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Isotopic shifts in complex crystals

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We obtain relations between the phonon frequencies of crystals related by isotopic substitution when several ion types are involved in the mode being probed. Also, when the rigid molecular-ion approximation applies to extended subunits of the basic lattice cell, we consider the effects of substitution on combined translational and librational modes, involving more than one type of extended ion. The Teller-Redlich product rule is obtained for arbitrary wave vector $\vec{q}$ as are inequalities on the sums of eigenvalues $\omega^2(\vec{q}r\gamma)$ associated with the rth irreducible representation of the little group $G^{\vec{q}}$.

I. INTRODUCTION

The identification of vibrational modes in solids via Raman scattering, inelastic neutron scattering, and infrared absorption, in conjunction with group-theoretical selection rules, is an established procedure. The high resolution available in the application of lasers to the optical techniques allows ready detection of frequency shifts induced by isotopic substitution, often in the form of deuteration of hydrogeneous samples. Comparison of the measured shifts with theory can be helpful in sorting out the modes in complex crystals. When the phonon mode being probed involves predominantly the substituted ion type, then in first approximation, the well-known relation

$$\tilde{\omega} = (M/\tilde{M})^{1/2}\omega \tag{1}$$

holds between the frequency $\tilde{\omega}$ of the phonon in the substituted lattice (ionic mass $\tilde{M}$) and its frequency ω in the original lattice (ionic mass M). If the ion type undergoing substitution is the *only one* partaking in the mode being probed, then Eq. (1) is exact. Similarly, if the extended rigid-molecule approximation applies to an ion complex of the type undergoing substitution and if the mode is *purely librational,* then

$$\tilde{\omega} = (I/\tilde{I})^{1/2}\,\omega\ . \tag{2}$$

(We temporarily assume that the moment-of-inertia ellipisoid is spherical, i.e., $I_{\lambda\lambda'} = \delta_{\lambda\lambda'} I$.) Again, as was the case with Eq. (1), Eq. (2) applies when *only* the ion type undergoing isotopic substitution partakes in the motion of the shifted mode under experimental investigation.

In this paper we discuss generalizations of these simple relations under less restrictive assumptions. For the case of point ions, we include the possibility that several atomic species are involved in the irreducible representation r (of the little group $G^{\vec{q}}$) that is associated with the atomic type t undergoing substitution. When the extended rigid-molecule approximation applies, we consider the effects of isotopic replacement on *combined* translational and librational modes involving more than one molecular type, making no model-dependent assumptions about the force constants. Moreover, we discuss these effects theoretically for modes at arbitrary wave vector $\vec{q}$, even though present experimental resolution in inelastic neutron scattering is such as to limit the detection of isotopic shifts away from $\vec{q} = 0$ (where the optical techniques detect multiphonon processes). (Model-independent selection rules for inelastic neutron scattering from combined translational and rotational modes have been given by Casella and Trevino.[1]) We obtain explicit extension to crystalline solids (for modes having wave vector $\vec{q}$) of the Teller-Redlich molecular product rule relating the frequencies of the vibronics in a molecule under isotopic substitution.[2] The extension of the Teller-Redlich rule to crystals is perhaps an obvious one, especially in the $\vec{q} = 0$ limit, where the crystal point group applies. It has, in fact, been so employed to aid in the analysis of Raman studies of isotopic shifts in the solid state, e.g., in the benzoquinones.[3] It is also natural to assume that at *arbitrary* $\vec{q}$, where the Seitz little group enters, one is again led to the product rule. We establish that this is indeed the case.[4] It is also clear from our analysis that the Steele-Whiffen[5] interlacing inequalities apply at arbitrary $\vec{q}$. Moreover, we derive additional inequalities under isotopic replacement between sums over $\omega^2(\vec{q}, r, \gamma)$ of modes which belong to the same irreducible representation r of $G^{\vec{q}}$. As with the product rule, we do so both for point ions in a crystal (Appendix A) and also when the extended rigid-molecule approximation applies to subunits of the primitive cell (Appendix B). To my knowledge, these latter inequalities, while intuitively appealing, are new.[6] When the mass or moment-of-inertia ratios differ appreciably from unity, they are readily satisfied. However, when these ratios lie close to unity, the inequalities provide tighter constraints on the symmetry assignments of the vibronic levels.

