991, 95, 1852)을 이용하여 계산하였다. T-Rittner 모형의 틀속에서 모형 퍼텐셜을 구축하여 해리에너지와 쌍극자 모멘트를 계산하였다. 이 연구의 결과는 실험값과 좋은 일치를 보여 주었다.

ABSTRACT. The bonded state polarizabilities of ions in the alkali halides are estimated by using the Seitz and Ruffa (SR) energy level analysis relation. The effective number of electrons N_{eff} in the Slater-Kirkwood formula are used for all members of an isoelectronic sequence. The effective dispersion coefficients C_6^{eff} are calculated by the use of the empirical formula (J. Chem. Phys. 1991, 95, 1852) estimating N_{eff} values to reproduce the experimental C_6^{eff} for atom-atom (or molecule) interactions. In the framework of the T-Rittner model the model potential is constructed and used to calculate the values of dissociation energy and dipole moment. The results obtained in the present study are in good agreement with the experiment one.

INTRODUCTION

Various electrostatic interaction models have been used extensively to describe the properties and bonding in diatomic ionic compounds¹⁻¹³. For highly ionic compounds, such as the alkali halide molecules, the most commonly known model is the Rittner model¹ which has been successfully applied to the ground state of these molecules.

According to this model the potential energy, $V(R)$ and dipole moment, $\mu(R)$ can be expressed as follows:

$$V(R) = V_{\text{rep}}(R) - \frac{e^2}{R} - \frac{e^2(\alpha_+ + \alpha_-)}{2R^4} - \frac{2e^2\alpha_+\alpha_-}{R^7} - \frac{C}{R^6} \quad (1)$$

$$\mu(R) = eR \left[1 - \frac{(\alpha_+ + \alpha_-) - \frac{4\alpha_+\alpha_-}{R^3}}{R^3 - \frac{4\alpha_+\alpha_-}{R^3}} \right]$$

$$= eR \left[1 - \frac{(\alpha_+ + \alpha_-)}{R^3} + \frac{4\alpha_+\alpha_-}{R^6} + \dots \right] \quad (2)$$

In Eq. (1) the first term is the overlap repulsive energy, the second is the Coulomb energy, the third and fourth terms are the polarization energies, and the last one is the van der Waals (vdW) energy. In Eq. (2) R is the internuclear distance, and α_+ and α_- are the polarizability of positive ion and negative ion respectively. In this model the ions are assumed to be polarizable spherical charge and multiple terms higher than dipole-dipole terms are neglected. Brumer and Karplus⁵(BK) have shown that the $2e^2\alpha_+\alpha_-/R^7$ in Eq. (1) and $4\alpha_+\alpha_-/R^6$ in Eq. (2) be neglected within the second-order perturbation theory. The model without these terms is known as T-Rittner model. The T-Rittner model has yield reliable binding(or dis-

sociation) energies and dipole moments where both values of accurate equilibrium bond distance and polarizabilities of ions in the molecule are available.

Shanker^{7-9,12,13} and his group published a series of papers on the properties such as electronic polarizabilities, potential functions, and spectroscopic constants for alkali halides using T-Rittner model. They discussed three main limitations in the T-Rittner model in terms of i) calculation of the electronic polarizabilities of ions fitting the experimental values of dipole moments, ii) calculation of overlap repulsive potential parameters using experimental values of vibrational frequencies, and iii) calculation of effective dispersion coefficients. These shortcomings were rectified by Kumar *et al.*⁹ They calculated the electronic polarizabilities of ions in molecules using the SR energy level analysis by considering the effect of Coulomb interaction suggested by Seitz¹⁴ and Ruffa.¹⁵ These polarizabilities thus calculated were used to evaluate the polarization energies and the vdW energies. For calculating the overlap repulsive energy they employed the exchange charge model^{15,17} to obtain the values of overlap repulsive potential parameters from the overlap integrals. Kumar and Shanker¹³(KS) have presented an extensive analysis using various potential functions for the overlap repulsive energy such as ion-independent (molecular dependent) and ion-dependent potential models. The van der Waals parameters which are effective dispersion coefficients were determined by the Kirkwood-Müller (KM) formula.

