

# INFRARED ABSORPTION FREQUENCY OF IONIC CRYSTALS

S. P. SRIVASTAVA, S. KUMAR AND M. P. MADAN

DEPARTMENT OF PHYSICS, UNIVERSITY OF LUCKNOW, INDIA.

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**ABSTRACT.** Relations are derived for the absorption frequency of ionic crystals in terms of various lattice properties following a simple and direct approach through the assumption of a few realistic interaction potential functions, in particular an exp : exp type of potential. The derived relations permit the use of room temperature input data and also consider the electronic polarizability which is neglected in the rigid ion approximation. The absorption frequencies have been computed utilizing recent data for various lattice properties. A very satisfactory agreement has been found with the measured values of the frequency as well as with the frequency computed from the frequency versus wave vector dispersion curves.

## INTRODUCTION

Born and his collaborators (1954) using a simple interionic force model correlated the cohesive energies with the lattice constants and the compressibility and obtained a reasonable degree of success. Szigeti (1949, 1951) and independently Odelevski (1950), using the simple Born model derived relations for the absorption frequency in connection with the theory of dielectric constants but found the results at variance with the experiment. The disagreement with the experiment was also noticed with regard to lattice vibration calculations based on simple Born model, in particular, when the frequency versus wave vector dispersion curves were compared with those determined experimentally by inelastic neutron scattering (Woods *et al.* 1960, 1963, Cowley *et al.* 1963). Szigeti (1951) pointed out that the failure of his relations indicated the distortion polarization of ions displaced relative to one another. Attempts to explain part of the deviations have been made by Born *et al.* (1954), Tolpygo (1950), Lundqvist (1955, 1957) and in terms of a more complicated model of dielectric polarization by Dick *et al.* (1958) and by Hanlon *et al.* (1959). Yamashita (1955) in their treatment of the dielectric constants of ionic crystals have also considered the connection between polarization of ions and the repulsive force between them. Woods *et al.* (1960, 1963) and Cowley *et al.* (1963) used a shell model originally developed by Dick *et al.* (1958) for the interpretation of their results from inelastic neutron scattering. Somewhat similar attempts to explain the experimentally observed dispersion curves have been made by Hardy (1959, 1961, 1962) and Hardy *et al.* Karo (1960).

Szigeti (1951) obtained two relations, the first connecting the absorption frequency  $\omega_0$  with the static and high frequency dielectric constants  $\epsilon$  and  $\epsilon_\infty$ , respectively, as

$$\epsilon - \epsilon_\infty = (\epsilon_\infty + 2)^2 \frac{4\pi N(ze^*)^2}{9m\omega_0^2} \quad \dots (1)$$

where  $m$  is the reduced mass of an ion pair and  $N$  the Avogadro Number, and the second connecting the absorption frequency with the compressibility  $\beta$  as

$$m\omega_0^2 \left( \frac{\epsilon + 2}{\epsilon_\infty + 2} \right) = \frac{3v}{\beta R_0^2} \quad \dots (2)$$

where  $v$  is the volume of the lattice cell and  $R_0$  the equilibrium interionic distance. Szigeti (1951) introduces the idea of an effective charge  $e^*$  to account for the distortion of ions by overlap forces. Attempts to compute the magnitude of  $e^*/e$  have been made among others by Szigeti (1951), Lundqvist (1955, 1957), Dick *et al* (1958) and Havinga (1961). Lundqvist has also investigated the effect of the second neighbour interactions neglected in the simple theory, by assuming a more complicated model involving three body as well as two body interactions. Three body interactions have also been discussed by Szigeti (1960, 1961), Karo *et al* (1963) and Hardy *et al* (1965). It should be pointed out that Szigeti relation (2) connecting the absorption frequency with the compressibility does not involve  $e^*$  and should still be correct in the approximation when ionic distortion is treated in terms of distortion dipoles determined by the nearest neighbour ionic separation. The deviation of the results of this equation from the experiment therefore should not be attributed to distortion moments and one must look for the explanation of discrepancies elsewhere.