As noted earlier, examples of the application of the product rule exist in the literature.[7] For the purpose of discussing our general results in terms of a relatively simple example, we shall on occasion refer to crystalline ammonium perchlorate in both the hydrogeneous and deuterated forms. The vibronic spectra of these substances have recently been examined via Raman scattering by Rosaco and Prask.[8] The deuterated form has also been investigated with inelastic neutron scattering by Chesser and Prask.[9] We work throughout in the harmonic approximation even though, for the example cited, the modes which are predominantly rotational have appreciable anharmonic couplings. We also neglect changes in the force constants resulting from the isotopic substitution.

Let the decomposition series for the vibrational reducible representation $\Delta^{\vec{q}}$ in terms of the irreducible representations $D^{\vec{q}r}$ at $\vec{q}$ be[10, 11]

$$\Delta^{\vec{q}} = \sum_r N_r D^{\vec{q}r} \ . \tag{3}$$

N_r denotes the number of times the rth irreducible representation occurs in $\Delta^{\vec{q}}$. If $N_r = 1$ for the symmetry projected states $\xi_\Lambda^{\vec{q}r\mu t}$ associated with a pointlike ion of atomic type t undergoing substitution, then the simple relation (1) applies exactly. Therefore, in Sec. II we shall mainly be concerned with the case $N_r > 1$. Similarly, if $N_r = 1$ for the irreducible representation associated with the translational motion of a rigid molecule having constituents undergoing substitution in each unit cell, then Eq. (1) again applies with M equal to the moleccular ion mass. If, moreover, $N_r = 1$ for each representation r', r'', ... associated with rotations about inequivalent inertial axes λ', λ'', ... of the molecular ion type undergoing substitution, then a simple generalization of Eq. (2) with I replaced by $I(\lambda)$ suffices. As remarked earlier, we shall be concerned mainly with more general conditions. Isotopic shifts in crystals within the rigid-molecule approximation when $N_r > 1$ are discussed in Sec. III.

II. PHONONS INVOLVING POINTLIKE IONS ONLY

To establish notation (which generally follows that in Refs. 1 and 11) we recall some well-known relations involving the mass-weighted force constants $C_{\Lambda\Lambda'}(\vec{L}-\vec{L}')$ and their Fourier transforms, i.e., the dynamical matrix $C_{\Lambda\Lambda'}(\vec{q})$. Here, $\Lambda = (t, n_t, \lambda)$ is a triple index where n_t labels different atoms of the same type t in the unit cell and $\lambda = 1, 2, 3$ is a Cartesian index. Thus

$$C_{\Lambda\Lambda'}(\vec{L}-\vec{L}') = M_t^{-1/2}\, \bar{C}_{\Lambda\Lambda'}(\vec{L}-\vec{L}')M_{t'}^{-1/2} \ , \tag{4}$$

where $\vec{L}$ and $\vec{L}'$ denote cell sites, M_t and $M_{t'}$ are masses, and $\bar{C}_{\Lambda\Lambda'}$ the unweighted force constants. From Eq. (4) the usual relation between the dynamical matrices,

$$\tilde{C}_{\Lambda\Lambda'}(\vec{q}) = (M_t M_{t'}/\tilde{M}_t \tilde{M}_{t'})^{1/2} C_{\Lambda\Lambda'}(\vec{q}) \ , \tag{5}$$

follows immediately. Employing projection operators, one constructs symmetry-adapted displacements $\xi_\Lambda^{\vec{q}r\mu t_i s_i}$ belonging to the μth row of the rth irreducible representation of $G^{\vec{q}}$. These are *independent of the masses*. Moreover, since symmetry operators always connect like atoms,

$$\xi_{t n_t \lambda}^{\vec{q}r\mu t_i s_i} = \delta_{t t_i}\ \xi_{t_i n_i \lambda}^{\vec{q}r\mu t_i s_i} \ . \tag{6}$$

(s_i is an additional index distinguishing independent states belonging to the same $\vec{q}r\mu t_i$.) Using these symmetry states, one constructs the symmetry-reduced (block diagonalized) dynamical matrix by computing the inner product

$$C^{t_1 s_1 t_2 s_2}(\vec{q}, r) = \sum_{\Lambda\Lambda'} (\xi_\Lambda^{\vec{q}r\mu t_1 s_1})^* C_{\Lambda\Lambda'}(\vec{q})\, \xi_{\Lambda'}^{\vec{q}r\mu t_2 s_2} \ . \tag{7}$$