The purpose of this paper has two parts. The first part is to see whether the use of effective dispersion coefficients (C_6^{eff}) through the Slater-Kirkwood (SK) formula is also valid in estimating the vdW energy and the binding energy for the alkali halide molecule. The m C_6^{eff} coefficient is an effective long-range interaction term including dipole-dipole, dipole-multipole, and multipole-multipole interactions. It describes the overall attraction in a distance range in the neighborhood of the potential well depth. The well-known Slater-Kirkwood for-

mula(in atomic unit) for the two chemical species A and B can be written as follows:

$$C_6^{\text{eff}}(AB) = \frac{3}{2} \frac{\alpha_A \alpha_B}{\left(\frac{\alpha_A}{N_A}\right)^{\frac{1}{2}} + \left(\frac{\alpha_B}{N_B}\right)^{\frac{1}{2}}} e^2 a_0^5 \quad (3)$$

where N_A and N_B are the effective numbers of electrons in A with polarizability α_A and B with α_B respectively. In general the number of electrons of the outer shells has been used for N_A and N_B . However Pitzer¹⁹ had already shown that the N values should be expected to exceed substantially the actual number of electrons in the outer shell. Koutselos and Mason²⁰ demonstrated that the value of N depends on the electronic structure of the atoms(or ions). They have shown that the transferability of the same value N within an isoelectronic sequence (eg. Cl^- , Ar, and K^+) is possible. To take into account correctly the effective number of electrons estimating the effective dispersion coefficient C_6^{eff} , the combined role played by both the outer shell and the inner-shell electrons should be considered. More recently Combi *et al.*²¹ developed the empirical formula to estimate the N values only in terms of inner and outer orbital electron numbers and showed that the C_6^{eff} values calculated from the SK formula with the N_{eff} value are in satisfactory agreement with the experimentally available C_6^{eff} coefficients:

$$\frac{N_{\text{eff}}}{N_{\text{ext}}} = 1 + \left(1 - \frac{N_{\text{ext}}}{N_{\text{int}}}\right) \left(\frac{N_{\text{int}}}{N_{\text{tot}}}\right)^2 \quad (4)$$

where N_{int} and N_{ext} are the numbers of total inner and total outer electrons and $N_{\text{tot}} = N_{\text{int}} + N_{\text{ext}}$. The second part is to see whether the use of best free ion polarizability values through the SK formula is also valid in estimating the vdW energy and the binding energy for the alkali halide molecule. Shanker *et al.*^{7,8} calculated the vdW energies through the SK formula using the bonded state polarizability values to estimate the binding energy and the dipole moment for the alkali halides. The Kirkwood-Müller formula is the other formula which is similar to the Slater-Kirkwood formula but does not involve N explicitly. The Kirkwood-

Muller formula^{22,23} is expressed as follows:

$$C_6^{eff}(AB) = \frac{6 \frac{mc^2}{N_0} \alpha_A \alpha_B}{\frac{\alpha_A}{|\chi_A|} + \frac{\alpha_B}{|\chi_B|}} \quad (5)$$

where m is the electron mass, c is the speed of light, N_0 is the Avogadro's number, χ_A (or χ_B) is the diamagnetic susceptibility.

Throughout this paper the following units are used, where 1a.u. (atomic unit) energy=1hartree=27.21139 eV= 4.359748×10^{-18} J= 2.194746×10^5 cm⁻¹; 1a.u. distance= $1a_0=0.5291772$ Å. The conversion factor for the dispersion coefficient C_6^{eff} is $1e^2a_0^5=0.5975360$ eV Å⁶. The conversion factor for the force constant k is $1 \frac{10^5 \text{dyne}}{\text{cm}} = 1 \frac{\text{mdyne}}{\text{Å}} = 6.423038 \times 10^2 \frac{\text{hartree}}{a_0^2}$. The conversions factor for the dipole mo-

ment $e\text{Å}=4.803243$ Debye. The conversion factors for the diamagnetic susceptibility expression are: 10^{-6} cm³/mol= $1.120589 \times 10^{-5}a_0^3$ and $6 \frac{mc^2}{N_0}=1.126732 \times 10^5$

hartree where m is the electron mass, c is the speed of light, and N_0 is Avogadro's number.

In the present study we employ

i) the SR energy level analysis method proposed by Seitz and Ruffa

ii) the Born-Mayer repulsive potential form to obtain overlap repulsive parameters and

iii) the SK formula to calculate the C_6^{eff} values using N_{eff} values proposed by Combi *et al* and best values of free ion polarizability.

The paper is organized as follows. In Sec. II we present the model and the method of analysis, and numerical calculations. Results are discussed and compared with available data in Sec. III.

