Neutron scattering from coherent admixtures of phonons with libronic excitations of diatomic impurities

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The coherent mixed-mode states are represented in an S-matrix formalism. In the small-$\vec{q}$ quasicontinuum region, the phonon field is expanded in terms of vector cubic harmonics, analogues of vector spherical harmonics. Tunneling states of the diatoms in a cubic crystal field are analyzed via group-theoretically projected tight-binding local oscillator states developed by Dick. Plausible level schemes are constructed by joining the strong-coupling spectrum they describe to the weak-coupling (free-rotator) spectrum. This semiphenomenological approach does not depend upon details of the generalized Devonshire hindering potential. It is found that the T-matrix elements connecting the phonons with the libronic or hindered-rotator excitations vanish in lowest nontrivial order unless the latter are of E_g or T_{2g} symmetry. Expressions for estimating the relative strengths of these allowed T-matrix elements are derived. Results are applied to neutron scattering experiments on dilute-impurity KCl:CN^- and KBr:CN^- and comparisons made with optical experiments on these systems. Of the usually considered ⟨100⟩ and ⟨111⟩ CN^- impurity models for these crystals, our analysis shows that the ⟨100⟩ model is eliminated by the neutron data, in agreement with earlier conclusions based upon optical and other experiments. The absence of a T_{2g} interaction as observed in the neutron experiments presents a difficulty for the ⟨111⟩ model if the libronically excited observed E_g and unobserved T_{2g} levels are split by an amount of the order of the ground-state tunnel splitting, i.e., $O(1\ \mathrm{cm}^{-1})$. Under this assumption, the same difficulty exists for the ⟨110⟩ model which we are also led to consider. The relative strengths of the T_{2g} to E_g couplings of the phonon to the libronic excitations are estimated for both the ⟨111⟩ and ⟨110⟩ models. Whereas the estimation procedure is perhaps too crude to distinguish between these two models on the basis of the neutron data alone, the fact that for either model the computed ratio of T_{2g} to E_g couplings is nearly equal to unity, under the assumption that the excited tunnel splittings are small, clearly suffices to rule out this latter assumption if either model is correct. It is concluded that the T_{2g} rotational excitations of the CN^- ions lie considerably above the observed E_g libronic excitations and that the former are lifetime broadened to the extent that formation of coherent mixed modes does not occur; hence the absence of neutron observed splitting of the phonon modes in the T_{2g} configuration. Our analysis of the Raman data lends support to this conclusion. Under the assumption of large excited-state splitting, our estimation procedure for the T_{2g}/E_g coupling ratio does not apply and the neutron data are compatible with either the ⟨111⟩ or ⟨110⟩ models. The earlier experiments favor the ⟨111⟩ model.

I. INTRODUCTION AND PREVIEW OF RESULTS

We consider the *coherent* resonant forward scattering of phonons from a random distribution of diatomic molecules in a cubic lattice, e.g., CN^- ions substituted for the halogens in KCl or KBr. In the forward direction the scattering leads to mixed modes, part phonon and part coherent excitation of the diatomic complexes to higher libronic tunneling (or hindered-rotator) states. Discussion is limited to the case of dilute impurities when their direct mutual interaction can be neglected. The problem is discussed conceptually in terms of an expansion of the phonon field into *vector cubic harmonics,* generalizations of the von der Lage–Bethe entities.[1] These are the analogues in a cubic environment of the vector spherical harmonics employed, e.g., to treat the scattering of photons from atoms or nuclei.[2] Our analysis is applicable to the study of coherent inelastic neutron scattering by the mixed modes, as has been experimentally observed and so interpreted by Walton, Mook, and Nicklow[3] for KCl:CN^- and by Rowe, Rush, Hinks, and Susman for KBr:CN^-.[4] These experiments observe splittings of the TA phonons due to coherent interaction with the libronic excitations of the CN^- ions. In both crystals a splitting is observed when the neutron produces an excitation with $\vec{q}$ along [110] which is polarized along [1$\bar{1}$0] (E_g configuration). No splitting is observed in either crystal when the neutron scatters such as to produce a phonon

with $\vec{q}$ along [100] and polarization vector along [010] (T_{2g} configuration).