Information about infrared absorption frequency  $\omega_0$  can also be obtained from the frequency  $\omega$  versus wave vector  $q$  dispersion curves (Woods *et al*, 1960, 1963, Cowley *et al*, 1963, Karo *et al*, 1963, Hardy *et al*, 1965, Kellermann 1940, 1941) and finding the transverse optical frequency at  $q = 0$ , which incidentally is a laborious procedure and provides an indirect description of the interionic forces. Szigeti's expressions as well as the frequency versus wave vector dispersion curves based on simple Born model or other complicated models of dielectric polarization (Woods *et al*, 1960, 1963, Cowley, *et al*, 1963, Dick *et al* 1958, Karo *et al* 1963, Hardy *et al* Karo 1965) are independent of the particular shape of the potential function or the potential parameters. In addition these expressions require the condition for the stability of a static lattice. They are strictly applicable only at very low temperatures and also if zero point vibrations are neglected. Deviations (Hass 1960) are found to occur when room temperature values are inserted in these relations.

Another approach which is simple and direct is through the assumption of a central pairwise potential function and the consideration of electronic polarizability which is neglected in the rigid ion approximation. Relations can then be derived for the absorption frequency in terms of various lattice properties. Further, as the various lattice properties are not directly observable for static lattices the relations can be modified so that they permit the use of room temperature values. In what follows, the determination of the absorption frequencies on the basis of more realistic potential forms in conjunction with various lattice properties has been made. The derived relations allow the use of room temperature data for the compressibility  $\beta$ , the interionic distance  $R_0$  and other lattice properties. Moreover, the values of  $R_0$  and  $\beta$  as well as of the Madelung term occurring in the potential function and as reported in Born *et al* (1954) and Huggins (1937) have undergone a rather important change. Since then a redetermination of these quantities has been made and a more reliable data is available (Cubicciotti 1959, Spangenberg 1956, Spangenberg *et al* 1957) which has been used in the present work.

#### INTERACTION POTENTIALS

A knowledge of the accurate potential energy function is very necessary for investigating the interaction potential approach which lays emphasis on the particular shape of the potential function. The potential energy  $\psi$  of the crystal per pair of ions can be written in the form

$$\psi = \phi_C + \phi_R \quad \dots (3)$$

where  $\phi_C$  is the Coulomb potential and is of the form  $\alpha'e^2/R$  where  $\alpha'$  is the Madelung's constant and  $e$  the electronic charge.  $\phi_R$  contains the energy contributions other than the electrostatic energy and includes the repulsive energies, the Van der Waals attractive energies and may include the zero-point energy. The forces included in  $\phi_R$  are of great importance for the absorption frequency, the compressibility and the other lattice properties. It is a reasonable approximation to take into account the forces between nearest neighbours only. If zero-point energy is included as a part of the lattice energy, the cohesive energy  $U$  per mole is given by

$$U = -[N\psi + \epsilon_0] \quad \dots (4)$$

where  $\epsilon_0$  is the zero-point energy per mole.  $\phi_R$  can be expected to be of the form

$$\phi_R = B \exp(-R/\rho) \quad \dots (5)$$

or may be taken to be of the type

$$\phi_R = B \exp(-R/\rho) - CR^{-6} \quad \dots (6)$$

when Van der Waals forces are also considered, where,  $B$ ,  $C$  and  $\rho$  are the potential parameters. The interatomic potential between two inert gas atoms has been studied intensively using the familiar Lennard-Jones 12:6 potential form as well