MODEL AND METHOD OF ANALYSIS

The model. The general form of a semiclassical potential function for ionic compound is

$$V(R) = V_{rep} - \frac{e^2}{R} - V_{pol} - \frac{C}{R^6} \quad (6)$$

In Eq. (6), the first term is the overlap repulsive energy, the second term is the Coulomb energy (electrostatic interaction energy), the third term is the polarization, and the last term is the van der Waals dipole-dipole energy. The overlap repulsive energy arises from the overlap of charge from the interacting species. Different forms of overlap repulsive potential V_{rep} have been proposed and tested in estimating the dissociation energy and the spectroscopic constants of alkali monohalides¹³. The polarization energy comes from the mutual polarization of the two ions. This model has various different forms which differ mainly in the forms of both polarization potential and overlap repulsive potential. Rittner¹ viewed alkali halides as consisting two mutually polarizable spheres of charge ± 1 in units of e separated by an internuclear distance R . Using the classical electrodynamics he proposed that V_{pol} has the form of

$$V_{pol} = \frac{e^2(\alpha_+ + \alpha_-)}{2R^4} + \frac{2e^2\alpha_+\alpha_-}{R^7}$$

The model with this form of polarization function is called as the Rittner model. From a quantum mechanical treatment Brumer & Karplus⁵ presented the fundamental ground for this model and also have demonstrated that the $2e^2\alpha_+\alpha_-/R^7$ term in Eq. (1) should be neglected within the second-order perturbations theory. The model without this term is known as truncated Rittner model or simply the T-Rittner model.

For the overlap repulsive potential the Born-Mayer potential form²⁴ has proven very successfully for describing a variety of atom-atom²⁵⁻²⁷, ion-atom²⁸, and atom-molecule²⁹ systems. The C constant in the van der Waals dipole-dipole energy form is in fact the dispersion coefficient for dipole-dipole interaction. As mentioned in Introduction the effective dispersion coefficient C_6^{eff} is an effective long range interaction term to describe the overall attraction in the well depth range. It might be therefore expected that the value of C_6^{eff} would be larger in value than the original C_6 value. This is in fact the case. The model potential function for the alkali halide then takes the form (in atomic

unit):

$$V(R) = Ae^{-bR} - \frac{1}{R} - \frac{(\alpha_+ + \alpha_-)}{2R^4} - \frac{C_6^{\text{eff}}}{R^6} \quad (7)$$

Rittner proposed that for the alkali halide molecules the dipole moment μ is related to a distance R by the equation as in Eq. (2). For large R we can expand the form of the second part in Eq. (2) in a Taylor series expansion. The T-Rittner model is Eq. (8) without the third term in the form of a Taylor series expansion in Eq.(2).

$$\mu(R) = eR - \frac{e(\alpha_+ + \alpha_-)}{R^2} \text{ or } \mu(R) = R - \frac{(\alpha_+ + \alpha_-)}{R^2} \quad (8)$$

in atomic unit

In fact the first term in Eq. (8) is a point dipole moment and the second term is a correction term to the point dipole model due to the overall interaction between ions.

Method of analysis. Ruffa¹⁵ derived the simple relation for calculating free ion polarizabilities using the Thomas-Kuhn sum rule in the frame of second-order perturbation theory. He also showed that the polarizabilities of ions in molecules differ from the corresponding free ion polarizability values due to the presence of the electrostatic potential. The effect of the potential on the atomic energy levels can be estimated by a classical procedure which has been used by Seitz¹⁴. The potential which comes mainly from the Coulombic interaction is negative at the cation site and positive at the anion site. Consequently the mean excitation energy of the cation in the molecule is diminished by this potential($e\Phi$) while the energy of the anion is expected to be increased by $e\Phi$. Ruffa's simple relation for the free ion or atom can be written as follows:

$$\alpha_f = \frac{e^2 h^2 n}{4\pi^2 m E_f^2} \text{ or } \alpha_f = \frac{n}{E_f^2} \text{ in atomic unit} \quad (9)$$

where e and m are the charge and mass of an electron respectively, h is the Plank's constant, and n is the total number of electrons in the ion. Kumar and Shanker¹³ used the free ion polarizabilities of Pauling³⁰ to calculate α_+ and α_- . For the values of

Table 1. Free ion polarizabilities α_f and characteristic energy parameters E_p for ions in atomic unit

Ion	α_f^a	E_p
Li ⁺	0.192	3.2275
Na ⁺	1.000	3.1623
K ⁺	5.470	1.8140
Rb ⁺	9.110	1.9879
Cs ⁺	15.720	1.8534
F ⁻	9.310	1.0364
Cl ⁻	26.590	0.8228
Br ⁻	35.230	1.0109
I	52.710	1.0122

^aSee Ref.34 for alkali ions and see Ref.31 for halide ions.