The group theory of the local-site complexes is treated in a way that does not depend upon the details of the generalized Devonshire model potential[5] and can, in principle, encompass many terms beyond the $l=4$, 6, and 8 cubic invariants usually employed. We do so by first constructing tight-binding libronic tunneling states for the diatoms in their cubic environment, a technique developed extensively by Dick,[6] which is appropriate in the strong-coupling regime. By adjoining the spectra of the strong- and weak-coupling (free-rotator) limits, we consider plausible level schemes which are confronted not only with the neutron data, but also with optical data as discussed extensively by Lüty[7] in his demonstration that the earlier assignment[8] of ⟨100⟩ minima for the CN^- orientations in KCl is incorrect. In the mixed-mode configuration the excited-tunnel-state (or hindered-rotator) component must have the *same* symmetry as the lowest nontrivial vector cubic harmonic in the partial-wave expansion of the phonon field. Hence, the absence of an E_g-type excitation among the lowest libronically excited tunnel states in the ⟨100⟩ model, coupled with the observation of interaction with neutron-generated states having $\vec{q}$ along [110] (and polarized along [1$\bar{1}$0]) in KCl:CN^- and KBr:CN^-,[3,4] provides further evidence against this model for these systems in the dilute regime.[9] Within the context of the Devonshire model this conclusion can also be deduced from the results of Beyeler.[10] Moreover, the data of Windheim on phonon interactions producing low-energy transitions within the tunnel-split libronic ground states indicate that the ⟨111⟩ model first proposed by Lüty for these systems is favored.[11]

We also address the question as to why interaction with T_{2g}-type excitations in the neutron experiments[3,4] for KCl:CN^- and KBr:CN^- is not observed when $\vec{q} \parallel [100]$ and $\vec{\xi} \parallel [010]$. (Here, $\vec{q}$ and $\vec{\xi}$ are the phonon wave vector and polarization, respectively.) The optically favored ⟨111⟩ model predicts the existence of a T_{2g} libronically excited tunnel mode for the CN^- in KCl and KBr, but it is not seen.[3,4] Although group theoretically allowed, the coupling between the T_{2g} libronic excitation and the phonons might, in principle, be much smaller than the observed E_g coupling. To investigate this problem we employ explicit tight-binding wave functions along with classical arguments in the long-wavelength approximation to estimate the relative magnitudes of the T-matrix elements coupling the phonons to the libronic excitations for the E_g and T_{2g} configurations. We do so under the assumptions that both excited states are sharp in energy and that their tunnel splitting is of the same order of magnitude as the tunnel splitting in the libronic ground states. As will be seen, we find that the ratio of the magnitudes of the relevant T-matrix elements is nearly equal to unity, whence both ought to be observable. The failure to observe a T_{2g} interaction in the cited neutron scattering experiments therefore implies that one of our input assumptions is incorrect. We tentatively interpret these experimental findings as indicating that for these systems the first excited T_{2g} mode lies considerably above the E_g excitation, whence additional decay channels are open and lifetime broadening prohibits its observation as a coherent mixed-mode state in the neutron experiments.

The ⟨110⟩ model is disfavored by the optical experiments.[7,11] Nonetheless, we examine this possibility in an effort to find an alternative explanation for the absence of an observed T_{2g} interaction in the neutron experiments. (This model allows the additional possibility of highly anisotropic local two-dimensional oscillator wells with concomitant nondegenerate subfrequencies, ω_1 and ω_2.) Again we find for the KCl:CN^- and KBr:CN^- systems that the T-matrix elements are not very different for the E_g vs T_{2g} couplings to the phonon, whence there is no motivation for abandoning the optically favored ⟨111⟩ model at this time.

Since we are interested here in general symmetry considerations associated with the coherent mixed-mode state, we find it convenient to work within the general S-matrix formalism rather than in terms of an explicit Hamiltonian formulation. Clearly, it is always possible to express the former in terms of the latter for the purpose of explicit quantitative calculation. A concrete interaction Hamiltonian has been utilized by de Raedt and Michel[12] who study the incoherent neutron scattering from rotational molecular motion in solids. A quantitative variational approach for determining the energy spectrum of molecular impurities in the intermediate-coupling regime has been given by Huller and Kroll.[13] Group-theoretical techniques for analyzing coherent inelastic neutron scattering from mixed libronic-translational modes in pure molecular crystals in the harmonic approximation (but, otherwise, in a model independent way) have been given by Casella and Trevino.[14] In the present analysis, the ions in the host lattice are restricted to be pointlike rather than extended molecules, but no restriction to small-amplitude rotary oscillations of the dilute diatomic impurities is made, although, in the strong-coupling regime, the constituents of the tight-binding tunneling states are quasiharmonic in character.

II. *S*-MATRIX FORMALISM OF THE MIXED-MODE STATES

We write $S=1+iT$ and let $|\Phi\rangle$ be a mixed-mode state. $|\text{phon},\vec{q},j\rangle$ is the phonon state with wave vector $\vec{q}$ and polarization $\vec{\xi}^{\vec{q}j}$. $|\text{ex},\vec{R}'\rangle$ denotes the resonant tunnel-split libronically excited state of the

diatomic impurity located at lattice site $\vec{R}'$. Then,

$$|\Phi\rangle = |\text{phon},\vec{q},j\rangle + i \sum_{\vec{R}'}{}' |\text{ex},\vec{R}'\rangle \langle \text{ex},\vec{R}'|T|\text{phon},\vec{q}j\rangle \tag{1}$$