(Warren and Whorlten have provided computer-generated symmetry reduced dynamical matrices for many well-known lattice structures.[10] An algorithm for determining the number of independent real matrix parameters, including the effects of time-reversal symmetry has been derived by this author[11] and applied in Ref. 12 to selected cases among those studied by Warren and Whorlton.) From the property (6) it follows that the sums on t and t' implied in Eq. (7) reduce to a single term, leading via Eq. (5) to the relation

$$\tilde{C}^{t_1 s_1 t_2 s_2}(\vec{q}, r) = \left(\frac{M_{t_1} M_{t_2}}{\tilde{M}_{t_1} \tilde{M}_{t_2}}\right)^{1/2} C^{t_1 s_1 t_2 s_2}(\vec{q}, r) \tag{8}$$

between the symmetry reduced dynamical matrices of the isotypically substituted and the original lattices. Even when $N_r > 1$, if only one atom type t_A undergoes isotopic substitution, and *if only that type occurs* among the $(N_r l_r)$-symmetry projected $\xi^{\vec{q}r\mu t_i s_i}$ associated with $\vec{q}r$, then the matrices scale,

$$\tilde{C} = x_A^2\, C \ , \tag{9}$$

where

$$x_A = (M_A/\tilde{M}_A)^{1/2} \ , \tag{10}$$

and Eq. (1) follows trivially. (l_r is the dimension of the rth irreducible representation, $D^{\vec{q}r}$ of $G^{\vec{q}}$, i.e., $\mu = 1, \ldots, l_r$. $M_A \equiv M_{t_A}$.)

For the general case, the *eigen*modes $\xi_\Lambda^{\vec{q}j}$ are linear combinations of the various symmetry projected states with coefficients which depend upon the masses as well as the force constants.

[$j=(r\mu\gamma)$ where γ is a "principal quantum number" labeling different eigenmodes belonging to the same $\vec{q}$, r, μ.] Nevertheless, from Eq. (8) one obtains

$$\det|\tilde{C}| = x_A^{2N_A} x_B^{2N_B} \cdots \det|C| \,, \tag{11}$$

where N_A, $N_B, \ldots$ are the numbers of times the isotopically substituted types t_A, $t_B, \ldots$ are represented among the $\xi^{\vec{q} r\mu t_i s_i}$ for fixed $\vec{q}$, r, *and* μ. From the eigenvalue equation

$$C(\vec{q}r)\xi^{\vec{q}j} = \omega^2(\vec{q}r\gamma)\xi^{\vec{q}j} \tag{12}$$

and Eq. (11), the product rule

$$\prod_{\gamma=1}^{N_r} \tilde{\omega}(\vec{q}r\gamma) = x_A^{N_A} x_B^{N_B} \cdots \prod_{\gamma=1}^{N_r} \omega(\vec{q}r\gamma) \tag{13}$$

follows directly [since the determinant of C (or $\tilde{C}$) equals the product of its eigenvalues].

In most cases of interest only one atom type, say t_A, undergoes isotopic substitution (e.g., in the deuteration of hydrogeneous samples), *even though several atomic species (including t_A) are represented among the symmetry projected states, $\xi^{\vec{q}r\mu t_i s_i}$ associated with a given $\vec{q}$, r, μ.* For this important special case, lettering $x_A \equiv x$ [cf., Eq. (10)], Eq. (13) reduces to a particularly simple form: the products of the frequencies of the substituted and original lattices are related by the factor x^{N_A}.

It is also possible to derive inequalities on the sums of eigenvalues $\omega^2(\vec{q}r\gamma)$. Consider the case $x<1$, which can always be realized by suitably redefining which isotope one associates with M vs $\tilde{M}$, if necessary. Then as demonstrated in Appendix A.

$$x^2 \sum_{\gamma} \omega^2(\vec{q}r\gamma) < \sum_{\gamma} \tilde{\omega}^2(\vec{q}r\gamma) < \sum_{\gamma} \omega^2(\vec{q}r\gamma) \qquad (x<1)\,. \tag{14}$$

III. VIBRONICS OF EXTENDED IONS IN THE RIGID-MOLECULE APPROXIMATION

We restrict attention to the case when isotopic substitution does not alter the symmetry group of the molecular inertial tensors. As mentioned in Sec. I we allow for the possibility of combined translational and rotational modes, involving more than one ion type, including one or more of the types with constituents undergoing isotopic replacement. To simplify the discussion and minimize the proliferation of indices, we first consider the case where the inertial tensors of the molecules are isotropic before and after replacement. Later, we relax this constraint, obtaining the crystal product rule for general inertial tensors.