α_f for the alkali ions Pauling's polarizabilities are bigger in values than Coker's³¹ one except α_f for K⁺ ion. Coker arbitrarily set sodium ion to have $\alpha_f = 0.158 \text{ \AA}^3$ instead of the best value of $\alpha_f = 0.148 \text{ \AA}^3$ and determined the other values from this assumption. The best free ion polarizability values for the alkali ions are lower than Coker's values³¹. In the present paper we make use of the best free ion polarizability values for the alkali ions and the Coker's values for the halide ions. The best values of α_f and the calculated values of E_p from Eq. (9) for various ions are reported in Table 1.

The combination form of Ruffa's simple relation¹⁵ with Seitz's concepts is called the Seitz and Ruffa (SR) energy level analysis. The resulting formula is expressed as follows:

$$\alpha_+ = \frac{e^2 h^2 n}{4\pi^2 m (E_p - e\Phi)^2} \text{ or } \alpha_+ = \frac{n}{(E_p - \Phi)^2} \text{ in atomic unit} \quad (10)$$

and

$$\alpha_- = \frac{e^2 h^2 n}{4\pi^2 m (E_p + e\Phi)^2} \text{ or } \alpha_- = \frac{n}{(E_p + \Phi)^2} \text{ in atomic unit} \quad (11)$$

where $\Phi = \frac{e}{R}$ or $\Phi = \frac{1}{R}$ in atomic unit.

The values of bonded state polarizabilities α_c and α_a calculated from Eq. (10) and (11) at $R=R_{eq}$, the experimental equilibrium bond distance, are given in Table 2 and compared with other values^{9, 13}. The calculated polarizabilities are used to es-

Table 2. Calculated bonded-state polarizabilities, α_+ and α_- in atomic unit

Molecule	α_+		α_-	
	A ^a	B ^b	A ^a	B ^b
LiF	0.2396	0.2429	5.2910	5.0007
LiCl	0.2274	0.2294	15.2993	14.8603
LiBr	0.2247	0.2227	22.8672	22.6076
LiI	0.2213	0.2227	35.4943	35.2544
NaF	1.1994	1.2822	5.8168	5.5406
NaCl	1.1584	1.2417	16.4218	16.0076
NaBr	1.1485	1.2282	24.0921	23.8494
NaI	1.1359	1.2147	37.0437	36.8133
KF	7.2997	7.7136	6.1026	5.8375
KCl	6.8965	7.2749	17.2598	16.8579
KBr	6.8048	7.1737	25.0626	24.8347
KI	6.6894	7.0522	38.4020	38.1900
RbF	11.6907	12.1811	6.2050	5.9455
RbCl	11.1358	11.5940	17.5516	17.1616
RbBr	11.0106	11.4590	25.3961	25.1788
RbI	10.8524	11.2903	38.8628	38.6557
CsF	20.3801	21.2849	6.2786	6.0264
CsCl	19.3319	20.1714	17.8256	17.4382
CsBr	19.1064	19.9217	25.7174	25.5028
CsI	18.8226	19.6248	39.3252	39.6815

^aPresent study. ^bSee Ref.9.

timate dipole moments μ at $R=R_{eq}$. Values of μ obtained from Eq.(8) are listed in Table 3 and com-

pared with experimental values⁵ as well as with others^{9,13}. The van der Waals energies, C_6^{eff}/R^6 can