The prime on the sum is included to indicate that the sum over lattice sites extends over only those occupied by a diatomic impurity. Employing the Wigner operator O_R, defined such that $O_R f(\vec{x}-\vec{R}') = f(\vec{x}-\vec{R}-\vec{R}')$, we find

$$O_R|\text{ex},\vec{R}'\rangle = |\text{ex},\vec{R}'+\vec{R}\rangle \tag{2}$$

and

$$O_R|\text{phon},\vec{q},j\rangle = e^{-i\vec{q}\cdot\vec{R}}|\text{phon},\vec{q},j\rangle . \tag{3}$$

Obviously, the subset $\{O_R\}$ of translations connecting the impurities does not constitute a group since the impurity sites do not themselves form a regular lattice. Nevertheless, for a given $\vec{R}'$, an O_R which leads from one impurity site to another satisfies the invariance condition

$$O_R^\dagger T O_R = T. \tag{4}$$

Hence, for such an O_R

$$\langle \text{ex},\vec{R}'|T|\text{phon},\vec{q},j\rangle = \langle \text{ex},\vec{R}'|O_R^\dagger T O_R|\text{phon},\vec{q},j\rangle . \tag{5}$$

In particular, letting $\vec{R} = -\vec{R}'$,

$$\langle \text{ex},\vec{R}'|T|\text{phon},\vec{q},j\rangle = \langle \text{ex},\vec{0}|T|\text{phon},\vec{q},j\rangle \exp(i\vec{q}\cdot\vec{R}'), \tag{6}$$

where the origin of coordinates, $\vec{0}$, is chosen to lie on a site occupied by an impurity. Thus, from Eq. (1)

$$|\Phi\rangle = |\text{phon},\vec{q},j\rangle + i\langle \text{ex},\vec{0}|T|\text{phon},\vec{q},j\rangle \sum_{\vec{R}'}{}' e^{i\vec{q}\cdot\vec{R}'}|\text{ex},\vec{R}'\rangle . \tag{7}$$

To investigate the phonon-impurity interaction we must examine the T-matrix element

$$\langle \text{ex},\vec{0}|T|\text{phon},\vec{q},j\rangle , \tag{8}$$

which appears in Eq. (7). The state $|\text{ex},\vec{0}\rangle$ is a libronically excited tunnel-split state in the strong-coupling regime and a free rotator in the weak-coupling limit. In any event, for finite coupling, it belongs to some irreducible representation of the full cubic group of the local site symmetry. (Even when a Jahn-Teller relaxation takes place, if tunneling is still possible, the full cubic symmetry of the site is restored.[15]) We defer further discussion of these states to Sec. III, turning instead to the decomposition of the phonon state in the perfect lattice.

Since we restrict attention to host lattices consisting of pointlike ions, the phonon is a pure vector field with no axial-vector component. It transforms irreducibly under the Seitz little group of the wave vector, generally a subgroup of the full cubic space group. In a real-space representation (in the Dirac sense) and in the elastic continuum limit, the acoustic field,

$$\vec{V}(\vec{x}) = \vec{\xi}\exp(i\vec{q}\cdot\vec{x}) \tag{9}$$

can be decomposed into *vector cubic harmonics*. This can be accomplished by expanding $\vec{V}$, as in the construction of vector spherical harmonics,[2] via the intermediate step,

$$\vec{V}(\vec{x}) = \vec{\xi}\sum_l (2l+1) i^l P_l(\hat{q}\cdot\hat{x}) j_l(kr). \tag{10}$$

Here, $k = |\vec{q}|$, $r = |\vec{x}|$, and $j_l(kr)$ is the usual spherical Bessel function in the expansion of $\exp(ikr\cos\theta)$. Since $\vec{\xi}$ transforms according to T_{1u} and since the Legendre polynomials $P_l(\cos\theta)$ can be reduced to the well-known scalar cubic harmonics transforming as Γ_i, it is clear that one can construct *vector cubic harmonics* which transform according to the reduction of the product $T_{lu}\times\Gamma_i$. The procedure is analogous to the construction of vector spherical harmonics[2] transforming according to the $D^{(J)}$ contained in the product $D^{(1)}\times D^{(l)}$ of the full rotation group. The analogy is not wholly complete in that the photon is purely transverse whereas the possibility of longitudinal phonons, of course, exists. We do not develop this subject exhaustively here, since, for our present purposes, we need consider only the lowest order terms $l=0$ and $l=1$ in Eq. (10).

The $l=0$ term in Eq. (10) corresponds to a displacement field of the elastic medium which, classically, produces no torque on the diatomic impurity. Quantum mechanically, there exists no corresponding transition amplitude to a libronically excited state in this order. [We rely on the absence of any long-range electric field $\vec{E}$ induced by the relevant acoustic modes, i.e., the absence of a torque produced on the diatomic impurity by any $\vec{\mu}\cdot\vec{E}$ coupling term in the Hamiltonian. ($\vec{\mu}$ is the dipole moment of the impurity.)]

