

COHESIVE ENERGY AND SPECTROSCOPIC CONSTANTS OF HEAVY METAL HALIDES AND SOME CHALCOGENIDES

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ABSTRACT:

Cohesive energy and spectroscopic constants such as vibrational anharmonicity constant ($\omega_e x_e$) and rotation vibration coupling constants (α_e) of heavy metal halides of Ag, Cu and some chalcogenides have been computed by using the different forms for the interaction potential energy. The potential consist of four short range overlap repulsive interaction part, Vander Waal's dipole-dipole interaction energy parts and polarization energy part and well known long range coulombian energy part. The relative contribution of different terms in the interaction energy have been obtained. Previous workers did not take into account of all terms. The results obtained are satisfactory and very close to the observed values. More over, the present calculation can be useful in predicting the validity and superiority of the one form of short range repulsive potential over the other.

KEYWORDS: Vibrational anharmonicity constant, rotational–vibrational coupling constant, chalcogenide, cohesive energy, short–range repulsive potential.

I. INTRODUCTION

Workers in this field have been continuously taking deep interest to ascertain the exact nature of the interaction potential energy in crystal and molecules. Some of them (Das and Kachhava 1977, Thakur *et al.* 1981, Shankar *et al.* 1982 and Hasan *et al.* 1998) considered only long range Coulombian energy and a repulsive interaction energy. Results obtained were not encouraging. Other investigators (Kumar & Kachhava, 1970 Kaur *et al.* 1986 and Ali & Hasan, 1991) did add Vander Waals dipole–dipole interaction energy term to the total energy term. Recently some investigators (Mandal & Ghatak, 2007 and Mandal & Thakur, 2013) included the polarization energy term excluding other terms. Exponential, Gaussian, Inverse and Logarithmic forms of overlap energy terms have been employed but the results obtained were far from satisfactory. The true nature of the exact form of interaction energy could not be ascertained, still the search for ideal potential is still going on.

In the pursuit of suitable interaction energy and overlap repulsive part, we have used the four different forms of short-range repulsive energy terms such as Born-Mayer (BM), Hellmann (HELL), Varshni–Shukla (VS) and Ali-Hassan (AH) interaction energy terms, in addition to polarization energy and Vander Waals dipole–dipole interaction energy term which were so far ignored in earlier calculations. The B.M. and H.M. models are quantum mechanical in nature and VS and AH models are empirical in nature. These potential have the ability to fulfill the conditions of ideal potential.

II. METHOD OF CALCULATION

The binding energy, harmonic and anharmonic spectroscopic constants have been computed through the analysis of interionic interaction. The important contribution to the interaction energy at the separating distance, r are manifested in the form

$$U(r) = \frac{-z_1 z_2 e^2}{r} - \frac{e^2 (\alpha_1 + \alpha_2)}{2r^4} - \frac{C}{r^6} + \frac{S}{r^m} \exp(-\lambda r^n) \quad (1)$$

Where the first term is the Coulombian interaction energy acting between the positive ion ($+Z_1e$) and negative ion ($-Z_2e$) and e is the electronic charge. The second term is the polarization energy. α_1 and α_2 are the molecular state polarizabilities of the cation and anion respectively. The third term is the Vander Waals

dipole-dipole energy. The last term is the short range repulsive interaction arising from the mutual overlap of electron clouds between two combining ions. Four forms of repulsive interactions used in this work are :

Born – Mayer Model

$$U_{SR} [BM] = S \exp(-\lambda r) \quad (2)$$

Hellmann Model

$$U_{SR} [HM] = \frac{S}{r} \exp(-\lambda r) \quad (3)$$

Varshni-Shukla Model

$$U_{SR} [VS] = \frac{S}{r^2} \exp(-\lambda r) \quad (4)$$

Ali-Hasan Model

$$U_{SR} [AH] = \frac{S}{r^2} \exp\left(-\lambda r^{\frac{3}{2}}\right) \quad (5)$$

Here S and λ are potential parameter to be obtained by applying molecular equilibrium and force constant conditions mentioned mathematically as,

$$\left(\frac{\partial U(r)}{\partial r}\right)_{r=r_e} = 0 \quad (6)$$

and

$$\left(\frac{\partial^2 U(r)}{\partial r^2}\right)_{r=r_e} = K_e = 4\pi^2 \omega_e^2 c^2 \mu_A \quad (7)$$

Where K_e is the molecular force constant, ω_e is the equilibrium vibrational frequency, c is the velocity of light μ_A is the reduced mass and r_e is the inter ionic separation. The Values of input data are taken from (Huber & Herzberg, 1973).

The Vander Waals constant C is computed through the expression.

$$C = \left\{ \frac{3}{2} \frac{e\hbar}{m^{\frac{1}{2}}} \right\} \times \frac{\alpha_1 \alpha_2}{\left[\left(\frac{\alpha_1}{N_+} \right)^{\frac{1}{2}} + \left(\frac{\alpha_2}{N_-} \right)^{\frac{1}{2}} \right]} \quad (8)$$

Here $\hbar = \frac{h}{2\pi}$ where h is the Planck's constant. N_+ and N_- are the effective numbers for anions and cations respectively, m is the electronic mass α_1 and α_2 are the molecular state polarizabilities taken from literature of (Tessmann, 1953).

