Lattice dynamical investigation of different parameters of RbBr

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ABSTRACT

In this communication the lattice dynamics and allied properties of RbBr crystal we have investigated theoretically by use of Van der Waal three body force shell model. Elemental rubidium has a NaCl-type crystal structure which is highly reactive, with properties similar to those of other alkali metals. The investigation of of the crystals depends on the motion of the constituent atoms, which can be achieved from the theoretical models of inter ionic potentials. The new proposed model, van der Waals three body force shell (VTBFS) come in existence ,which incorporates the effects of the van der Waals interaction with long-range Coulomb interactions, three-body interactions and short-range second neighbour interactions in the framework of rigid shell model (RSM). The obtained theoretical results for Debye temperature variation, two phonons IR/Raman spectra, third order elastic constants (TOEC), fourth order elastic constants (FOEC) and the pressure derivatives of second order elastic constants (SOEC) for RbBr are very close agreement with experimental result.

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INTRODUCTION

In the last two decays a considerable interest has been shown by theoretical and experimental workers in the investigation of lattice dynamical behavior Rubidium Bromide (RbBr). The knowledge of phonon dispersion curves (PDC), Debye temperature variation, two phonons IR/Raman spectra, third order elastic constants (TOEC), fourth order elastic constants (FOEC) and the pressure derivatives of second order elastic constants (SOEC) and Cauchy discrepancy (C_{12}-C_{44}) have been of fundamental importance. According to the Quantum theory of cohesion, the ionic crystals possess Van der Waals and many body interactions. This has motivated us to incorporate the effects of van der Waals interactions and three-body interactions in the framework of ion polarizable (RSM) with short-range interactions effective up to the second neighbour. Therefore, the most realistic model for complete harmonic dynamical behaviour of the crystals under consideration can be developed by introducing the effect of van der Waals interactions (VWI) and three-body interactions (TBI) in the framework of RSM. The present model is known as van der Waals three-body force shell model (VTBFSM). This model considers all possible interactions for explaining the harmonic properties of RbBr. Due to availability of experimental data on the availability of a lot of experimental measured data on elastic constants [1-4], dielectric constants [5], phonon dispersion curves [6-10], Debye temperatures variation [11], two phonon IR and Raman spectra [12,13], third and fourth order elastic constants and their pressure derivatives [14,15], for RbBr crystal their interpretations by means of various theoretical models [7,10,16-43], has motivated the present author to the basic need for a lattice dynamical model for the satisfactory description of their interesting properties.

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2.Theory
The schematic representation of RbBr crystal structure shown in Fig.-1**.**The essential formalism of VTBFSM is the inclusion of VWI and TBI in the framework of RSM. The interactions system of present model thus consists of long-range screened Coulomb, VWI, three-body interactions and short-range overlap repulsion operative up to the second -neighbor's ions. Looking into the adequacy of the interaction system, the present model successful approach for the dynamical descriptions of RbBr crystal.
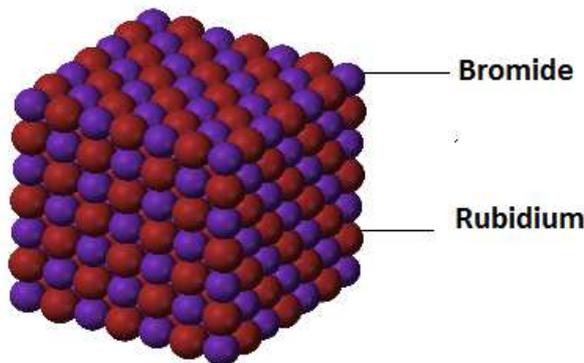
Rubidium Bromide Structure Fig-1

The general form of present model can be derived from the crystal potential energy per unit cell, given by

$$\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI} \tag{1}$$

where, the potential energy terms on the right hand side are expressed as ,Φ^C is Coulomb interaction potential. This interaction potential is long-range in nature. An ionic crystal can be regarded as made up of positive and negative ions separated by a distance $\left|\vec{r}_{ij}\right|$, where $\vec{r}_{ij}$ is a vector joining the ions i and j. According to electrostatic theory, the Coulomb energy of interaction of i-th ion with j-th ion is written as $\Phi^C(\vec{r}_{ij})$. Thus, total Coulomb energy for the crystal is

$$\Phi^C(r) = \sum_j{}' \Phi^C\left(r_{ij}\right) = \sum_j{}' \varepsilon_{ij} \frac{e^2}{\left|\vec{r}_{ij}\right|} \tag{2}$$

where, the prime means summation over all ions except $i=j$, ε_{ij} will be +1, if i and j are like ions and –1, if they are unlike. If we consider infinite lattice, the Coulomb potential energy for the whole crystal is given as

$$\Phi^C = \alpha_M \frac{Z^2 e^2}{r_0} \tag{3}$$

where, α_m is the Modelung constant whose value for NaCl-type lattice is –1.7476 and r_0 is the equilibrium nearest neighbour distance. Second term Φ^R is short-range overlap repulsion potential. The most commonly used analytical expressions for the repulsive energy are given by the inverse and exponential power laws such that

$$\Phi^R\left(r_{ij}\right) = a r_{ij}{}^n \qquad \text{(Born Potential)} \tag{4}$$

$$\Phi^R\left(r_{ij}\right) = b \exp .(- r_{ij} / \rho) \qquad \text{(B-M) Potential} \tag{5}$$

where, a (or$b$) and η(orρ) are the Born exponents called the strength and hardness parameters, respectively.