In component form, the generalized projected symmetry states can be written as $\xi_{\Lambda}^{\vec{q}r\mu t_i \chi_i s_i}$. Now, $\Lambda=(t, n_t, \chi, \lambda)$ where χ is a dichotomous variable, employed in Ref. 1, which designates either a translation ($\chi=T$) or a rotation ($\chi=\theta$). $\lambda=1, 2, 3$ designates a principal moment axis for each molecule in the unit cell when $\chi=\theta$ and a common Cartesian axis (fixed with respect to the crystalline axes) when $\chi=T$.[13] From the properties of the projected symmetry states (cf. Rao and Trevino[14]) it follows that

$$\xi_{t n_t \chi \lambda}^{\vec{q}r\mu t_i \chi_i s_i} = \delta_{t t_i}\, \delta_{\chi\chi_i}\, \xi_{t_i n_i \chi_i \lambda}^{\vec{q}r\mu t_i \chi_i s_i} \,. \tag{15}$$

The obvious generalization of Eq. (5) is

$$\tilde{C}_{\Lambda\Lambda'}(\vec{q}) = (B_\Lambda B_{\Lambda'}/\tilde{B}_\Lambda \tilde{B}_{\Lambda'})^{1/2} C_{\Lambda\Lambda'}(\vec{q}) \,, \tag{16}$$

where

$$B_\Lambda = \begin{cases} M_t \,, \text{ when } \chi = T \,, \\ I(t,\lambda) \,, \text{ when } \chi = \theta \,. \end{cases} \tag{17}$$

$I(t,\lambda)$ denotes the λth principal moment of inertia of the molecular type t. The inner product is defined as in Eq. (7) and, using Eq. (15) and Eq. (16), one finds

$$\tilde{C}^{t_1\chi_1 s_1,\, t_2\chi_2 s_2}(\vec{q}r) = \sum_{\lambda\lambda'} \sum_{n_1 n_2} (\xi_{t_1 n_1 \chi_1 \lambda}^{\vec{q}r\mu t_1 \chi_1 s_1})^* \left(\frac{B(t_1\chi_1\lambda)B(t_2\chi_2\lambda')}{\tilde{B}(t_1\chi_1\lambda)\tilde{B}(t_2\chi_2\lambda')}\right)^{1/2} C_{t_1 n_1 \chi_1 \lambda,\, t_2 n_2 \chi_2 \lambda'}(\vec{q})\, \xi_{t_2 n_2 \chi_2 \lambda'}^{\vec{q}r\mu t_2 \chi_2 s_2} \,. \tag{18}$$

When χ_1 and χ_2 are both translations, $B(t_i, T, \lambda) = M_i$, the mass of the molecular ion of type t_i, and the result (8) follows straightforwardly from Eq. (18), the only difference being that M_i now represents the mass of the extended molecular ion rather than that of the point ion (atom). For rotations, B_Λ depends on λ in general. For the special case (presently under consideration) of molecules with spherical inertial ellipsoids, $I(t,\lambda)$ equals $I(t)$ independent of λ, whence it is again straightforward to obtain the result

$$\tilde{C}^{t_1\theta s_1,\, t_2\theta s_2}(\vec{q}r) = \left(\frac{I(t_1)I(t_2)}{\tilde{I}(t_1)\tilde{I}(t_2)}\right)^{1/2} C^{t_1\theta s_1,\, t_2\theta s_2}(\vec{q}r) \,. \tag{19}$$

The off-diagonal components (e.g., $\chi_1=\theta$, $\chi_2=T$) also factor. Next, define

$$y_A \equiv [I(t_A)/\tilde{I}(t_A)]^{1/2}\,, \tag{20}$$

and let $P_A, P_B, \ldots$ and $Q_A, Q_B, \ldots$ be the number of times translational and rotational states, respectively, associated with molecular types t_A, $t_B, \ldots$ are represented among the $\xi^{\vec{q} r \mu t_i \chi_i s_i}$ for a given $\vec{q}$, r, and μ. Then, the appropriate generalization of Eq. (13) becomes

$$\prod_{\gamma=1}^{N_r} \tilde{\omega}(\vec{q} r \gamma) = x_A^{P_A} y_A^{Q_A} x_B^{P_B} y_B^{Q_B} \cdots \prod_{\gamma=1}^{N_r} \omega(\vec{q} r \gamma)\,. \tag{21}$$