Hence, the lowest nontrivial order in the expansion of $\vec{V}(\vec{x})$ which induces a torque on the diatom is the $l=1$ term in Eq. (10). This term can be written in the form

$$\vec{V}_1(\vec{x}) = A_1(r)\vec{\xi}\,\vec{q}\cdot\vec{x} . \tag{11}$$

Here, $A_1(r) = 3i\,j_1(kr)/kr$ is a radial factor that plays no role in the following considerations. Since, for an allowed rotation α

$$O_\alpha\vec{V}(\vec{x}) = \alpha\vec{V}(\alpha^{-1}\vec{x}) , \tag{12}$$

it follows that:

$$O_\alpha\vec{V}_1(\vec{x}) = A_1\ \alpha\vec{\xi}\ (\alpha\vec{q})\cdot\vec{x} . \tag{13}$$

In component form, we may write

$$V_{1\mu}(\vec{x}) = B_{\mu\nu}x^\nu , \tag{14}$$

where

$$B_{\mu\nu} \equiv A_1 \xi_\mu q_\nu \ . \tag{15}$$

Thus,

$$O_\alpha V_{1\mu}(\vec{x}) \equiv V'_{1\mu}(\vec{x}) = B'_{\mu\nu} x^\nu \ , \tag{16}$$

where

$$B'_{\mu\nu} = \alpha_{\mu\mu'} \alpha_{\nu\nu'} B^{\mu'\nu'} \ . \tag{17}$$

The decomposition of the second-rank tensor $B_{\mu\nu}$ into tensors transforming irreducibly under the full cubic group specifies the representation content of $\vec{V}_1(x)$. This allows a determination of the lowest-order nontrivial matrix elements $\langle \mathrm{ex},\vec{0}|T|\mathrm{phon},\vec{q},j\rangle$. For $\vec{q}\|[110]$ and $\vec{\xi}\|[1\bar{1}0]$

$$B_{\mu\nu} \sim \xi_\mu q_\nu \sim (x-y)(x+y) = (x^2-y^2) \sim \psi_2^{E_g} \ , \tag{18}$$

whereas, for $\vec{q}\|[100]$ and $\vec{\xi}\|[010]$,

$$B_{\mu\nu} \sim \xi_\mu q_\nu \sim yx \sim \psi_3^{T_{2g}} \ . \tag{19}$$

Here,"~" reads "transforms as". [The row indices on the states $\psi_2^{E_g}$ and $\psi_3^{T_{2g}}$ are, of course, a matter of convention. In the conventions employed here the partner $\psi_1^{E_g} \sim (3)^{-1/2}(x^2+y^2-z^2)$ and the partners ψ_1 and ψ_2 in the T_{2g} set transform as yz and zx, respectively.]

Given the invariance of the T matrix [Eq. (4)], one sees from Eqs. (7) and (17) that, in lowest order, the only states $|\mathrm{ex},\vec{R}'\rangle$ which can mix coherently with the phonons are those which belong to either E_g or T_{2g}. This is a peculiar feature of the coherent mixed-mode state: Phonons can induce *incoherent* transitions between a much broader class of impurity states Γ_i and Γ_f provided only that the products $\Gamma_f \times E_g \times \Gamma_i$ or $\Gamma_f \times T_{2g} \times \Gamma_i$ contain the identity representation A_{1g}. However, these transitions do not lead to the modified phonon dispersion curves exhibited by the mixed-mode states observed in the neutron scattering experiments of Refs. 3 and 4. We remark that the importance of the E_g and T_{2g} states can be seen intuitively in that the local strain induced by the phonon is also a second rank tensor.

III. LIBRONIC TUNNELING STATES — ESTIMATES OF THE T-MATRIX ELEMENTS

A. General considerations

Since the formalism of the tight-binding tunneling states of diatomic molecules in a cubic lattice has been discussed in some detail by Dick,[6] we shall give only a brief review here. To construct the libronic ground states, one applies projection operators belonging to the various irreducible representations of the cubic group to states u_i which transform under O_α in the same way as the unit vectors $\hat{u}_i$ which specify the various minimum energy orientations of the diatomic molecule within the postulated set, e.g., $\langle 111\rangle$.[16] To generate the libronic first-excited states, not only the $\hat{u}_i$, but also the directions $\hat{\theta}'_i$ and $\hat{\theta}''_i$ transverse to $\hat{u}_i$, about which librations in the local wells take place, must be specified. The first-excited tunneling states are of the form

$$\psi' = \sum_i A_i' u_i \theta_i' \tag{20a}$$

and

$$\psi'' = \sum_i A_i'' u_i \theta_i'' \ , \tag{20b}$$

where the A_i are constants and θ'_i and θ''_i signify states which librate about $\hat{\theta}'_i$ and $\hat{\theta}''_i$, respectively. As recognized by Devonshire within the context of his original V_4 potential,[5] still other qualitatively different states of the local two-dimensional oscillators exist. These could also be employed to construct tight-binding tunneling wave functions, but these generally lie still higher in energy and will not be considered further here. This completes our review of this method.