$$\Phi^R = M \beta_{+-} b \exp\left[(r_+ + r_- - r)/\rho\right] + 1/2 M \, 'b$$
$$\left[\beta_{++} \exp(2 r_+ / \rho) + \beta_{--} \exp(2 r_- / \rho)\right]\exp\left(- r'/\rho\right) \tag{6}$$

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where M and M' are the number of first and second-neighbours and r' is the distance between the second neighbours β_{ij} are the Pauling coefficients [43,45] defined as

$$\beta_{ij} = 1 + (Z_i / n_i) + (Z_j / n_j) \tag{7}$$

with Z_i and n_i as the valence and the number of outer electrons of the i-th ion, r_+ and r_- are the ionic radii of the positive and negative ions. This interaction potential is expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0} \left[\frac{2n}{Z} f(r)_0 \right] \tag{8}$$

where, the term $f(r)_0$ is a function dependent on the overlap integrals of the electron wave-functions and the subscript zero on the bracket indicates the equilibrium value of the quantities inside. Φ^{TBI} is also long-range in nature hence it is added to the Φ^C. Using the crystal energy expression (1) the equations of motion of two cores and two shells can be written as

$$\omega^2 \underline{M} \; \underline{U} = (\underline{R} + \underline{Z_m} \; \underline{C'} \; \underline{Z_m}) \; \underline{U} + (\underline{T} + \underline{Z_m} \; \underline{C'} \; \underline{Y_m}) \; \underline{W} \tag{9}$$

$$O = (\underline{T}^T + \underline{Y_m} \; \underline{C'} \; \underline{Z_m}) \; \underline{U} + (\underline{S} + \underline{K} + \underline{Y_m} \; \underline{C'} \; \underline{Y_m}) \; \underline{W} \tag{10}$$

Here $\underline{U}$ and $\underline{W}$ are vectors describing the ionic displacements and deformations, respectively and $R = \underline{T} = \underline{S}.\underline{Z_m}$ and $\underline{Y_m}$ are diagonal matrices of modified ionic charges & shell charges, respectively. The elements of matrix $\underline{Z_m}$ consists of the parameter $\underline{Z_m}$ giving the modified ionic charge.

$$\tag{11}$$

$\underline{C'}$ is the modified long-range interaction matrix given by

$$\underline{C'} = \underline{C} + (Z_m^{-2} \; Zr_0 \hat{f_0}') \; \underline{V} + (Z^2 Z_m^{-2}) \underline{D} \tag{12}$$
$$Z_m = Z\xi = \pm Z\sqrt{1+(12/Z)f_0}$$

By using equation (13) for secular determinant the frequency can calculate.

$$\left| \underline{D}(\vec{q}) - \omega^2 \; \underline{M} \; \underline{I} \right| = 0 \tag{13}$$

Here $\underline{D}(q)$ is the (6×6) dynamical matrix .If we consider only the second neighbour dipole-dipole van der Waals interaction energy, then it is expressed as:

$$\Phi_{dd}^{vwI}(r) = - S_v \qquad\qquad = \Phi^v(r) \tag{14}$$

$$\left| \frac{C_{++} + C_{--}}{6r^6} \right|$$

Where, S_v is lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively. The equation for calculation of short-range parameters for the nearest neighbours and the next nearest neighbours, are given as the respectively.

$$B_{12} = \frac{4 r_0^2}{e^2} \left[\frac{d}{dr} \Phi_1^{(R)}(r) \right]_{r=r_0} , \quad A_{12} = \frac{4 r_0^3}{e^2} \left[\frac{d^2}{dr^2} \Phi_1^{(R)}(r) \right]_{r=r_0} \tag{15}$$

$$\sqrt{2} (B_{11} + B_{22}) = \frac{4(r_0 \sqrt{2})^2}{e^2} \left[\frac{d}{dr} \Phi_2^{(R)}(r) \right]_{r=r_0 \sqrt{2}}$$

$$\sqrt{2} (A_{11} + A_{22}) = \frac{4(r_0 \sqrt{2})^3}{e^2} \left[\frac{d^2}{dr^2} \Phi_2^{(R)}(r) \right]_{r=r_0 \sqrt{2}}$$

