

## Phonon dispersion curves of CsCN

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**Abstract.** The motivation for the present work was gained from the recent publication on phonon dispersion curves (PDCs) of CsCN from the neutron scattering technique. We have applied the extended three-body force shell model (ETSM) by incorporating the effect of coupling between the translation modes and the orientation of cyanide molecules for the description of phonon dispersion curves of CsCN between the temperatures 195 and 295 K. Our results on PDCs in symmetric direction are in good agreement with the experimental data measured with inelastic neutron scattering technique.

**Keywords.** Phonon dispersion curves (PDCs); translational–rotational coupling (TR); neutron diffraction.

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### 1. Introduction

Cesium cyanide is an ionic molecular crystal with a pseudo-cubic (CsCl, Pm3m) high temperature phase in which the CN<sup>−</sup> ions are orientationally disordered. At 193 K, CsCN transforms discontinuously into a trigonal (R3̄m) structure [1,2]. The CN<sup>−</sup> ions are aligned now along the three-fold axis, corresponding to what were the  $\langle 111 \rangle$ -axes in the cubic phase [2]. The space group of the low temperature phase implies that the CN<sup>−</sup> ions are still disordered with respect to head and tail. The additional striking features, exhibited by CsCN might be due to its strong Cauchy discrepancy ( $C_{12}-C_{44}$ ) whose magnitude is several times larger than that of the cesium halide [3].

The special interest in CsCN lies in the fact that this exhibits the CsCl structure and it can be expected that the reorientational dynamics differ significantly from those of NaCl structure alkali cyanide which have been extensively studied theoretically and experimentally [4–25]. These investigations showed anomalous dispersion effects in the acoustic branches.

The present work was inspired in part by the result of inelastic neutron scattering experiment in CsCN [15,16]. These experiments have established the existence of low frequency transverse acoustic (TA) phonons propagating along  $[q\ 0\ 0]$  and

$[q\ q\ 0]$  directions. Earlier, we have applied ETSM for the lattice mechanical properties of other alkali cyanides [20–25] successfully. Motivated by the success of ETSM to explain the lattice mechanical properties of alkali cyanide having rock-salt structure, we have applied the same for the dynamical studies of CsCN having CsCl structure.

The essential theory of ETSM is given in §2. The results on PDCs have been given in §3 and discussed in the same section.

## 2. Essential formulation

The interaction potential used to derive the framework of the present ETSM can be expressed as [21]

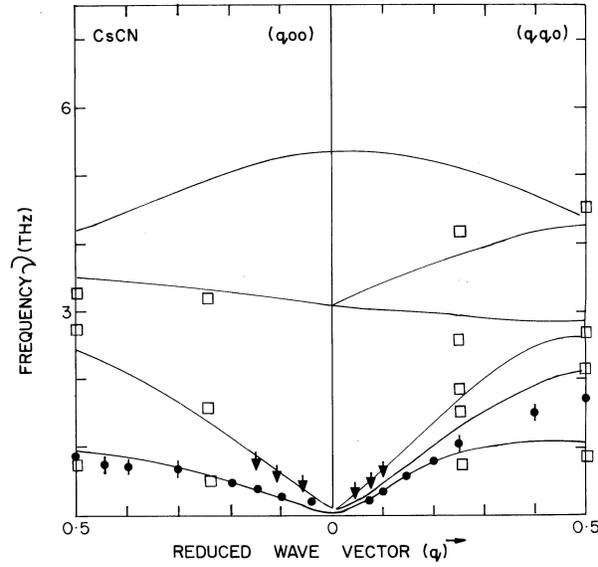
$$\begin{aligned} \phi = & -\frac{e^2}{2} \sum_{kk'} Z_k Z_{k'} e^2 r_{kk'}^{-1} \left[ 1 + \sum_{kk'} f_k(r_{kk'}) \right] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} \\ & - \sum_{kk'} d_{kk'} r_{kk'}^{-8} - b \sum_{kk'} \beta_{kk'} \exp \left\{ \frac{r_k + r_{k'} - r_{kk'}}{\rho} \right\} + \phi^{\text{TR}}. \end{aligned} \quad (1)$$

The first two terms represent the long-range Coulomb and three-body interaction (TBI) [26]. The third and fourth terms are vdW coefficients due to dipole–dipole and dipole–quadrupole (d–q) interactions. The fifth term is Hafemeister and Flygare (HF) type short-range (SR) overlap repulsion [26] extended up to the second neighbour ion with  $\beta_{kk'}$  as Pauling coefficient,  $\rho$  and  $b$  are the range and hardness parameters [22,24],  $\phi^{\text{TR}}$  is the contribution due to translational–rotational coupling [5,18,27,28].

