Theoretical interpretation of the second-order Raman spectra of caesium halides
A.M. Karo, J.R. Hardy, I. Morrison

To cite this version:
A.M. Karo, J.R. Hardy, I. Morrison. Theoretical interpretation of the second-order Raman spectra of caesium halides. Journal de Physique, 1965, 26 (11), pp.668-676. <10.1051/jphys:019650026011066800>. <jpa-00206333>

HAL Id: jpa-00206333
https://hal.archives-ouvertes.fr/jpa-00206333
Submitted on 1 Jan 1965

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
THEORETICAL INTERPRETATION
OF THE SECOND-ORDER RAMAN SPECTRA OF CAESIUM HALIDES

By A. M. KARO (1), J. R. HARDY (2) and I. MORRISON (3),

Résumé, — Les auteurs ont calculé les spectres Raman du second ordre de CsCl, CsBr et CsI. Pour les deux derniers, on peut comparer leurs résultats avec les spectres observés. On constate que les spectres prévus en admettant une polarisabilité et un chevauchement des ions sont en bien meilleur accord avec l'expérience que ceux obtenus en traitant ces ions comme des charges rigides ponctuelles.

Par la première méthode, l'accord général est remarquablement exact, même sans tenir compte de l'influence du vecteur d'onde sur le tenseur de polarisabilité de Raman.

La raison probable en est que les principaux pics dans le spectre théorique proviennent de la superposition de points critiques dans les courbes de dispersion à deux phonons, qui se trouvent sur les axes de symétrie. Les présents résultats semblent montrer que le spectre Raman observé fournit une image assez exacte de la densité d'états à deux phonons, et peut servir pour vérifier et préciser le calcul théorique de la matrice dynamique.

Il apparaît également que des spectres à haute résolution, obtenus à basse température, révélaient beaucoup plus de détails, si les spectres calculés sont dignes de foi.

Abstract. — The results of calculation of the second-order Raman spectra of CsCl, CsBr, and CsI are presented. For the last two crystals the results can be compared with observed spectra. It is found that the spectra derived by allowing for the polarizability and overlap deformation of the ions are in much better agreement with the experimental results than those derived by treating the ions as rigid point charges. In the first case the overall agreement is remarkably close, even though no allowance has been made for the wave-vector dependence of the Raman polarizability tensor.

The probable reason for this is that the main peaks in the theoretical spectra arise from superpositions of critical points in the two-phonon dispersion curves which occur along symmetry axes. The present results tend to support the view that the observed Raman spectra provide a reasonably close mapping of the two-phonon density of states and can be used both to test and refine theoretical calculation of the dynamical matrix.

Also, it appears that low-temperature, high-resolution spectra should reveal considerably more detail if the computed spectra are reliable.

Introduction. — The alkali halide crystals are probably the best examples of solids whose valence electrons can be adequately described by the "tight binding" approximation, since the perturbation of the free-ion functions is relatively small and is due primarily to first-neighbour overlap effects. It is thus possible, as was done by Löwdin [1] following Landshoff [2], to calculate the cohesive energy quantum mechanically from the zero-order (i.e. free ion) wave functions and obtain very close agreement with the observed values.

Thus, it would seem that the effects of configuration mixing are relatively small, whereas the cohesion of the inert gas solids, where the isolated atoms have a closed-shell electronic configuration, is only possible because of the admixing of excited states by the crystal perturbation, resulting in the Van der Waals attraction.

In an earlier paper [3] we have presented the results of a systematic treatment of the lattice dynamics of most of the NaCl-structure alkali halides. The aim of this work was to remove the main shortcomings of Kellermann's original theory by the inclusion of the effects of electronic distortion in the harmonic potential function in so far as they alter the dipole-dipole component of this potential.

Thus, we retained his assumption of a central repulsion, effective between first neighbours only, to describe the short-range component of the potential.

As regards the electronic distortion, we recognised two components:
(a) The field-induced polarization dipoles, given by the product of the self-consistent crystal polarizability of the particular ion being considered, and the effective field at the centre of that ion, where the dipole is assumed to be situated.