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The modified expressions for the electrical and mechanical polarizabilities are as:

$$\alpha_i = \frac{(Y_i Z_m)^2 e^2}{R_0 + K_i}, (i = 1,2) \text{ and } d_i = \frac{R_0 (Y_i Z_m)}{R_0 + K_i} = -\frac{\alpha_i R_0}{Z e^2 (Y_i Z_m)}, (i = 1,2) \qquad (16)$$

The elastic properties in term elastic constants (C_{11}, C_{12}, C_{44}) calculated by using the equation as

$$\frac{4 r_0^4}{e^2} C_{11} = \left[-5.112 Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204 \; \xi'^2 \right] \qquad (17)$$

$$\frac{4 r_0^4}{e^2} C_{12} = \left[0.226 Z_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204 \; \xi'^2 \right] \qquad (18)$$

$$\frac{4 r_0^4}{e^2} C_{44} = \left[2.556 Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22}) \right] \qquad (19)$$

In view of the equilibrium condition [$(d\Phi/dr)_0 = 0$] we obtain $B_{11} + B_{22} + B_{12} = -1.165 Z_m^2$.

where
$$Z_m^2 = Z^2 \left(1 + \frac{12}{Z} f_0 \right) \quad \text{and} \quad \xi'^2 = Z r_0 f_0' \qquad (20)$$

The term f_0 is a function dependent on the overlap integrals of the electron wave functions and the subscript zero indicates the equilibrium value. Debye's model define the frequency distribution function which is given by

$$\Theta_D = h\nu_m / K \qquad (21)$$

To determine the combined density of states for each polarization is given by

$$D(\omega) = dN/d\omega = (VK^2/2\pi^2) \cdot dK/d\omega \qquad (22)$$

where $N = (L/2\pi)^3 (4\pi K^3/3)$, K is wave vector and $L^3 = V$.

RESULTS AND DISCUSSION

By use of Van der Waal three body force shell model (VTBFSM) the input data and model parameters have calculated in Table-1. The phonon frequencies in the first Brillouin zone, to compute the variations of Debye temperatures with specific heats in Fig-1. The observed Raman spectra has been interpreted with the help of phonon density of state (PDS) approach and critical point analysis, using the above spectrum. Debye temperature variations and combined density of state (CDS) curves for (RbBr) through use of VTBFSM have been computed at different temperatures for Θ_D against the absolute temperature (T) plotted ,are shown in Fig.-1 for RbBr. The calculated (Θ_D– T) curve for RbBr has given excellent agreement with the experimental value [25].Though the agreement is almost better with our model, VTBFSM, there is a slight discrepancy between theoretical and experimental results at higher temperatures due to the exclusion of the effect of anharmonicity in the present model. The third order ,forth order elastic constant, their pressure derivatives and Cauchy-Discrepancy for RbBr reported in Table-2 and Table-3. Which gives strength to author for complete structural descriptions and dynamical study of RbBr crystal. Theoretically calculated results for the two-phonon Raman spectra shown in table-2. This will provide a complete test for the validity of the present model for the all range of the spectra.

Table.1 Input data and model parameters for RbBr C_{ij} (in 10^{11} dyn/cm²), ν (in 10^{12} Hz), ρ (10^{-8} cm), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm³) and C_{++}, C_{--} (in 10^{-60} erg cm⁶)

Input data for RbBr		Model parameters for RbBr	
Properties	**Values for RbBr**	**Properties**	**Values for RbBr**
C_{11}	3.863[a]	$r_0 f_0'$	0.024

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C_{12}	0.474[a]	Z_m^2	0.842
C_{44}	0.405[a]	A_{12}	12.843
$v_{LO}(\Gamma)$	3.88[b]	B_{12}	-1.431
$v_{TO}(\Gamma)$	2.840[b]	A_{11}	-2.640
$v_{LO}(L)$	2.896[b]	B_{11}	7.141
$v_{TO}(L)$	2.092[b]	A_{22}	2.236
$v_{LA}(L)$	2.801[b]	B_{22}	-7.043
$v_{TA}(L)$	2.092[b]	d_1	0.101
r_o	3.399[b]	d_2	0.204
α_1	1.679[c]	Y_1	-2.644
α_2	4.091[c]	Y_2	-2.971
C_{++}	133[c]		
C_{--}	503[c]		

Ref-a-[5],b-[6], c-[16]

Table. 2 Two phonon Raman peaks, TOEC and FOEC (in units 10^{12} dyn / Cm^2), Pressure derivatives of SOEC and TOEC (dimensionless) for RbBr