Knowing the representation content of the ground and first-excited libronic tunneling states,[6] and of the free-rotator states,[5] one can consider various plausible level schemes which reduce to these in the limits of large and small generalized coupling constants g^2. In Fig. 1, we exhibit such plots for (a) the $\langle 111\rangle$ model and (b) the $\langle 110\rangle$ model. For clarity, only the ground state A_{1g} and relevant ground and low-lying excited E_g and T_{2g} levels are shown. Also, for each

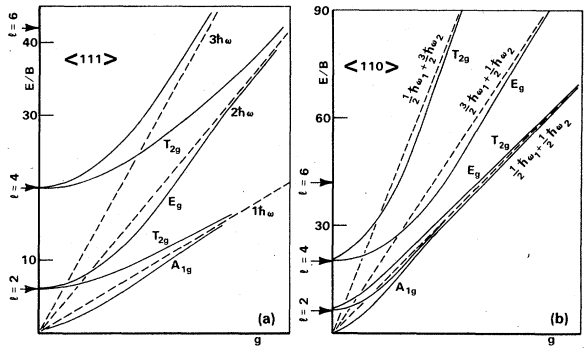

FIG. 1. Schematic of ground A_{1g} and low-lying E_g and T_{2g} energy levels for (a) the $\langle 111\rangle$ model and (b) the $\langle 110\rangle$ model vs generalized coupling to the hindering potential. For each value of g, the zero of energy is chosen at the bottom of the local oscillator well; hence, somewhat unconventionally, the curves rise with increasing g for large g. $B = \hbar^2/2\mu d^2$ is the diatomic rotational constant. l is the angular momentum when $g=0$. The dashed curves represent asymptotic values approached by the tight-binding local oscillator states in the strong-coupling regime. Only qualitative features are illustrated (See text). As pictured in (b), $\omega_2 = 3\omega_1$. Note scale difference between (a) and (b).

value of g, the zero of energy is chosen to be at the bottom of the local wells so that the curves rise with increasing g. The first-excited libronic tunneling states for the $\langle 111\rangle$ model are pictured in Fig. 2 (E_g) and Fig. 3 (T_{2g}). The arrows in these figures depict the linear motions $\vec{\theta}_i' \times \frac{1}{2}\vec{d}_i$ or $\vec{\theta}_i'' \times \frac{1}{2}\vec{d}_i$ of, say, the C atom in the CN^- molecule where $\vec{d}_i$ points, say, from N to C. Also shown in these figures are the relevant long-wavelength phonons which couple coherently to these local excitations.

We estimate the relative magnitudes of the T-matrix elements (8) for the two cases by means of the following partially classical arguments. [Quantum aspects are retained in that the relative phases and magnitudes of the local states, i.e., the A_i in Eqs. (20), are taken into account.] (i) The degree to which the phonons couple to the libronically excited states depends in part on the relative orientations of the linear displacements of, say, the C atoms in each local well relative to the polarization vector of the phonon. Thus, as seen in Fig. 2, the $[1\bar{1}0]$ displacements associated with the TA E_g mode propagating along [110] couple at full strength to those associated with the C atoms at the positions 1, 4, $\bar{1}$, and $\bar{4}$ in the tight-binding state $\psi_2^{E_g}$. In contrast, the displacements of the C atoms at 2, 3, $\bar{2}$, and $\bar{3}$ couple not at all. This suggests introducing factors $(\hat{\xi}\cdot\hat{s}_i)$ where $\hat{s}_i = \hat{\theta}_i \times \hat{d}_i$ are the unit vectors along the linear displacements pictured. (ii) For each orientation $\hat{u}_i$ the linear displacements of, say, the N atoms (not shown in the figures) are equal and opposite to those of the C atoms. Hence, in the infinite-wavelength ($\vec{q}=0$) limit, the sum of the direction cosines over both C and N atoms vanishes, expressing the absence of torque on the CN^- molecules in this limit. To account for the mitigating effect of finite wavelength, the sum on direction cosines $(\hat{\xi}\cdot\hat{s}_i)$ is restricted to terms involving only the displacements of, say, the C atoms, but with each cosine multiplied by a factor $\vec{q}\cdot\vec{d}_i$. (These factors vanish in the infinite-wavelength limit.) Each product is then multiplied by the quantum factor A_i and summed.[17] A similar sum is performed for the T_{2g} configuration shown in Fig. 3. In this way we obtain an expression from which we can estimate the ratio of the magnitudes of the T-matrix elements

$$|T^{T_{2g}}/T^{E_g}|_{\langle 111\rangle} = \tfrac{1}{3}^{1/2}(|\vec{q}^{\,R}_{[100]}|/|\vec{q}^{\,R}_{[110]}|) \quad . \qquad (21)$$