Table 3. Dipole moments in Debye

Molecule	A ^a	B ^b	C ^c	D ^d
LiF	6.284	5.902	5.993	6.20
LiCl	7.085	7.000	7.084	7.13
LiBr	7.226	6.936	7.055	7.17
LiI	7.429	7.047	7.113	7.38
NaF	8.123	7.904	7.949	8.06
NaCl	8.972	9.094	9.146	9.17
NaBr	9.092	9.148	9.175	9.31
NaI	9.210	9.327	9.348	9.57
KF	8.558	8.407	8.391	8.57
KCl	10.238	10.391	10.400	10.46
KBr	10.603	10.699	10.693	10.84
KI	11.050	11.184	11.184	11.40
RbF	8.513	8.434	8.391	8.53
RbCl	10.483	10.756	10.751	10.80
RbBr	10.86 ^e	11.156	11.140	11.27
RbI	11.48 ^e	11.753	11.741	11.93
CsF	7.849	7.816	7.733	7.86
CsCl	10.358	10.828	10.794	10.84
CsBr	10.82 ^e	11.377	11.337	11.45
CsI	12.100	12.158	12.126	12.30
Avg. error		0.211	0.196	0.238
Max. error		0.557	0.517	0.630
% error		2.349	2.144	2.180

^aExperimental values from Ref.5. ^bPresent study. ^cSee Ref.9. ^dSee Ref.13. ^eSee Ref.37.

Table 4. Free ion polarizability values, α_A and diamagnetic susceptibility values χ_A and effective number of electrons N_{eff}

Ions	α_A^a (a_0^3)	$ \chi_A $ (10^{-6} cm ³ /mole) ^b	N_A^c	N_{eff}^d
Li	0.192	0.6	1.3285	2.0000
Na ⁺	1.00	5	17.7130	7.0400
K ⁺	5.47	13	21.8903	8.4938
Rb ⁺	9.11	20	31.1096	11.4568
Cs ⁺	15.72	31	43.3135	12.7956
F	9.31	11	9.2085	7.0400
Cl ⁻	26.59	26	18.0128	8.4938
Br ⁻	35.23	36	26.0642	11.4568
I	52.71	52	36.3468	12.7956

^a α_A value used in present study. ^bFrom Ref.9

^cValues obtained from $n N_A = (4 \frac{mc^2}{N_0})^2 \frac{\chi_A^2}{\alpha_A}$ where N_0 is the Avogadro's number.

^dValues calculated from $\frac{N_{\text{eff}}}{N_{\text{ext}}} = 1 + (1 - \frac{N_{\text{ext}}}{N_{\text{int}}})(\frac{N_{\text{int}}}{N_{\text{ext}}})^2$; present study.

be estimated from the various types of formulas such as Slater-Kirkwood type¹⁸, Kirkwood-Müller type^{22,23}, London type³², and Salem's type³³. Among the four types of formulas the Slater-Kirkwood formula involves N_{eff} but the Kirkwood-Müller formula does not involve N_{eff} . These two formulas can be written as follows:

$$C_6^{\text{eff}}(\text{AB}) = \frac{\frac{3}{2} \alpha_A \alpha_B}{\frac{1}{\Omega_A} + \frac{1}{\Omega_B}} \quad (12)$$

From Eq.(3) Ω_A in the Slater-Kirkwood formula, is given by

$$\Omega_A = \left(\frac{N_A}{\alpha_A}\right)^{1/2} \quad (13)$$

In the Kirkwood-Müller formula (Eq.(5)), Ω_A is given by

$$\Omega_A = \frac{4 mc^2 \chi_A}{N_0 \alpha_A} \quad (14)$$

These different expressions for Ω_A (or Ω_B) can be used to get the relation between N_A and χ_A . From Eq.(13) and (14) the following relation is obtained.

$$N_A = \frac{\left(\frac{4 mc^2}{N_0}\right) \chi_A^2}{\alpha_A} \quad (15)$$

Combi *et al*²¹ proposed the empirical formula to estimate the N_A values in order to reproduce the experimental C_6^{eff} in the SK formula. The empirical formula (Eq.(4)) to calculate the N_A values is employed in our study. The N_A values calculated by Eq. (4) are reported in Table 4 and compared with the corresponding values⁹ obtained from Eq. (15). The ratios of the N values of the same ions to that of a reference one, K⁺ ion are compared and the results are given in Table 5. The effective dispersion coefficients C_6^{eff} are calculated using Eq. (3) with the free ion polarizability values and the calculated values of N_A in our present study. The van der Waals energies C_6^{eff}/R^6 are also reported in Table 6 and compared with other values.⁹

The last term which we need to estimate the dissociation (binding) energy is the overlap repulsive

Table 5. The ratios of effective electron number of ions to those of K⁺ (or Cl⁻) ions

Ions	Ratio	
	A ^a	B ^b
Li ⁺	0.2355	0.2429
Na ⁺ (or F)	0.8288	0.7539
K ⁺ (or Cl)	1.0000	1.0000
Rb ⁺ (or Br)	1.3488	1.1358
Cs ⁺ (or I)	1.5065	1.3161

^aPresent study. ^bSee Ref.20.