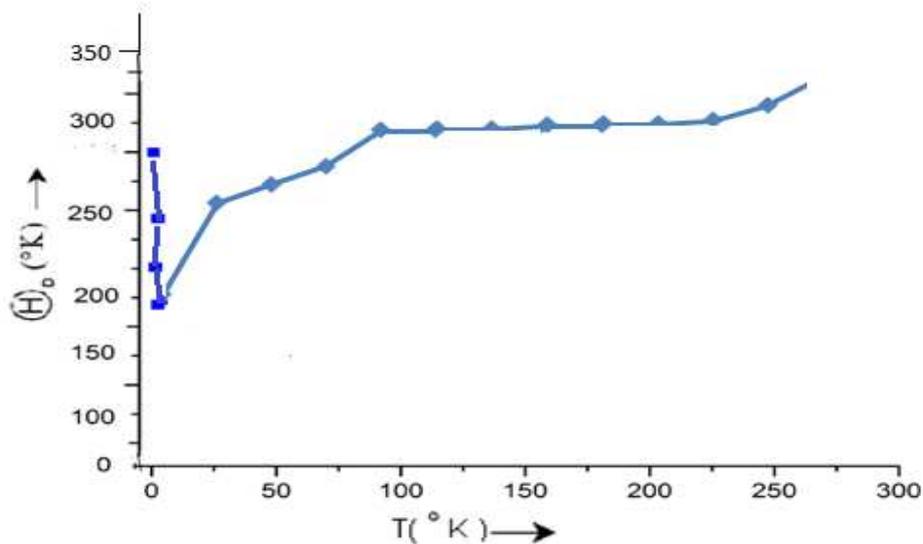| Raman Active -(Present study)			TOEC and FOEC (in units 10^{12} dyn / Cm^2)		Pressure derivatives of SOEC and TOEC (dimensionless)	
Frequency In (THz)	Branch	Values (cm^{-1}) by [VTBFSM]	Property	RbBr (Present)	Property	RbBr (Prsent)
1.48	2TA(X)	132	C_{111}	67.2315	dK'/dP	5.905
1.86	TO(X)–TA(X)	62	C_{112}	-0.1437	dS'/dP	6.433
1.98	LO(X)–TA(X)	66	C_{123}	0.0530	dC'_{44}/dP	-0.432
2.96	LA(X)+TA(X)	92	C_{144}	0.05479	dC'_{111}/dP	-576.743
3.54	2LA(X)	118	C_{166}	-0.1536	dC'_{112}/dP	-2.330
3.84	TO(X)+TA(X)	128	C_{456}	0.05456	dC'_{166}/dP	2.342
4.14	2TA(L)	138	C_{1111}	76.5485	dC'_{123}/dP	1.435
2.07	TO(L)+TA(L)	69	C_{1112}	0.3357	dC'_{144}/dP	-0.634
-------	2TO(L)	-----	C_{1166}	0.2231	dC'_{456}/dP	1.430
2.07	LO(L)+TA(L)	69	C_{1122}	0.4516		
-------	LO(L)+TO(L)	------	C_{1266}	0.4596		
5.70	2TO(Δ)	62	C_{4444}	0.3234		
5.70	2TO(X)	190	C_{1123}	-0.1256		
5.94	2LO(X)	198	C_{1144}	-0.1035		
3.75	LO+TA(Δ)	125	C_{1244}	-0.1125		
1.20	LA-TA(Δ)	40	C_{1456}	-0.1073		

Fig.1. Debye temperature variations for RbBr

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Table.3-Cauchy-Discrepancy (in units 10^{12} dyne/cm^2) for lattice dynamics of RbBr

Property	$C_{112}-$ C_{166}	$C_{123}-$ C_{456}	$C_{144}-$ C_{456}	$C_{123}-$ C_{144}	$C_{1112}-$ C_{1166}	$C_{1122}-$ C_{1266}	$C_{1122}-$ C_{4444}	$C_{1123}-$ C_{1144}	$C_{1123}-$ C_{1456}	$C_{1123}-$ C_{1244}
Values for RbBr	0.0099	-0.00156	0.00023	-0.00179	0.1126	-0.008	0.1282	-0.0221	-0.0183	-0.0131

CONCLUSION

The theoretically investigated value of Debye temperature and Raman spectra explain correctly by use of calculated results of model parameter. A successful interpretation of these spectra has provided the next best test of any model for higher range of frequency spectra. The calculation of TOEC, FOEC with pressure derivative and Cauchy-Discrepancy reported in Table .2 & 3 successfully .The interpretation of Raman spectra achieved from PDS approach and critical point analysis may be considered satisfactory in all cases. The theoretical results have been calculated for different frequency and reveal better agreement [10-14].Therefore, the inclusion of van der Waals interaction is essential for the complete description of the phonon dynamical behaviour of Rubidium crystals. The basic idea about the RbBr crystal has taken by [46] and author highly thanks him. Some researchers also have been successfully reported theoretical result for other alkali halides using the same model [40-51].

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