In Eq. (21) the superscript R on the wave vectors of the two TA modes signifies the values of $\vec{q}$ at which the phonon and libronic excitations resonate (more precisely, the centroids of narrow ranges of $\vec{q}$ within which mode mixing is strong).[18] Invoking the Wigner-Eckart theorem, the subscripts 3 and 2 on the T-matrix elements have been omitted. The subscript $\langle 111\rangle$ on the ratio denotes the model being considered.

A similar estimate has been made for the case where the minima lie along the $\langle 110\rangle$ directions. The result is

$$|T^{T_{2g}}/T^{E_g}|_{\langle 110\rangle} = \tfrac{2}{3}^{1/2}(|\vec{q}^{\,R}_{[100]}|/|\vec{q}^{\,R}_{[110]}|) \quad . \qquad (22)$$

These results are not limited to the examples chosen, but apply to any diatomic molecule in a cubic lattice. In Sec. III B the ratios are evaluated for specific cases.

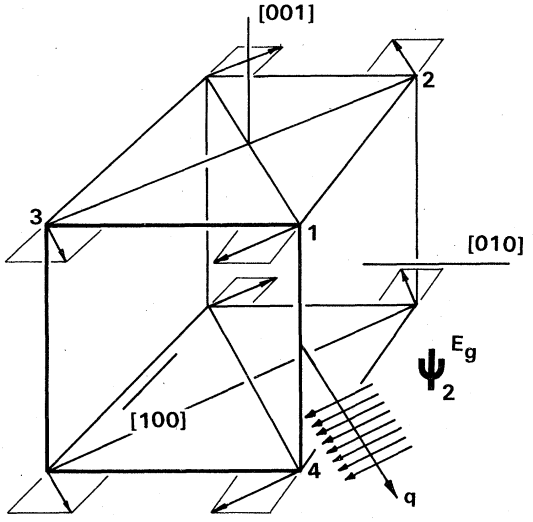

FIG. 2. Correlated linear motions of the A ions for the first excitation of the libronic E_g tunneling state $\psi_2^{E_g}$ of the diatomic molecule AB. The long-wavelength TA phonon with $\vec{q}\parallel[110]$ and $\vec{\xi}\parallel[1\bar{1}0]$ is also shown.

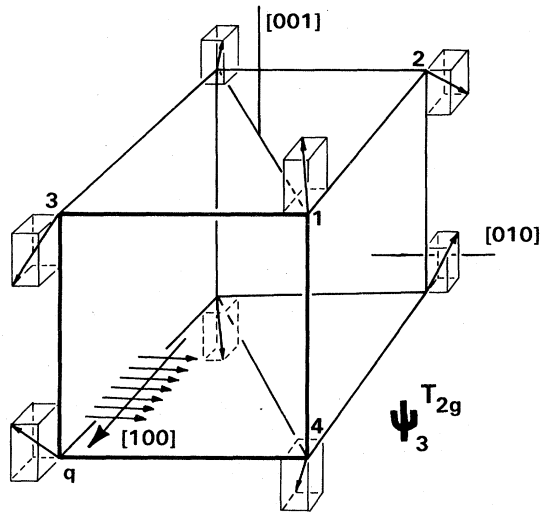

FIG. 3. Correlated linear motions of the A ions for the first excitation of the libronic T_{2g} tunneling state $\psi_3^{T_{2g}}$ of the diatomic molecule AB. The long-wavelength TA phonon with $\vec{q}\parallel[100]$ and $\vec{\xi}\parallel[010]$ is also shown.

B. Application to KCl:CN$^-$ and KBr:CN$^-$

The ratio of the resonant wave vectors in Eq. (21) is estimated for these systems via the following method: (i) In the [110] TA configuration (E_g) $\vec{q}_R$ is determined experimentally from the neutron scattering data.[3,4] Since no interaction is observed in the [100] TA configuration (T_{2g}), we assume, for the moment, that the tunnel splitting of the libronic first-excited states is of the same order of magnitude as that among the libronic ground states, i.e., small compared with the libronic excitation energy: $O(1\ \mathrm{cm}^{-1})$ vs $O(1\ \mathrm{meV})$. Thus, in zeroth approximation, the postulated T_{2g} excitation energy is taken to be the same as that observed for the E_g state. From either the dilute CN$^-$ doped or pure KCl and KBr phonon spectra along [100],[19,20] one can then obtain $\vec{q}_R$ for the hypothetical interaction of the phonon with the T_{2g} libronic excitation. As stated in the Introduction, the ratio (21) is nearly equal to unity for both systems. (The values of the ratio for the ⟨111⟩ model are 0.8 for KCl:CN$^-$ and 1.0 for KBr:CN$^-$.) Hence, the absence of an observed interaction in either system in the [100] TA configuration at an energy close to that at which a splitting is observed in the [110] TA configuration cannot readily be attributed to weaker coupling of the phonon to the (postulated) nearby T_{2g} state. It might be argued that this reasoning is limited by its reliance on the tight-binding nature of the states. However, if the excited E_g and T_{2g} levels lie close in energy, then the approximation is presumably a rather good one. Hence, the contradiction persists.