as by the other potential forms such as the Buckingham-Corner, the exp : six and more recently by the exp:exp potential form. Alkali halides are the closest to the theoretical model for ionic crystals having rare gas structures. In view of the apparent success of these potentials in explaining the behaviour of inert gas atomic structures,  $\phi_R$  can also be given a form based on these potentials provided the potential parameters are determined independently and directly using the observed lattice properties. This restriction is important because it has been shown by Rittner (1951) that the earlier attempts to calculate the binding energies and other properties of alkali halide gas molecules from Born lattice theory assuming that the repulsion constants are the same for gas molecules as for the crystals are certainly not valid. A few of the properties of some ionic crystals using simple inverse forms that is  $BR^{-12}$  for the repulsive energy and  $CR^{-6}$  for the attractive energy (Lennard-Jones potential) were studied by Sharma and Madan (1961, 1964). However, the expressions for the Van der Waals terms ( $-CR^{-6}$ ,  $-DR^{-8}$ , etc.) are not very satisfactory for closely situated atoms when the overlap is predominant, though the dipole-dipole potential probably reproduces the correct order of magnitude. A more realistic form is perhaps desirable to express this attractive contribution to the total lattice energy. As such, of particular interest is the exp : exp form for the interaction energy. This potential was used initially to explain the vibrational spectra of diatomic molecules, but has not been tried for ionic crystal lattices. Here we have considered this potential to examine the characteristic frequencies and other lattice properties. In order to test its suitability as an ionic potential we have also investigated, for comparison, the potentials given by equations (5) and (6) as well as the Lennard-Jones potential. Using an exp : exp form, the equation for  $\phi_R$  is written in a simplified form as

$$\phi_R = Be^{-2R/\rho} - Ce^{-R/\rho} \quad \dots (7)$$

where  $B$ ,  $C$  and  $\rho$  are the potential parameters.

#### ESTIMATION OF LATTICE FREQUENCIES

Many of the macroscopic properties of crystals can be obtained from the dynamic motions of their lattice particles. The statistical mechanics of such motions gives the expressions for the free energy of the system which in turn can be related with the total internal energy  $E$  and the entropy by the thermodynamical relations (Born *et al*, 1954) such that we can write

$$E = U + E_{vib} \quad (8)$$

Here  $U$ , the lattice energy is a function only of the interatomic distances or of volume in the adiabatic approximation (Dobbs *et al* 1957).  $E_{vib}$  represents the thermal energy excluding the zero-point energy. The zero-point energy which is also dependent only on volume, is included in  $U$  (see equation (4)). The ions in the crystal are held in their respective positions by the forces included in the

representation of  $U$ . Usually the derivatives of  $U$  are evaluated at absolute zero and in the absence of zero-point energy. In order to be able to use the room temperature values of lattice properties, the derivatives should be evaluated at the mean positions which the atoms actually occupy at the temperature  $T$ . For this purpose one can use the expressions given by Hildebrand (1931), obtained from equation (8) as (using  $\psi$  instead of  $U$  for convenience)

$$\left( \frac{d\psi}{dR} \right)_{R=R_0} = \frac{3vT\alpha}{\beta R_0} \quad \dots (9)$$

and

$$\left( \frac{d^2\psi}{dR^2} \right)_{R=R_0} = \frac{9v^2}{\beta R_0^2} F_{TP} \quad \dots (10)$$

where  $\alpha$  is the thermal expansion coefficient and  $F_{TP}$  is a temperature dependent factor which is very nearly equal to unity. The expression for this is given in Cubicciotti (1959). When there is a small displacement of the lattice of positive ions relative to the lattice of negative ions, there is a change in the internal energy of the crystal. The contributing effect is mainly contained in the change  $\delta\phi_R$  (Szigeti 1951, Krishnan *et al*, 1951). The energy change is

$$\delta\phi_R = \frac{1}{2} m \omega_r^2 r^2 \quad \dots (11)$$

where  $r$  is the displacement of the two kinds of ions relative to each other, and  $m\omega_r^2 = f$ , the force constant. Neglecting anharmonicity the frequency  $\omega_r$  is given as

$$\omega_r = \sqrt{\frac{f}{m}} \quad \dots (12)$$

To evaluate  $f$ , one has to add up the interactions of one of the ions with its nearest neighbours. Starting with the appropriate equation for the interaction potential, the force constant could be estimated as a coefficient of  $r$  in the expansion of  $d\psi/dR$  as a power series in  $r$ . The potential parameters are then evaluated with the help of the relations (9) and (10). Thus for a crystal of NaCl type, using the exp:exp potential (equation (7)) we obtain

$$f = \frac{1}{3} \left[ \frac{1}{\rho R_0} \left( \frac{\alpha' e^2}{R_0^3} - \frac{3vT\alpha}{\beta R_0} \right) (3R_0 - 2\rho) - \frac{2}{\rho^2} \left( \frac{\alpha' e^2}{R_0} - E' \right) \right] \quad \dots (13)$$

where  $E'$  are the energy values which are derived from the experimental energy values listed by Seitz (1940) considering the zero-point energies (Cubicciotti 1959). Alternatively, one could proceed following Krishnan *et al* (1951) and Born

et al (1954) and obtain  $f$  in terms of the first and second derivatives of  $\phi_R$  as

$$f = \frac{1}{3} \left[ \phi_{R''} + \frac{2}{R_0} \phi_{R'} \right] \quad (14)$$