These self-consistent polarizabilities were taken from the compilation of Tessman, Kahn and Shockley [5] whose work also provides independent support for treating the electronic polarization in this way because, not only were they able to find a clearly defined set of characteristic polarizabilities, but also their most consistent set was...
obtained by assuming that the effective polarizing field was that acting at the ion centres in an array of point dipoles.

(b) The "deformation" polarization, which we restricted to the negative ions, and regarded as independent of the field-induced polarization. Its existence, as was first observed by Szigeti [6], is a logical consequence of the presence of the overlap repulsion, which must distort the ions to some extent. In a polar vibration this distortion has a resultant odd multipole component and, in particular, a dipole component. Since we consider only first-neighbour repulsion, it follows that this dipole is determined by the configuration of the negative ion and its six first-neighbour positive ions. Thus, by a generalization of Szigeti's [6] original work on uniformly polarized crystals, we could derive the deformation dipole (D. D.) moment on any given ion in an arbitrarily distorted crystal.

The results of these D. D. calculations for the NaCl structures were very different from the rigid ion (R. I.) results, both as regards calculated frequency spectra and frequency \( v \) wave vector \( (\omega, v, q) \) dispersion curves. In particular, the D. D. \( (\omega, v, q) \) curves for NaI and KBr agree closely with those obtained from the original "shell model" calculations [7, 8] which, in turn, agree with the measured [8, 9] dispersion curves much better than the R. I. results.

The most striking improvements are those which occur near the zone boundary, particularly for longitudinal modes propagating along [100] directions. These are remarkable for two reasons: first, they are predicted, not "forced" by the choice of input parameters; and second, the net changes in the individual frequencies produced by correction for both types of electronic polarization are relatively small differences between very much larger changes produced by the individual polarization mechanisms acting separately. It seems to us important to emphasize these two points, particularly the second, since they provide good evidence for asserting that the D. D. approximation is not too far from an exact description of the effective potential function governing the nuclear motion. Conversely, one can argue that since the eigenfrequencies for a given crystal are very sensitive to the dipolar part of this potential, while the basic assumptions of the D. D. approximation, if valid for one alkali halide, should be reasonably valid for the whole sequence, it is of considerable importance to verify that the validity of the D. D. theory is not confined to either one particular compound or to only those alkali halides with the NaCl structure. In our earlier work [3] we were able to verify the first of these points; however, we have not previously investigated the caesium halides and that is the object of the present paper.

Owing to the large neutron absorption cross-section of caesium there seems very little prospect of the direct determination of dispersion curves, and one will have to resort to more indirect tests of the theory, the best of which, at present, seems to be that provided by the second-order Raman spectrum. For both NaCl and CsCl structures this is the lowest-order spectrum, since the first-order line is forbidden. We shall restrict our attention to that part of the spectrum which arises from double phonon creation, and we shall also assume that all the crystal normal modes are in their ground state. Consequently, our results are only directly comparable with observed spectra measured at 0 °K. In practice, even at 300 °K, these combination bands are generally distinct from any difference bands which may be present, and as a first step, we can compare our predicted spectra with the available experimental measurements made at room temperature. What we actually calculate is the "two-phonon density of states" \( \rho(\omega_1 + \omega_2) \) which gives the number of pairs of phonons, of equal and opposite \( q \) vectors such that the combination frequency \( (\omega_1 + \omega_2) \) lies between \( \omega \) and \( \omega + \Delta \omega \). Thus, the only selection rule we include is the conservation of crystal momentum. Obviously this cannot provide a full theory of the Raman spectrum, since the strength of a given combination \( 1 + 2 \) must also depend on the matrix element \( M(12)^2 \). Recently Cowley [10] has used an extended shell model [11] to make a full calculation of the Raman spectra of NaI and KBr. However, this theory is used to derive the Raman spectra from the measured [8, 9] dispersion curves, since these are fitted at the outset by adjusting the extra parameters introduced by the extension of the shell model.