An obvious way out is that the excited T_{2g} state lies considerably higher in energy than the observed E_g excitation. Since the tight-binding approximation no longer applies, then neither does the estimate (21) for the ratio of the T-matrix elements. On the other hand, if the ratio does not deviate a great deal from unity, one might still expect to observe the T_{2g} excitation, unless it lies sufficiently far above the rotational barrier potential that lifetime broadening prohibits the formation of the coherent mixed-mode state.

Another avenue which was explored consists of temporarily ignoring difficulties encountered by the ⟨110⟩ model with other experiments[7,11] and repeating the above exercise for it. As can be seen from Eq. (22), the ratio of T_{2g} to E_g T-matrix elements is even larger (by a factor $\sqrt{2}$) than the corresponding ratio for the ⟨111⟩ model for each system. Hence, if the first-excited libronic state tunnel splittings are small, the failure to observe the phonon-impurity interaction in the [100] TA configuration of the neutron scattering experiments is even more difficult to understand within the ⟨110⟩ model. (A redeeming feature of the ⟨110⟩ model is that the anisotropy of the local wells allows a natural understanding of a large T_{2g}-E_g level separation among the first-excited libronic levels. See Fig. 1.)

Returning to the ⟨111⟩ model, one might ask whether such a large T_{2g}-E_g splitting is compatible with other experiments. The infrared measurements do not relate to this question since only internal degrees of freedom of the diatomic molecule are excited and the external libronic *ground*-state tunnel splittings are therefore reproduced in the stretch-mode excitations. However, the Raman scattering measurements of Durand and Lüty[7] are germane since they include transitions to the libronic excitations. We first note that the existance of a large peak observed in the T_{2g} ⟨100⟩⟨010⟩ Raman-scattering configuration does *not*, in itself, contradict the absence of an observed T_{2g} level in the coherent neutron scattering experiments. As discussed fully in Sec. II, the latter requires the existance of a sharp libronic T_{2g} excitation to mix with the phonon. However, as discussed there in connection with incoherent neutron scattering by the impurities, the observation of a peak in the T_{2g} Raman configuration requires only that A_{1g} be contained in the product $\Gamma_f \times T_{2g} \times \Gamma_i$. Since E_g is present in the decomposition of $T_{2g} \times T_{2g}$, we may expect a large T_{2g} peak in the Raman scattering resulting from the transition from the T_{2g} component of the tunnel-split libronic *ground* state ($\Gamma_i = T_{2g}$) to the *same* libronically excited E_g state observed in the neutron scattering experiments ($\Gamma_f = E_g$). This E_g level is also observed in the Raman measurements with the E_g configuration as a transition from the A_{1g} absolute ground state. With this interpretation, both sets of data for KCl:CN$^-$ are in acceptable agreement as regards the libronic E_g excitation.[21] It is also worth noting that a second strong peak in the T_{2g}-configured Raman scattering associated with the transition from the ground A_{1g} to the libronically excited T_{2g} level would be expected in the vicinity of the first peak, if the excited E_g-T_{2g} tunnel splitting were small with both levels sharp. Experimentally, this second peak is present only weakly and lies about 1.0 meV above that associated with the transitions from the ground T_{2g} to excited E_g level.[22] This weak, broad peak in the KCl:CN$^-$ Raman spectrum *may* be due to the T_{2g} level that is unobserved in the neutron scattering experiments. Its position (1.0 meV above the E_g) is consistent with the conclusion, based upon our earlier estimates, that for either the ⟨111⟩ or ⟨110⟩ models the E_g-T_{2g} separation must be considerably larger than the ground-state tunnel splitting, $O(1\ \mathrm{cm}^{-1})$. Its breadth is also consistent with the interpretation that a sharp libronically excited T_{2g} state coherently mixed with the phonons does not exist; hence the absence of a splitting in the coherent inelastic neutron spectrum in the T_{2g} configuration is readily understood. Presumably, the same mechanisms are operative with regard to the neutron scattering experiments on KBr:CN$^-$.