It can be verified easily that equations (13) and (14) are essentially equivalent. Equation (14) is more convenient for computational purposes. Similarly using the potential forms represented by equations (5) and (6) we obtain for the force constant  $f$  as

$$f_{eq.(5)} = \frac{1}{3\rho R_0} \left[ \frac{\alpha'e^2}{R_0} - E' \right] \left( \frac{R_0}{\rho} - 2 \right) \quad (15)$$

and

$$f_{eq.(6)} = \frac{1}{3} \left[ \frac{1}{\rho R_0} \left( \frac{\alpha'e^2}{R_0} - E' + \frac{C}{R_0^6} \right) \left( \frac{R_0}{\rho} - 2 \right) - \frac{30C}{R_0^8} \right] \quad (16)$$

whereas for the Lennard-Jones 12:6 potential  $f$  has the value

$$f_{L-J} = \frac{1}{3R_0^2} \left[ 17R_0 \left( \frac{\alpha'e^2}{R_0^2} - \frac{3vT\alpha}{\beta R_0} \right) - 7 \left( \frac{\alpha'e^2}{R_0} - E' \right) \right] \quad (17)$$

The values of the force constants thus determined are given in table 1, where they have been compared with each other. The force constant  $f$  is entirely

Table 1  
Values of force constants  $f \times 10^{-4}$

Crystals	(Eq. 13)	(Eq. 17)	(Eq. 16)	(Eq. 15)
LiF	6.60	8.10	6.84	6.75
LiCl	4.31	5.94	4.41	4.26
LiBr	3.83	5.59	3.87	3.37
LiI	3.25	4.90	3.33	2.21
NaF	5.55	6.22	6.34	6.25
NaCl	4.31	4.81	5.30	5.12
NaBr	3.63	4.10	4.28	4.09
NaI	3.08	4.05	2.98	2.65
KCl	3.12	3.49	4.10	3.95
KBr	2.40	2.85	4.33	4.18
KI	2.22	2.50	3.84	3.28
RbCl	3.35	3.50	4.59	3.71
RbBr	2.94	3.02	4.32	3.38
RbI	2.65	3.06	2.71	2.08
CsCl	3.07	3.25	3.43	2.57
CsBr	2.74	2.57	3.07	2.89
CsI	2.44	2.87	2.06	—

determined from a knowledge of  $\phi_R$  and is for the type of displacement in which the electronic polarizability in the crystal is ignored. The electronic polarizability is considered by taking into account the polarization of the medium (Born *et al* 1954, Szigeti 1951, Lyddane *et al* 1941) and an expression for the force constant can be obtained (Born *et al* 1954) as

$$\frac{f}{m} = \frac{\epsilon+2}{\epsilon_{\infty}+2} \omega_0^2 \quad \dots \quad (18)$$

Equation (18) is derived by considering a lattice of polarizable ions, which contribute to the local polarization, firstly, a moment due to their displacement from lattice sites and secondly, the moments induced in the ions by the effective field representing the Coulomb interaction. In addition, one can also consider the electronic dipole moment created by local distortions when a positive ion approaches a more polarizable negative ion and which affects the field in the overlapping regions (Szigeti 1951, Mott *et al* 1948). Following Szigeti's idea of an effective charge  $e^*$  one can derive an expression for the force constant  $f$  in terms of the dielectric constants and the distance  $R_0$ . The result is

$$f = \frac{2\pi(e^*)^2}{9R_0^3} \cdot \frac{(\epsilon_{\infty}+2)(\epsilon+2)}{(c-\epsilon_{\infty})} \quad \dots \quad (19)$$

