

Infrared eigen frequency and characteristic Debye temperature of a few heavier halides.

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Using the Lennard-Jones (12:6) potential energy function the necessary equation for the force constant and infrared eigen frequency  $\nu_0$  have been derived. The calculated values of  $\nu_0$  and Debye  $\Theta_D$  have been compared with the experimental data. The calculated results reveal the appropriateness of the Lennard-Jones potential model for heavier salts.

INTRODUCTION

The interatomic forces play a important role in predicting the various properties of matter. The behaviour of the forces for ionic crystals was studied in the early stage by Mie (1903), Gruneisen (1912, 1926), Born (1923), Born & Mayer (1932), and in the later stage by Cubicciotti (1959, 1951) Sharma & Madan (1961, 1962), Chatterjee (1963), Kachhava & Saxena (1965, 1966), Gohel & Trivedi (1967) and others and has been summarised by Kittel (1956) and by Born & Huang (1954). In an ionic crystal the degree of ionisation of the constituent atoms is often such that the electronic configuration of all ions corresponds to closed electronic shells, as in the case of inert gas atoms. Assuming this, Sharma and Madan (1964a, 1964b) have computed the various properties of alkali and metal halides. In the present paper we have extended the use of the Lennard-Jones (12:6) potential model in calculating some other properties, viz., infrared eigen frequency  $\nu_0$  and characteristic Debye temperature  $\Theta_D$  of a few heavier halides.

COMPUTATION OF CRYSTAL PROPERTIES

Using the Lennard-Jones (12:6) potential model in conjunction with the Coulomb term, the expression for the energy per unit cell can be written as :

$$\phi(r) = - \frac{\alpha Z^2 e^2}{r} + \frac{B}{r^{12}} - \frac{C}{r^8} - \frac{D}{r^6} + \epsilon_0 \quad \dots(1)$$

where  $\alpha$  is the Madelung constant,  $Ze$  is the charge on an ion,  $r$  is the interionic distance,  $B$  is the repulsive parameter,  $\frac{C}{r^8}$  is the dipole-dipole interaction term,  $\frac{D}{r^6}$  is the dipole-quadrupole interaction term, and  $\epsilon_0$  is the zero-point energy.

The experimental values of  $r$ ,  $\phi(r)$  and  $\epsilon_0$  can be substituted in equation (1) to determine  $B$  if we have a knowledge of  $C$  and  $D$  from other means. Estimates of  $C$  and  $D$  obtained from an analysis of optical data were employed to determine  $B$  (Mayer 1933; Mayer & Levy 1933; Bleich 1934). The values of  $B$  are given in table 1.

The force constant  $f$  is given by

$$f = \frac{1}{3} \left[ \frac{2\phi'(r)}{r} + \phi''(r) \right] \quad \dots(2)$$

in which  $\phi'(r)$  and  $\phi''(r)$  are the first and second derivatives, respectively, of the overlap potential between a positive and a negative ion. Substituting for  $\phi'(r)$  and  $\phi''(r)$  in equation (3) we at once get

$$f = 44 \cdot \frac{B}{r^{14}} - 10 \cdot \frac{C}{r^8} - \frac{56}{3} \cdot \frac{D}{r^{10}} \quad \dots(3)$$

Using  $C$  and  $D$  from optical data and  $B$  from equation (1) we can compute the force constant which is tabulated in table 1.

(A) *Infrared absorption frequency*

The characteristic infrared eigen frequency  $\nu_0$  of the ionic crystals is the frequency of the lattice of positive ions moving as a unit relative to the lattice of negative ions. Taking polarisation into consideration,  $\nu_0$  can be calculated from

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{f}{\mu} \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right)} \quad \dots(4)$$

where  $\mu$  is the reduced mass of the ions,  $\epsilon_0$  is the static dielectric constant and  $\epsilon_\infty$  is the high frequency dielectric constant.

Substituting for,  $f$ , we get

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{\left( 44 \cdot \frac{B}{r^{14}} - 10 \cdot \frac{C}{r^8} - \frac{56}{3} \cdot \frac{D}{r^{10}} \right) \left( \epsilon_\infty + 2 \right)}{\mu(\epsilon_0 + 2)}} \quad \dots(5)$$

Here  $C$  and  $D$  can again be taken from optical data of Mayer (1933), Mayer & Levy (1933) and Bleich (1934) and  $B$  from equation (1).