The potential parameters obtained then are used to obtain the rotation vibration coupling constant (α_e) and vibrational anharmonicity constant ($\omega_e x_e$) by using the expressions

$$\alpha_e = - \left(\frac{X_3 r_e}{3} + 1 \right) \frac{6 B e^2}{\omega_e} \quad (9)$$

And

$$\omega_e x_e = \left[\frac{5}{3} X_3^2 - X_4 \right] \times \frac{h}{64 \pi^2 c \mu} \quad (10)$$

Where X_2 , X_3 and X_4 are second third and fourth order differentiation of potential energy function U (r) In general

$$X_p = \frac{\left(\frac{\partial^p \phi(r)}{\partial r^p} \right)_{r=r_e}}{\left(\frac{\partial^2 \phi(r)}{\partial r^2} \right)_{r=r_e}} \quad (11)$$

Where p denotes the order of differentiation. The binding energy W is computed by

$$W = -NU(r)$$

Where N is the Avogadro's number

III. RESULTS AND DISCUSSION

Input data used in the calculation are the equilibrium separation r_e , Vander Waals constant C, N_+ and N. They are depicted in table 1. The calculated values of potential parameters for Born-Mayer (BM), Hellmenn (HELL), Varshni-Shukla (VS) and Ali-Hasan models are given in table 2.

The short range repulsive potential for the four models are evaluated and contained in table 3. The computed values of binding energy for the heavy metal halide (Ag and Cu) and some chalcogenides are shown in table 4

The vales are very close to the experimental values establishing the very usefulness of the model. The values of (α_e) and $(\omega_e x_e)$ are presented in table 5 and 6 respectively.

The short range repulsive interaction yields almost 36 % contribution to binding energy on the average. The polarization energy contributes approximately 18 % to the total binding energy for all models. It is observed that contribution from polarization energy term is significant. The earlier workers have ignored this term the sequence of contribution of % repulsive part is readily found in this order.

HELL (37 %) > VS (36.6 %) > BM (36.5) > AH (35%)

Like wise the percentage contribution of polarization energy is 18 % for AH model, 18.3 % of VS model, 18.5 % of HELL model and 19.2 % for BM model. Our calculations firmly establish the place of polarization energy & short range repulsive potential and the discrepancies between the theoretical and experimental data in certain cases may be attributed to the uncertainties involved in the value of input data and the limitation of the method used.

IV. CONCLUSION

The complex repulsion core of BM, HELL, VS and AH has more realistic approach in explaining the molecular properties of partially ionic and partially covalent bond. The agreement between the calculated values and the experimental values is in general good and may therefore, gives as an indication of the extent up to which the theoretical value of those properties for which there are no measurement can be relied upon.

Table 1: Input data and computed Vander Waals (C) constant for Alkali heavy metal halides and chalcogenides

Molecules	r_e (A°)	C $10^{-60}(\text{erg cm}^6)$	N_+	N.
TiO	1.6202	20.7269	6	8
SrO	1.9198	96.3899	28	8
ZrO	1.7514	38.2625211	6	8
PbS	2.2868	949.4475	22	14
CaS	2.3178	265.3657	12	14
TiS	2.0825	46.1684	6	14
SnSe	2.325	852.4176	22	24
PbSe	2.4022	1143.05316	22	24
SnTe	2.5228	1036.03095	22	24
PbTe	2.5549	1397.867	22	24
AgF	1.98317	69.1346	28	9
AgCl	2.2807	242.7145	28	15
AgBr	2.39309	358.7842	28	25
AgI	2.54462	485.7714	28	25
CuCl	2.05118	168.4418	23	15
CuBr	2.1734	249.52304	23	25
CuI	2.33832	361.9744	23	25

Table 2: Calculated values of potential parameter (λ)

Molecules	B.M. (Å^{-1})	HELL (Å^{-1})	VS (Å^{-1})	AH (10^{+12} cm)
TiO	3.1376	2.5628	1.81558	1.2317
SrO	2.4988	2.008	1.6298	0.7407
ZrO	2.9606	2.431	1.7426	0.97551
PbS	2.7022	2.3092	1.7985	0.86304
CaS	2.0633	1.6563	1.1267	0.40915
TiS	2.21856	1.7631	1.17	0.6111
SnSe	2.507	2.1166	1.6093	0.7706
PbSe	2.2637	1.881	1.3838	0.6573
SnTe	2.349	1.9903	1.5241	0.6993
PbTe	2.4569	1.9047	1.4423	0.6595
AgF	3.803	3.3633	2.791	1.4136
AgCl	3.3427	2.9609	2.4637	1.1628
AgBr	3.2183	2.8515	2.382	1.0966
AgI	3.0427	2.8098	2.2568	1.0069
CuCl	3.5106	3.0828	2.5261	1.2625
CuBr	3.2625	2.8578	2.3313	1.1333
CuI	3.1266	2.7522	2.2648	1.0589