It can be seen from equation (18) that a knowledge of  $\omega_0$  is necessary for the determination of  $f$ , whereas, for equation (19) we need in addition to the experimental data on dielectric constants, the values of  $e^*$  and  $R_0$ . The effect of local distortions due to the neighbouring ions is eliminated in equation (18) and as such it is preferred. Hardy (1961) also indicates that equation (18) is obeyed better than equation (19) particularly for crystals containing light ions. Equations (13) and (15) to (17) in conjunction with equation (18) may now be subjected to test in computing the infrared absorption frequencies. These are tabulated in table 2. The experimental frequencies reported are those given by Barnes (1932) and Jones *et al* (1961). As mentioned earlier, the parameters occurring in various relations for interaction potentials as well as for  $f$  are determined using relations (9) and (10).  $C$ , the Van der Waals constant, in expression (6) can be evaluated from the above conditions or its value as given by Huggins (1937) from a careful analysis of optical data can be used.  $\beta$  and other terms used were those reported by Cubicciotti (1959) except the  $\alpha$  values which are those listed by Weyl (1955) and Kumar (1959, 1960). It can be seen from the table that for crystals containing lighter ions, the exp:exp potential is definitely better than the Lennard-Jones potential. Exp. model or modified exp. model gives satisfactory results only for a few crystals. As we proceed down the table, we see that Lennard-Jones potential gives quite good results for crystals containing heavier ions. This is in confirmation with our earlier findings (Sharma *et al* 1961). However, one

cannot fail to notice that the exp:exp potential also yields equally good results for these crystals leading to the conclusion that this potential is definitely better

Table 2  
Values of absorption frequencies  
 $\omega_0(10^{13}\text{sec.}^{-1})$

Crystals	Exptl. (Barnes 1932)	Exptl. (Jones <i>et al.</i> , 1961)	exp : exp	Lennard- Jones 12 : 6	Modified exp.	exp.
LiF	5.78	—	5.22	5.78	5.32	5.28
LiCl	—	—	4.04	4.74	4.09	4.02
LiBr	—	—	3.79	4.58	3.81	3.56
LiI	—	—	3.68	4.47	3.68	3.00
NaF	4.64	—	3.87	4.10	4.14	4.11
NaCl	3.09, 3.09*	—	3.22	3.41	3.58	3.49
NaBr	2.52	2.55	2.66	2.83	2.89	3.83
NaI	2.20	2.20	2.34	2.68	2.30	2.17
KCl	2.67, 2.68*	2.71	2.51	2.64	2.87	2.82
KBr	2.13	2.18	1.88	2.05	2.52	2.48
KI	1.85	1.91	1.74	1.85	2.29	2.12
RbCl	2.22	2.24	2.20	2.24	2.57	2.31
RbBr	1.65	1.69	1.62	1.65	1.98	1.79
RbI	1.45	1.42	1.45	1.55	1.45	1.28
CsCl	1.85	1.87	1.81	1.87	1.92	1.66
CsBr	1.41	1.39	1.49	1.45	1.58	1.54

\* Hass (1960).

than the other ionic interaction models for the whole family of alkali halides considered here and should be preferred for the calculation of lattice properties. The present computed values of the absorption frequency of those alkali halides which have been considered by Karo *et al* (1963), Hardy *et al* (1965), Woods *et al.* (1960, 1963) and Cowley *et al* (1963) can be compared with the values obtained from frequency versus wave vector dispersion curves for  $q = 0$  by them. It is seen in general (from their curves) that the agreement is very reasonable and the deviations observed by us from the experimental measurements using the  $f$  values from exp:exp model or Lennard-Jones 12:6 model appear to be roughly of the same nature and magnitude as that noticed by them. We did not hope to produce as good an agreement between the theory and experiment as that found by using the dispersion curve approach, nevertheless in view of the present simple and direct approach it is significant that we appear to confirm their results within a few percent. We consider that the agreement verifies that the general



picture and main features of our approach are correct and our theory leads to results which are in general in reasonable agreement with the experimental data that exist, and also with the values obtained from dispersion curves.