Table 6. Effective dispersion coefficients, $m C_6^{eff}$ and van der Waals interaction energies in atomic unit

Molecule	$C_6^{eff} (e^2 a_0^5)$		vdW energy (10^{-3} hartree)	
	A ^a	B ^b	A ^a	B ^b
LiF	1.8367	1.7845	-2.757	-2.678
LiCl	3.6832	4.5118	-1.188	-1.455
LiBr	4.9172	6.3622	-1.033	-1.337
Lil	6.4889	9.4486	-0.7609	-1.108
NaF	9.1462	11.8003	-3.936	-5.078
NaCl	18.5839	29.0461	-2.357	-3.684
NaBr	24.8044	40.7257	-2.220	-3.645
NaI	32.8546	59.3761	-1.816	-3.284
KF	39.1240	50.5791	-8.194	-10.578
KCl	84.8313	128.1844	-5.181	-7.822
KBr	113.0884	181.1596	-4.930	-7.893
KI	152.7072	266.3083	-4.183	-7.293
RbF	62.3116	79.5449	-9.993	-12.766
RbCl	136.5450	202.6377	-6.402	-9.495
RbBr	181.9903	286.3115	-6.129	-9.637
RbI	246.5584	421.3218	-5.267	-8.997
CsF	97.2070	131.1953	-12.824	-17.325
CsCl	217.8777	336.1042	-7.939	-12.255
CsBr	290.2623	474.8007	-7.580	-12.405
CsI	396.0777	704.2459	-6.551	-11.653

^aPresent study. ^bSee Ref.9.

potential in the framework of the T-Rittner model. Various types of overlap repulsive potentials are proposed and tested for the alkali halide system¹³. The Born-Mayer repulsive potential²⁴ is employed in the present study. Because of the difficulty in determining a priori A and b values we shall use Eq. (7) in conjunction with the equilibrium condition and the experimental values of vibrational frequency,

$$\frac{dV(R)}{dR} = 0 \text{ at } R = R_{eq} \quad (16)$$

and

$$\frac{d^2V(R)}{dR^2} = k = 4\pi^2 \bar{\mu} c^2 \omega_e \text{ at } R = R_{eq} \quad (17)$$

where k is the force constant, $\bar{\mu}$ the reduced mass of ion pair, and ω_e the vibrational frequency. The data on R_{eq} and k used in calculations are listed in Table 7. The resulting relations obtained from both Eqs. (16) and (17) can be used to calculate the overlap repulsive parameters A and b. The calculated overlap repulsive parameters A and b are

shown in Table 8 and compared with other values.⁹

The analytical potential in the T-Rittner model is in fact formed and used to estimate the dissociation energies for the 20 alkali halides. The dissociation energies thus calculated from Eq. (7) are tabulated in Table 9 and compared with others.^{5,9,13}

RESULT AND DISCUSSION

We have employed the SK energy level analysis^{14,15} to estimate the bonded state polarizabilities of ions in the alkali halide molecules. The bonded state polarizabilities thus calculated differ in values than those of free ion polarizabilities.

Table 2 shows the calculated bonded state polarizabilities based on the SR energy level analysis along with the other values.⁹ The values obtained here differ slightly from those reported by Kumar et al⁹ since those authors used the Coker's free ion polarizabilities³¹ rather than the best values of the free ion polarizabilities used in this study. This can be explained by the fact that the positive free ion

Table 7. Experimental equilibrium, bond distance R_{eq} , vibrational frequency ω_e and force constant k

Molecule ^a	R_{eq} (a ₀)	ω_e (cm ⁻¹)	k (10 ⁵ dyne/cm) ^b
LiF	2.9553	910.25	2.5013
LiCl	3.8186	643.31	1.4248
LiBr	4.1015	563.16	1.2040
LiI	4.5200	498.16	0.9729
NaF	3.6394	536.1	1.7614
NaCl	4.4613	364.60	1.0864
NaBr	4.7281	298.49	0.9357
NaI	5.1238	259.20	0.7704
KF	4.1035	426.04	1.3658
KCl	5.0392	279.80	0.8501
KBr	5.3305	219.17	0.7382
KI	5.7596	186.53	0.6111
RbF	4.2902	373.27	1.2744
RbCl	5.2661	233.34	0.7946
RbBr	5.5647	169.46	0.6920
RbI	6.0034	138.51	0.5750
CsF	4.4321	352.56	1.2173
CsCl	5.4921	214.17	0.7482
CsBr	5.8057	149.66	0.6534
CsI	6.2648	119.178	0.5432