Table 3: Calculated values of potential parameter $\frac{s}{r^m} \exp(-\lambda r^n)$ in (10^{-12} erg cm)

Molecules	BM	HELL	VS	AH
TiO	15.2559	15.05	15.693	14.3487
SrO	14.1176	13.9496	14.6316	14.6827
ZrO	13.927717	13.5288	14.0825	13.1928
PbS	13.721	13.5001	13.8708	13.09132
CaS	10.87	10.794	10.627	12.541
TiS	19.1989	18.9916	20.003	18.6578
SnSe	14.253	14.034	14.4696	13.624
PbSe	15.59	15.371	15.9325	15.634
SnTe	11.922	11.7338	12.08716	11.3889
PbTe	12.195	13.049	13.4655	12.6736
AgF	3.432	2.999	3.0529	2.9055
AgCl	3.2904	3.2363	3.2933	3.1326
AgBr	3.34151	3.28933	3.34215	3.1814
AgI	3.1873	3.0279	3.18729	3.035
CuCl	4.2742	4.2028	4.28586	4.0695
CuBr	4.3422	4.2697	4.35696	4.8505
CuI	4.01687	3.94969	4.0253	3.8242

Table 4: Calculated values of cohesive Energy W (kcal mol^{-1})

Molecules	BM	HELL	VS	AH
TiO	2995.454	3008.042	2969.314	3050.282
SrO	2406.875	2417.029	2375.651	2372.839
ZrO	2732.213	2756.245	2722.998	2776.603
PbS	1897.666	1910.997	1888.656	1935.611
CaS	1941.7188	1946.296	1956.348	1841.068
TiS	2237.948	2250.43	2189.467	2270.534
SnSe	2163.762	2176.748	2150.532	2201.466
PbSe	2054.625	2003.189	1978.133	2025.836
SnTe	2028.305	2039.688	2018.367	2060.414
PbTe	2378.492	2392.254	2358.445	2376.422
AgF	699.469	725.59	693.661	731.222
AgCl	653.893	657.151	653.784	663.394
AgBr	640.274	643.4169	634.215	643.894
AgI	609.016	618.564	609.017	618.138
CuCl	736.131	740.419	735.468	748.448
CuBr	700.698	705.07	699.814	670.083
CuI	413.412	534.709	672.63	684.742

Table 5: Calculated values of rotation- vibration Coupling constant α_e (in cm^{-1})

Molecules	BM	HELL	VS	AH	Exp.
TiO	0.00258	0.003035	0.002588	0.003958	0.00301
SrO	0.0016	0.001853	0.001431	0.001734	0.00219
ZrO	0.001867	0.001412	0.001699	0.0024	0.00198
PbS	0.000408	0.000363	0.00042	0.000695	0.000435
CaS	0.0006399	0.0005304	0.0005382	0.0004859	0.000837
TiS	0.0013059	0.0011515	0.0008737	0.001222	0.0009
SnSe	0.01669	0.021158	0.008869	0.015968	0.0001704
PbSe	0.0001925	0.0001099	0.0001781	0.0001367	0.00012993
SnTe	0.00010054	0.0000825	0.000094	0.00009309	0.0000543
PbTe	0.00002062	0.00001699	0.00002875	0.00005675	0.00006743
AgF	0.001786	0.0021016	0.002371	0.002583	0.0019206
AgCl	0.0006428	0.000739	0.0007841	0.0007926	0.000594
AgBr	0.00024	0.0002756	0.0002932	0.0003217	0.0002282
AgI	0.0002196	0.00015889	0.0001848	0.0002023	0.0001413
CuCl	0.0009375	0.001169	0.0012787	0.001361	0.000996
CuBr	0.00037687	0.0004987	0.0005526	0.0005077	0.0004521
CuI	0.0002794	0.00034341	0.0003242	0.0004312	0.003229

Table 6: Calculated values of vibrational anharmonicity constant ($\omega_e x_e$) (cm^{-1})

Molecules	BM	HELL	VS	AH	EXP
TiO	2.3121	3.1516	3.6595	4.5457	4.498
SrO	1.3031	2.2241	2.23715	3.1379	3.96
ZrO	1.8709	2.5238	2.0301	2.2863	3.14
PbS	0.8927	0.90723	1.5304	1.0717	1.3
CaS	0.7144	0.751	1.1573	0.995	1.78
TiS	0.7329	0.8093	1.1908	1.377	1.95
SnSe	0.4475	0.48868	0.55264	0.6202	0.736
PbSe	0.2725	0.3233	0.3186	0.4137	0.5101
SnTe	0.2477	0.3934	0.30026	0.38083	0.5
PbTe	0.2637	0.2845	0.2867	0.2873	0.43
AgF	2.59698	3.05393	3.1085	3.4129	2.593
AgCl	1.3359	1.27935	1.7877	1.6047	1.17
AgBr	0.62766	0.8693	0.6757	0.8401	0.6795
AgI	0.4793	0.5455	0.61308	0.5996	0.445
CuCl	1.9596	1.6413	1.6801	2.1432	1.58
CuBr	0.8552	0.9213	0.9267	1.19736	0.96
CuI	0.6537	0.7026	0.849	0.8892	0.6

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