Using the experimental values of the absorption frequency  $\omega_0$ , Szigeti (1951) calculated the compressibilities employing equation (2) using however, the room temperature data. The equation (2) is obtained with the aid of equation (18) and the relation

$$\frac{1}{\beta} = \frac{R_0^2 f}{3v} \quad \dots (20)$$

Odelevski (1950), Dick *et al* (1958), Hanlon *et. al* (1959) and Lundqvist (1955, 1957) have proposed generalisations of the Szigeti formula (2) to take into account different aspects of dielectric polarization. Hass (1960) using these different proposed formulae finds that his experimental data is in good agreement with frequencies calculated using the Szigeti formula (2). The formulae of Odelevski and Lundqvist when combined also give comparable results, though its appropriateness for all the alkali halides is doubtful. Thus it is prefer-

Table 3  
Values of compressibilities

Crystals	$\frac{\beta_{\text{calc.}}}{\beta_{\text{obs.}}}$ (a)	$\frac{\beta_{\text{calc.}}}{\beta_{\text{obs.}}}$ (b)	$\frac{\beta_{\text{calc.}}}{\beta_{\text{obs.}}}$ (c)	$\frac{\beta_{\text{calc.}}}{\beta_{\text{obs.}}}$ (d)
LiF	0.82*	1.05*	1.00	1.00
NaF	0.70*	0.85*	0.83	1.01
NaCl	1.13*(1.12)	1.08*(1.08)	0.99	1.03
NaBr	1.03	1.14	1.13	1.01
NaI	1.16	1.14	1.05	1.03
KCl	0.91(0.93)	0.94(0.96)	0.96	1.07
KBr	0.97	0.95	0.95	1.30
KI	0.98	0.98	0.99	1.18
RbCl	0.96	0.92	0.89	1.00
RbBr	0.94	0.89	0.83	0.99
RbI	1.04	0.95	0.66	1.02
CsCl	0.94	0.91	0.87	1.00
CsBr	0.94	0.96	0.87	0.98

(a) Using equation (21) with experimental values of frequency (Jones *et al.*, 1961).

(b) Using Szigeti equation but recent data.

(c) Szigeti (1951).

(d) Calculated from equation (21) using the exp : exp potential.

Values marked \* and in parentheses are those for which the experimental frequencies have been taken from Barnes (1932) and Hass (1960), respectively.

able to use the Szigeti relation (2). However, this relation was derived without considering the specific form of the potential. A relation similar to equation (20) connecting the compressibility and the force constant (and hence the absorption frequency) but permitting the use of room temperature values of  $R_0$  and  $\beta$  can also be derived. Such a relation is useful but cannot be used to test the appropriateness of a particular ionic potential. Using equation (14) and equations (9) and (10) it can be shown that

$$\frac{1}{\beta} = \frac{R_0^3 f}{3\nu(F_{TP} + \frac{2}{3}T\alpha)} \quad \dots (21)$$

The values of the compressibilities thus calculated are given in table 3. In this table are also given the values of  $(\beta_{calc.}/\beta_{obs.})$  following Szigeti when recent data for absorption frequency (Barnes 1932, Jones *et al* 1961),  $R_0$  and  $\beta$  (Cubicciotti 1959) are considered. For comparison old values of Szigeti (1951) are also listed in column 4. We have also listed in this table the values of the ratio, taking  $\beta_{calc.}$  by using the  $f$  values obtained from the interionic potential (column 2, table 1). Even though  $\beta_{obs.}$  were one of the experimental data in addition to the experimental  $E'$ ,  $R_0$  and  $\alpha$  values used for the determination of potential parameters, it is of some use to obtain these values to see how well the force constants obtained from different lattice properties taken together reproduce a single lattice property. When a comparison is made between columns 2 and 3 it is seen that the values of compressibility using modified equation (21) agree more with the experimental values for most of the crystals. The agreement is slightly inferior to value calculated using Szigeti relation for only a few crystals such as LiF and NaF. This is mainly due to the large deviation from unity of the factor  $F_{TP}$  for these crystals. It may be remarked that these new redetermined values computed using recent data show a better agreement with experiment over the old values of Szigeti.

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