Our problem is rather different, since what we would like to know is whether it is possible to use the Raman spectra as a means of discriminating between various potential functions in the absence of any other data.

We have already investigated NaCl [12] by calculating \( \rho(\omega_1 + \omega_2) \) for both R. I. and D. D. potentials and found, somewhat surprisingly, that the D. D. curve reproduced the experimental spectrum of Welsh et al. [13] remarkably well. Not only were the main peaks in approximately the correct positions, but the general shape of the curve was correct; whereas, the R. I. density had a completely different shape and bore no resemblance to the observed spectrum.

This result indicates that one should certainly investigate the caesium halides in the same way, complementing the calculation of \( \rho(\omega_1 + \omega_2) \) with the calculation of combined dispersion curves, \( (\omega_1 + \omega_2) v_1 q \), along symmetry directions. In this way it is possible to assign the various features of the distribution function to critical points on the dispersion surfaces. Also, there is the practical
point that, to reveal all the details of \( p(\omega_1 + \omega_2) \), one needs a very fine mesh of sample \( \mathbf{q} \) vectors, and it seems best to push the calculations to the computational limit in this respect before introducing selection rules. This difficulty is likely to be most pronounced for CsBr and CsI, on which we shall concentrate our attention (there seem to be no measurements available for CsCl itself, and CsF has the NaCl structure and does not concern us here), since the ionic masses are comparable for CsBr and almost equal for CsI.

In this paper we shall confine ourselves to the presentation of results for Raman spectra and dispersion curves; the details of the calculation will appear in a later paper which will contain a systematic account of the whole of the work. It is, however, worth mentioning here that the final dynamical matrix has the same form as that for the NaCl structure [14], but the various constituent matrices are modified. Apart from the fact that the dipole-dipole coupling coefficients have had to be rederived for the CsCl structure, the matrix which describes the short-range interactions is also modified, together with that which specifies the deformation dipole.

**Results.** — These will be presented separately for CsBr and CsI together with the appropriate experimental data. Unfortunately, the characteristic temperatures of the phonons involved are such that the observed Stokes and anti-Stokes components at 300 °K have nearly the same intensities because of the high degree of thermal excitation. Thus, although it is still possible to discriminate between combination and difference bands, one must remember that the observed relative intensities are not directly comparable with the theoretical values, since at high temperature the observed line strengths are

\[
\propto \frac{p(\omega_1 + \omega_2)}{\omega_1 \omega_2}
\]

which implies a strong relative enhancement of the low-frequency end of the spectrum.

**Caesium bromide.** — In figures 1 and 2 we show the computed densities of states (R. C. D. S.) and combined dispersion curves, first for the rigid ion (R. I.) model and second with both field-induced and deformation polarization of the ions included. The repulsive interaction is confined to first neighbours, the T. K. S. [5] polarizabilities are used, and it is assumed that the deformation dipole experiences the field at the negative ion centre.

---

**Fig. 1.** — Two-phonon density of states histogram and dispersion curves for CsBr computed for rigid ions (R. I.). Inset shows the corresponding smoothed curve with the positions of the observed features (see fig. 2).
Inset into figure 2 we also show the observed spectrum [15] with the various features marked a, b, c, etc... The corresponding points on the theoretical spectra are also indicated. The actual R. C. D. S. curves are smoothed through a histogram obtained from a sample of 64 000 q vectors in the whole reduced zone, while the dispersion curves are plotted using a sample of points five times as dense along the symmetry directions.

As in the case of NaCl [12] the two curves look very different, and the D. D. results are in much better overall agreement with the experimental data. The only really significant discrepancy is the presence of the peak at $1.8 \times 10^{13}$ s$^{-1}$ in the calculated spectrum, but it is possible that this occurs at too low a frequency because the $TO (X) + TA (X)$ combination is misplaced, since the present model does not allow us to fit $\omega_0$, the $T. O.$ frequency at $\Gamma$. To remove this discrepancy we will have to introduce non-Coulomb second-neighbour interactions and it should be possible, assuming that these are central, to determine the relative magnitudes of the $++$ and -- components, by fitting the observed values of $\omega_0$ and this transverse-mode combination frequency at $X$.