IV. CONCLUSIONS

A. General

(i) A coherent admixture $|\Phi\rangle$ of phonon and libronically excited diatomic-impurity tunneling state describes an elementary excitation which is probed by coherent inelastic neutron scattering, as observed in Refs. 3 and 4. (ii) $|\Phi\rangle$ is conveniently described within a general S-matrix framework [cf. Eq. (7)]. (iii) For cubic crystals, a partial-wave decomposition of the acoustic-phonon field in terms of *vector cubic harmonics* leads quite transparently to the conclusion that only E_g and T_{2g} libronically excited tunneling states can contribute to $|\Phi\rangle$ in lowest nontrivial order. (iv) By connecting the group theoretically projected tight-binding local oscillator spectrum with the free-rotator levels, plausible level schemes can be constructed for intermediate coupling (cf. Fig.1). These can be tested phenomenologically, independently of the details of the hindering potential. For example, the $\langle 100\rangle$ model does not admit an E_g state among the first-excited libronic tunneling states. (v) When the tunnel splittings are small compared with the libronic excitation energy, one can employ the tight-binding states (cf. Figs. 2 and 3) to estimate the relative strengths of the E_g and T_{2g} T- matrix elements in $|\Phi\rangle$. Results for the $\langle 111\rangle$ and $\langle 110\rangle$ models are given by Eqs. (21) and (22), respectively.

B. Application to dilute CN^- in KCl and KBr

(vi) Since the $\langle 100\rangle$ model does not admit an E_g state among the tunnel-split first excited libronic states, and since the only libronic excitation observed in the neutron scattering is of type E_g, the $\langle 100\rangle$ model is eliminated by these data. This result is in accord with earlier optical experiments[7] as well as others.[11] (vii) Within either of the $\langle 110\rangle$ and $\langle 111\rangle$ models, if the tunnel splittings of the first libronic excitations are of the same order as those of the libronic ground state, then, applying the estimation procedure outlined in Sec. III leads to the conclusion that the T_{2g} and E_g libronic excitations ought couple to the phonons with roughly equal strengths. The failure to detect a splitting of the TA phonons with neutrons scattered in the T_{2g} experimental configuration for both crystals therefore implies that either (a) both the $\langle 110\rangle$ and $\langle 111\rangle$ models are also eliminated or (b) the T_{2g} rotational excitations do not partake in the coherent state discussed in Sec. II. We assume the latter is true and are led to conclude that the T_{2g} excitation lies considerably above the E_g libronic level, i.e., well above the rotational barriers whence broadening effects destroy the coherence. Our analysis of earlier Raman data[7] in Sec. III lends support to this conclusion. (viii) The neutron data alone do not allow us to distinguish between the $\langle 110\rangle$ and the optically favored $\langle 111\rangle$ model.

Note in proof. Since this paper was submitted, Holuj and Bridges[23] have reported on microwave determination of the tunnel splittings of the libronic *ground* state in KCl:CN^-. They find the T_{2g} component lies 0.29 meV above the A_{1g} component. This result is consistent with our interpretation (Sec. III B) of the Raman data,[7] given the insights afforded by the neutron scattering[3,4] and our selection rule (Sec. II). Taking the difference between the A_{1g} (ground) $\rightarrow E_g$ (excited) and the T_{2g} (ground) $\rightarrow E_g$ (excited) transition energies as observed in the Raman work[22,24] we obtain the value 0.23 meV for the $T_{2g}-A_{1g}$ ground-state tunnel splitting. The two determinations are considered consistent (error assignments are incomplete).

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[17]The A_i can be chosen real. Moreover, possible minus signs have been absorbed in the definitions of the $\hat{\theta}_i$. Hence, as pictured in Figs. 2 and 3, the relative phases are all positive. (This convention is possible because the totally symmetric A_{1g} state does not occur among the first-excited libronic tunneling states. If it did, our prescription would lead to unconventional minus signs appearing in $\psi^{A_{1g}}$. The θ_i are absent for the libronic ground states, whence it is still possible to have all relative phases positive in $\psi^{A_{1g}}$.) For the $\langle 111 \rangle$ E_g and T_{2g} excitations pictured, $A_i = (\frac{1}{3})^{1/2}$ for all i. The A_i are less trivially related in the $\langle 110 \rangle$ model.

[18]Strictly, since the impurities are distributed at random, the mixed-mode state $|\Phi\rangle$ given by Eq. (7) does not have a sharp $\vec{q}$ [$O_R|\Phi\rangle \neq \exp(-i\vec{q}\cdot\vec{R})|\Phi\rangle$.] Operationally, $\vec{q}$ is defined via the momentum transfer of the scattered neutron in the region where mode mixing is strong. Roughly speaking, $|\Phi\rangle$ has approximately the same $\vec{q}$ as its phonon component $|\text{phon},\vec{q}j\rangle$ in this region.

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