^aBased on: ⁷Li, ²³Na, ³⁹K, ⁸⁵Rb, ¹³³Cs, ¹⁹F, ³⁵Cl, ⁷⁹Br, ¹²⁷I. ^bValues calculated from $k=4\pi^2c^2\bar{\mu}^6\omega_e^2$ where $\bar{\mu}$ is a reduced mass.

polarizability values used by Kumar *et al.*⁹ are slightly larger than ours. Coker³¹ arbitrarily set sodium ion to have the polarizability values of $\alpha=0.158 \text{ \AA}^3$ instead of the accurate value of $\alpha=0.148 \text{ \AA}^3$ and determined the values of other alkali ion from this assumption. We have adopted the values of free ion polarizability for alkali ions suggested by Mahan.³⁴

The calculated dipole moments in the frame of the T-Rittner model¹ are given in Table 3 along with the others^{9,13} and the experimental values⁵. Electric dipole moments provide a very critical test for ionic models. All the calculated dipole moments are in good agreement with experimental ones. The dipole moment within the framework of the Rittner model are also calculated but are not reported here. The dipole moments in the Rittner model are always smaller than the corresponding the T-Rittner values which give better agreement with experiment as pointed out by Brumer and Karplus⁵. This is due to the existence of the dipole-dipole interaction considered in the Rittner model but not in the T-Rittner model. In Eq. (8) the dipole moment expression shows that the first term

in Eq. (8) is from the point ion model and the second term in Eq. (8) is a correction term to the point ion model. The dipole moments calculated from the point ion model are expected to be larger than the experimental values.

The calculations of van der Waals energies based on the Kirkwood-Müller formula need the knowledge of both the polarizability α_A and the diamagnetic susceptibility χ_A which can all be calculated if the wave function for atom (or ion) A is available. There is a significant variation in the values of χ_A obtained by the different approaches. Experimental values for alkali ions and halide ions are not known. The Slater-Kirkwood formula on the other hand require the knowledge of both the polarizability α_A and the effective number of electrons N_A which can be estimated in a various way. Salem³³ claimed that the SK formula underestimates the dispersion energy. However the SK formula can yield satisfactory result particularly if one uses N_A (or N_B) as adjustable parameters.³⁸ The method employed in estimating N_A values in this work is the relation of Eq. (4) proposed by Combi *et al.*²¹. The values of the effective number

Table 8. Overlap repulsive potential parameters b and A in atomic unit

Molecule	b (a_0^{-1})		A (hartree)	
	This work	Ref.9	This work	Ref.9
LiF	1.9769	2.0999	29.4866	41.2869
LiCl	1.6647	1.7698	37.6364	53.2142
LiBr	1.5624	1.7015	39.1247	63.9946
LiI	1.4523	1.5796	42.9019	70.8758
NaF	1.8978	2.0045	54.7277	79.5919
NaCl	1.6311	1.7350	65.0093	101.3822
NaBr	1.5348	1.6746	63.5905	118.3557
NaI	1.4289	1.5564	65.4384	120.8788
KF	1.7497	1.7698	70.8230	85.5556
KCl	1.5525	1.5891	97.2376	127.9893
KBr	1.4725	1.5383	96.7185	148.6327
KI	1.3824	1.4498	101.1918	161.2481
RbF	1.7076	1.6853	82.6743	86.7024
RbCl	1.5277	1.5294	117.4230	135.3292
RbBr	1.4583	1.4823	120.5130	156.8901
RbI	1.3753	1.4036	128.1998	172.9461
CsF	1.6467	1.5749	89.2372	80.7388
CsCl	1.4943	1.4538	139.8183	136.2467
CsBr	1.4354	1.4149	148.1480	158.0369
CsI	1.3619	1.3431	163.2052	179.5979

of electrons N_A with the polarizability α_A are listed in Table 4 and compared with N_A values obtained from Eq. (15) with the diamagnetic susceptibility χ_A used in Ref. 9. The results show that N_A values calculated from the use of both χ_A and α_A are significantly larger than the corresponding values obtained from the empirical formula (Eq.(4)). Koutselos and Mason²⁰ have demonstrated that the same value of effective electron numbers N_A appeared in the SK formula can be used for all members of an isoelectronic sequence. The N_A value for atom A estimated from the empirical formula is definitely different from that for the same atom A in the scheme of Koutselos and Mason²⁰ because of the different approaches chosen. Therefore we compared the ratios of the N_A value of the same ions to that of a reference one. Table 5 shows that the results are in satisfactory agreement with those of Koutselos and Mason.^{20,21}