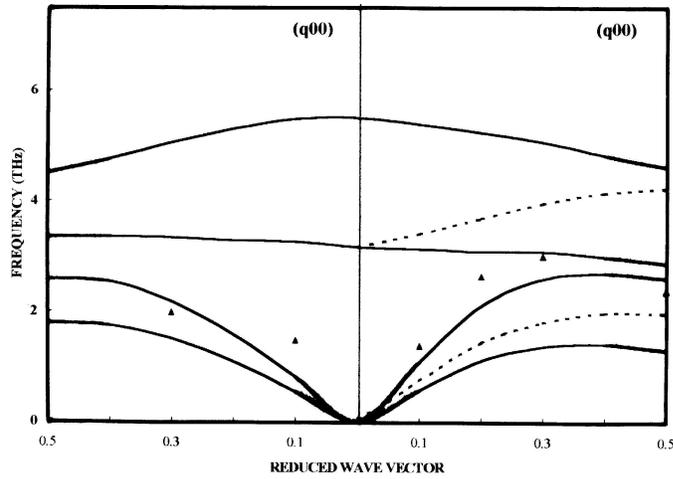
## 3. Results and discussion

Using the input data listed in table 1 and van der Waals coefficients directly used from [21] at 295 K, we have computed the four potential parameters  $b, \rho, f(r_0), r_0 f'(r_0)$  and four model parameters  $d_1, d_2, Y_1$  and  $Y_2$  in the ETSM framework. Here  $d$  and  $Y$  are distortion polarizabilities and shell charge parameters. We have calculated the values of translational–rotational coupling coefficients on the lines given in our earlier paper [21].

The phonon dispersion curves at temperatures 295 and 223 K obtained from ETSM have been displayed in figures 1 and 2 and compared with inelastic neutron scattering data [15,16] for CsCN. On inspection, these figures show that the overall agreement between the neutron scattering data and theoretical results are quite satisfactory for both the temperatures 295 and 223 K. Both the optic and acoustic branches have shown reasonably good agreement with the measured neutron scattering data [15,16] along  $[q\ 0\ 0]$  and  $[q\ q\ 0]$  directions. This is not surprising as the present model is capable to take proper account of both the elastic (Cauchy violation) as well as the dielectric (polarizability) properties on which these branches depend. Both the inelastic neutron scattering data [15,16] and our theoretical results at 295 and 223 K have shown that there are no anomalous dispersion effects



**Figure 1.** Phonon dispersion curves along  $[q\ 0\ 0]$  and  $[q\ q\ 0]$  directions for CsCN at 295 K obtained from ETSM. The closed circles ( $\bullet$ ), open squares ( $\square$ ) and triangles ( $\blacktriangle$ ) are the inelastic neutron scattering data [15,16].



**Figure 2.** Phonon dispersion curve along  $[q\ 0\ 0]$  and  $[q\ q\ 0]$  directions for CsCN at 223 K. The triangles ( $\blacktriangle$ ) are the inelastic neutron scattering data [16].

in the transverse acoustic (TA) branch in  $[q\ 0\ 0]$  and  $[q\ q\ 0]$  contrary to the findings in NaCN [4,20], KCN [4,20] and RbCN [7,20]. In all these NaCl-type cyanides, the frequencies in the  $(1\ 0\ 0)$  TA branch show a transition from a fast to slow relaxation case. Our calculations have shown the low frequencies of TA phonon propagating

**Table 1.** Input data and TR coupling coefficient for CsCN at 295 K.

Properties	Values	TR coupling coefficients	Values
$r_0$ (Å)	3.68 <sup>a</sup>	$A_R$ ( $10^{-4}$ dyn)	-0.098
$C_{11}$ ( $10^{11}$ dyn cm <sup>-2</sup> )	2.11 <sup>b</sup>	$B_R$ ( $10^{-4}$ dyn)	0.403
$C_{12}$ ( $10^{11}$ dyn cm <sup>-2</sup> )	1.18 <sup>b</sup>	$A_Q$ ( $10^{-4}$ dyn)	0.578
$C_{44}$ ( $10^{11}$ dyn cm <sup>-2</sup> )	0.40 <sup>b</sup>	$B_Q$ ( $10^{-4}$ dyn)	-0.472
$\alpha_+$ (Å) <sup>3</sup>	3.34 <sup>c</sup>	$\chi_{44}$ ( $10^{12}$ dyn cm <sup>-1</sup> )	0.122 <sup>e</sup>
$\alpha_-$ (Å) <sup>3</sup>	1.80 <sup>d</sup>	$\chi_{11}$ ( $10^{12}$ dyn cm <sup>-1</sup> )	-3.68 <sup>e</sup>

a - [29], b - [30], c - [31], d - [32], e - [33].

in the  $[q\ 0\ 0]$  direction can be explained on the basis of interaction potential used in ETSM. Contrary to the results of NaCN, KCN and RbCN (rock-salt structure alkali cyanides), the results obtained are insensitive to the choice of charge distribution for the anion. Reduction in the quadrupole moment leads to an increased preference for (1 1 1) orientations of the CN<sup>-</sup> ion, but the predicted PDCs are largely unaffected. The preference for (1 1 1) orientations reflects an increased tendency for the anions to point towards neighbouring cations. Same effect, but involving (1 0 0) orientation is seen in NaCl structure alkali cyanides. In these cyanides, however, this change in order is accompanied by large changes in other observable properties. The difference between the NaCl structure alkali cyanide and CsCN is presumably due to the difference in crystal structure. Since the ions are more closely packed in CsCN (eight-fold rather than six-fold coordination), modest changes in the local order are unlikely to have large effects.

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