It is evident that we expect better measu-
ments to reveal a great deal of extra structure; certainly the present experimental data are not good enough to rule out the presence of the weaker features, particularly at the high-frequency end of the spectrum. The combined dispersion curves are extremely complex and show a large number of almost degenerate singularities, and one can see that the various peaks do not generally occur exactly at symmetry-point combination frequencies. This is because the dispersion curves are often very flat over the zone surface and the strong features arise from superpositions of extrema which, although close in frequency to a symmetry point combination, are nowhere near it in q space. This result seems particularly important since it supports the contention that it is the density of states which determines the spectrum rather than the matrix element, and it indicates that selection rules only valid at symmetry points will not greatly affect the Raman spectrum.

It would seem fair to regard the present results as encouraging and an indication that the D. D. theory is not too far from the truth. Furthermore, it appears that we can use the present results as a basis for including short-range, second-neighbour interactions between both types of ion, and it is extremely useful to be able to determine their relative magnitudes as one expects them to be of comparable size.

This refinement is certainly well worth making because there is certainly no guarantee that it will produce a better fit to the whole Raman spectrum or indeed as good a fit as the present D. D. curve. Should it prove successful in this respect, we will then have strong evidence to support the assumption that the second-neighbour forces can be derived from two-body central potentials.

This is important from the viewpoint of extending our theoretical understanding of the effective potential function, since we would like, if possible, some assurance that any shortcomings of the present theory are not primarily due to failure to treat second-neighbour interactions (e.g. Van der Waal’s forces) in a more refined manner. If this can be established, then further refinement of the dipolar approximation will be justified.

Caesium iodide. — The computed R. C. D. S. and combined dispersions curves for this crystal are shown as figure 3 (R. I.) and figure 4 (D. D.). Once again we show the positions of the observed room-temperature peaks on the theoretical spectra,

![Fig. 3.](image-url)
together with the actual experimental spectrum [16] (inset in fig. 4) taken at 300°K. In this case the experimental data are somewhat better than the results for CsBr [15], and we have also indicated the positions of certain "shoulders" in the observed spectrum which appear to be more clearly defined than some of the high-frequency peaks.

It is again evident that the (D. D.) R. C. D. S. curve is in much better agreement with the experimental results. Moreover, the fit to those features which are reliably established is remarkably good, although the high frequency end of the spectrum probably contains a significant contribution from the third-order Raman spectrum. If this is so it strengthens the case for concentrating our attention on the clearly defined shoulders at this end of the spectrum. These are almost certainly due to second-order processes owing to their relatively high intensities, and it is gratifying to find that their presence is predicted by the (D. D.) R. C. D. S spectrum.

As in the CsBr spectrum, the theoretical $TO(X) + TA(X)$ combination at $1.5 \times 10^{13}$ s$^{-1}$ occurs at too low a frequency, and the arguments regarding the inclusion of second-neighbour forces

---

**Fig. 4.** — Computed two-phonon histogram and dispersion curves for CsI; D. D. model. Insets show smoothed theoretical distribution and the observed spectrum [16]. Features marked with a query are either doubtful or possible third-order lines.
also apply to CsI. Once again, the positions of the major peaks do not tally exactly with those of symmetry point combinations, and for the same reasons as were given for CsBr, each peak arising from a superposition of sharp critical points lying along symmetry directions.

It is interesting to observe that the predicted multiplet structure of the two strongest peaks is confirmed experimentally. It also seems clear that an improved spectrum taken at low temperatures should reveal considerably more structure if the present theoretical results are generally correct.