The effective dispersion coefficients C_6^{eff} (Table 6) in the present study are in general smaller than those⁹ calculated from the KM formula. The van der Waals energy values are assumed to be in the same trend. We calculate the C_6^{eff} values under the

column B in Table 6 by using the bonded state polarizability values under the column B in Table 2.

The C_6^{eff} values under the column A in Table 6 are obtained by using the free ion polarizability values listed in Table 1. The C_6^{eff} values are smaller than those reported under the column A in Table 6 if the bonded state polarizability values under the column A in Table 2 are employed. As an example, the C_6^{eff} value of CsI calculated by the use of the bonded state polarizability values ($\alpha_{Cs^+}=18.8226a_0^3$, $\alpha_I=39.3252a_0^3$) is $374.3501e^2 a_0^5$ instead of $C_6^{eff}=396.0777e^2 a_0^5$ under the column A in Table 6. Most striking is the accuracy of the SK formula, especially for the heavier atoms in which the assumed distinction between inner and outer electrons is more valid than in the lighter ones³⁵. This is the case. As an example in the use of data in Table 4, the C_6^{eff} value of $I^- \cdot I^-$ pair is $1026.7e^2 a_0^5$ through the SK formula while the corresponding C_6^{eff} value is $1730.3e^2 a_0^5$ through the KM formula.

The overlap repulsive potential parameters are listed in Table 8. Table 8 shows that the repulsive

Table 9. Dissociation energies to ions in eV

Molecule	A ^a	B ^b	C ^c	D ^d
LiF	7.983	7.946	7.914	7.814
LiCl	6.648	6.375	6.366	6.314
LiBr	6.409	6.018	6.019	6.002
LiI	6.015	5.560	5.577	5.542
NaF	6.674	6.637	6.601	6.535
NaCl	5.750	5.544	5.542	5.546
NaBr	5.538	5.282	5.277	5.277
NaI	5.217	4.936	4.935	4.931
KF	6.036	6.029	6.010	5.889
KCl	5.117	4.992	4.952	5.000
KBr	4.926	4.749	4.735	4.757
KI	4.601	4.437	4.427	4.440
RbF	5.793	5.852	5.785	5.594
RbCl	4.918	4.824	4.813	4.753
RbBr	4.727	4.593	4.579	4.549
RbI	4.419	4.291	4.280	4.215
CsF	5.659	5.785	5.763	5.854
CsCl	4.870	4.694	4.679	4.718
CsBr	4.709	4.462	4.445	4.701
CsI	4.384	4.160	4.146	4.180
Avg. error		0.168	0.185	0.206
Max. error		0.455	0.438	0.473
% error		3.101	3.453	3.544

^aExperimental values from Ref.5. ^bPresent study. ^cSee Ref.9. ^dSee Ref.13.

hardness parameter b are in fairly good agreement with those⁹ calculated from the exchange charge model which are listed in the column. The dissociation energies relative to the separated ions listed in Table 9 are in good agreement with the experimental ones⁵. The calculated values of molecular spectroscopic constants are not reported in this work.

The important point to be emphasized in this work are

i) the calculation of the effective dispersion coefficients C_6^{eff} through the empirical formula estimating N values which are elaborately devised to reproduce the experimental C_6^{eff} and

ii) the use of the best free ion polarizability values instead of using the bonded state polarizability values through the SK formula.

Our approach to those purposes are seemed to be justified in the calculations of the binding (dissociation) energies and dipole moments within the framework of the T-Rittner model. In con-

clusion the T-Rittner model has a singularity at $R = (4\alpha_+ \alpha_-)^{1/6}$ and is therefore clearly not valid for values of R in the neighborhood of this point. The Rittner model is therefore expected to be a good approximation only when the condition, $R^6 > 4\alpha_+ \alpha_-$ is satisfied. This is not the case³⁰ for the alkaline-earth monohalides due to the larger polarizabilities of the alkaline-earth ions. For alkali halides this condition is satisfied very well.

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