The values of  $\nu_0$  calculated from equation (5) are presented in table 1. The experimental values of  $\nu_0$  for the considered halides are also included in table 1 for comparison. It is interesting to note that  $\nu_0$  calculated from force constant compares well with the observed values of  $\nu_0$ . Specially in the case of TlCl and TlBr, the agreement is very good and this clearly indicates the adequacy of the Lennard-Jones potential model for the heavier ionic crystals.

TABLE 1. REPULSIVE PARAMETER  $B$ , FORCE CONSTANT  $f$  AND INFRARED EIGEN FREQUENCY  $\nu_0$  OF SOME HEAVIER HALIDES

| Substance | $B \times 10^{104}$<br>(from equation 1) | $f \times 10^{-4}$<br>(from equation 3) | $\nu_0 \times 10^{-12}(\text{sec}^{-1})$ |                            |
|-----------|--|---|--|----------------------------|
|           |  |   | Exp.<br>[Born & Housing<br>(1954)].      | Cal.<br>(Using equation 5) |
| CuCl      | 4.660                                    | 11.730                                  | 5.67                                     | 6.037                      |
| CuBr      | 6.772                                    | 8.071                                   | 5.27                                     | 4.597                      |
| CuI       | 8.056                                    | —                                       | —  | —                          |
| AgCl      | 45.290                                   | 9.610                                   | (3.09)                                   | 4.812                      |
| AgBr      | 59.940                                   | 6.998                                   | (2.29)                                   | 3.192                      |
| AgI       | 41.300                                   | —                                       | —  | —                          |
| TlCl      | 419.700                                  | 7.068                                   | 2.58                                     | 2.732                      |
| TlBr      | 604.700                                  | 6.522                                   | (1.85)                                   | 1.966                      |

Gohel & Trivedi (1967) have also calculated the lattice energies of some heavier ions using the Lennard-Jones potential energy function which clearly supports the adequacy of Lennard-Jones (12:6) model for a heavier salts.

TABLE 2. CALCULATED AND EXPERIMENTAL VALUES OF DEBYE  $\psi_D$  FOR SOME HEAVIER HALIDES

| Substance | $\psi_D$ experi-<br>mental** | $\psi_D$ Theoretical<br>(Using<br>Eq. 6) | $\psi_D$ refl.*<br>(Infrared) | $\psi_D$ abs.*<br>(Infrared) | $\psi_D$ elastic* | $\psi_D$ Black-<br>mann* & Joshi* | $\psi_D$ Mitra |
|-----------|------------------------------|--|-------------------------------|------------------------------|-------------------|-----------------------------------|----------------|
| CuCl      |                              | 289.80                                   |                               |                              |                   |                                   |                |
| CuBr      | 183                          | 220.70                                   |                               |                              |                   |                                   |                |
| AgCl      | 144                          | 231.10                                   |                               |                              |                   |                                   |                |
| AgBr      |                              | 153.20                                   |                               |                              |                   |                                   |                |
| TlCl      |                              | 131.10                                   | 157                           | 123                          | 125               | 100                               | 164            |
| TlBr      |                              | 94.39                                    | 123                           | —                            | 114               | 71                                | 117            |

\* Mitra & Joshi (1960 b)

\*\* Reddy (1963)

(B) Characteristic Debye temperature  $\psi_D$

A number of relations have been given connecting the Debye characteristic temperature  $\psi_D$  and the compressibility by Blackman (1942),

Mitra & Joshi (1960a) and by others. Once the value of  $\gamma_0$  is calculated,  $\phi_D$  can be computed from the relation

$$\phi_D = \frac{h\nu_0}{k} \quad \dots(6)$$

where  $h$  is the Planck's constant and  $k$  is the Boltzmann's constant.

The calculated values of  $\phi_D$  using equation (6) are given in table 2 for a few heavier halides along with the values determined by various other methods for the sake of comparison. The agreement between the calculated and observed values of  $\phi_D$  is quite satisfactory considering the approximations involved in the theory.

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