Discussion. — In figure 5 we show the predicted R. C. D. S. spectrum and combined dispersion curves for CsCl (D. D. theory). Unfortunately, there are no experimental data with which to compare these so that we have no test of the validity of our theory for a crystal where the positive ion is very much heavier than the negative ion. This statement is also true for the NaCl-structure alkali halides, although in our earlier paper [3] we were able to account for the specific heat data for KF; however, the present work indicates that comparison of theoretical and experimental Raman spectra would provide a more stringent test. For this purpose RbCl would seem to be the best material, both theoretically and experimentally.

The main reason for making these extensive tests is to understand, as far as possible, the behaviour of the "deformation dipole moments". These are the least well-defined parameters in the theory. First of all there is no real evidence that the overlap deformation is adequately represented by point dipoles, and secondly, if one accepts the point-dipole approximation, then there remains the problem of where these are located. At present we are forced to put them at the ion centres, since we are only able to derive the fields at these points. As Cowley et al. [11] have pointed out, it is possible that an intermediate position would be better and this can be tested, to some extent, by assuming that the deformation polarization experiences the effective field at the positive ion centre and it is proposed to do this.

Equally important is the question of whether or not the deformation is confined to the negative ion. If this is not so, then the net deformation dipole is the resultant of two opposed dipoles. In the work on KCl [14] it was found that the dispersion curves and frequency spectra were critically sensitive to any division of this kind, so much so that one could say that overlap deformation of the positive ion must be negligible, at least for the K and Na halides.

FIG. 5. — Computed two-phonon spectrum and dispersion curves for CsCl (D. D.) model.
Obviously, this assumption needs testing for more extreme cases such as CsCl.

At present these calculations remain to be carried out, but in figure 6 we show three sets of single-phonon dispersion curves computed for CsI. In this case the first two are standard R. I. and D. D. results, but the third set has been derived by including only field-induced polarization.

![Fig. 6. Single-phonon dispersion curves for CsI along Δ, Λ and Σ for:
(a) Rigid ions (R. I.),
(b) Polarizable deformable ions (D. D.),
(c) Ions polarizable by the local field, but not by overlap deformation (P. D.).](image)

It will be observed that the neglect of deformation polarization has much less effect on the stability of the CsCl lattice than on that of the NaCl structure, since the latter is nearly or completely unstable if one omits the deformation polarization. This result tends to support the theoretical explanation, given elsewhere [17], of the instability under pressure of the NaCl phase of RbI, since this was based on the behaviour of the dipolar forces in the NaCl phase.

**Discussion**

M. BURSTEIN. — It is appropriate at this time, after the presentation of the theoretical papers of Cowley and of Hardy and Karo to state that progress in the interpretation of infrared and Raman lattice vibration spectra has been jointly dependent on the contributions of both experimentalists and theorists. Without theoretical (or
experimental neutron phonon dispersion curves, it would not be possible for the experimentalists to give an adequate interpretation of the data. The experimental data also provide the theorists with a means of establishing more precisely the models they are using. This is in fact reminiscent of the work on semiconductors, where the joint effects of experimentalists and theorists made it possible to elucidate in some detail the energy band structure of semiconductors. The detailed energy band calculations of Herman, Philips and others were guided by information provided by experimentalists and vice versa.

M. Cowley. — I would like to suggest that calculations of joint density of states are easier if the extrapolation of Gilat and Dolling is used.

M. Hardy. — One finds in the combined density of states critical points not associated with combinations of single phonon critical points, but with critical points in the two phonon dispersion curves (Ref. to London) and also we have found in the single phonon density of states of NaCl, certain sharp maxima and minima associated with second derivative singularities.

However, one must beware of using matrix elements which are overconstrained, e.g. one which satisfies a point selection rule, but also vanishes throughout the zone (1).

(1) A somewhat fuller account of the present work has now been prepared as a Lawrence Radiation Laboratory Report (Ref. No U C R L-14398) showing, among other things, detailed critical point assignments. Copies of this report are available on request.

REFERENCES

[12] Karo (A. M.) and Hardy (J. R.), To be published.
[14] Hardy (J. R.), Phil. Mag., 1962, 7, 315.