When isotopic substitution occurs in a crystal with molecular subunits having nonspherical inertial ellipsoids, $I(t, \lambda)$ depends nontrivially on λ. However, since symmetry operators always carry rotations about a given principal axis to rotations about an *equivalent* principal axis, the ξ's are such[14] that nonvanishing contributions to the sums on λ and λ' appearing in Eq. (18) are restricted when $\chi = \theta$ to values for which the ratio $I(t, \lambda)/\tilde{I}(t, \lambda)$ is invariant. For example, for an inertial ellipsoid of revolution, each sum reduces to one extending over *either* the two equivalent axes *or* only the third. For the most general case, the result is

$$\prod_{\gamma=1}^{N_r} \tilde{\omega}(\vec{q} r \gamma) = x_A^{P_A} \left(\prod_{\lambda} y_{A\lambda}^{Q_{A\lambda}}\right) x_B^{P_B} \left(\prod_{\lambda} y_{B\lambda}^{Q_{B\lambda}}\right) \cdots \times \prod_{\gamma=1}^{N_r} \omega(\vec{q} r \gamma)\,, \tag{22}$$

where λ runs over inequivalent principal moment axes. Here,

$$y_{A\lambda} = [I(t_A, \lambda)/\tilde{I}(t_A, \lambda)]^{1/2} \tag{23}$$

and $Q_{A\lambda}$ is the number of times a rotational mode associated with molecular type t_A about an axis equivalent to the λth axis occurs among the symmetry projected states with a given $\vec{q}$, r, and μ.

As an example of the product rule we consider its application to crystalline ammonium perchlorate in the hydrogeneous versus deuterated forms, treating each ammonium and perchlorate complex as rigid. In this example only one ion type (ammonium) partakes in the isotopic substitution. Moreover, the moment-of-inertia ellipsoids are spherical before and after the substitution. Hence, Eq. (22) reduces to Eq. (21), which simplifies further to the following relation:

$$\prod_{\gamma=1}^{N_r} \tilde{\omega}(\vec{q} r \gamma) = x^P y^Q \prod_{\gamma=1}^{N_r} \omega(\vec{q} r \gamma)\,. \tag{24}$$

For this example $x \simeq (18/22)^{1/2}$ and $y \simeq (\frac{1}{2})^{1/2}$. P and Q are the numbers of $\xi^{\vec{q} r \mu t_i \chi_i s_i}$, with $t_i = \mathrm{NH}_4$ (or ND_4) having $\chi_i = T$ and $\chi_i = \theta$, respectively, for fixed $\vec{q}$, r, and μ. As mentioned earlier, Rosasco and Prask have examined shifts in the Raman spectra between both isotopic forms.[8] For modes having A_g symmetry ($N_r = 6$, $P = 2$, and $Q = 1$), these authors find that experimentally Eq. (24) is satisfied only approximately. They attribute the discrepancy ($\simeq 20\%$) to a breakdown of the harmonic approximation in connection with the rotations of the ammonium ions.[15] Their work will be reported more completely elsewhere.[8]

Finally, we remark generally that whenever the inertial tensor is isotropic and only one ion type undergoes isotopic substitution, i.e., when Eq. (24) applies, one can also obtain the following inequalities (Appendix B):

$$\min \begin{Bmatrix} x^2 \sum_{\gamma} \omega^2(\vec{q} r \gamma) \\ y^2 \sum_{\gamma} \omega^2(\vec{q} r \gamma) \end{Bmatrix} < \sum_{\gamma} \tilde{\omega}^2(\vec{q} r \gamma) < \sum_{\gamma} \omega^2(\vec{q} r \gamma)\,, \tag{25}$$

where $x < 1$ and $y \leqslant 1$. [As in the case of point ions, it can always be arranged for the condition $x < 1$ to be satisfied by redefining $\tilde{M}$ vs M if necessary. This, in turn, implies $y \leqslant 1$. (The case $y = 1$ occurs when the isotopically substituted nucleus lies only at the center of the extended ion.)][16]

IV. CONCLUSIONS

Under isotopic substitution of one or more atom types t_A, $t_B, \ldots$ in a crystal lattice, the phonon frequencies $\tilde{\omega}$ and ω of the substituted and original lattices are related by the product rule (13) where x_A, $x_B, \ldots$ are defined as in Eq. (10). Eq. (13) involves only frequencies belonging to the same irreducible representation r of the little group $G^{\vec{q}}$ at wave vector $\vec{q}$. When some atom complexes can be treated as approximately rigid, the frequencies of the combined translational and librational modes before and after substitution are related by Eq. (22). $y_{A\lambda}$, $y_{B\lambda}, \ldots$ are defined by Eq. (23) and, as in the case of point ions, x_A, $x_B, \ldots$ are defined by Eq. (10), except that M_A, $\tilde{M}_A, \ldots$ now signify the masses of the entire molecular ions. Expressions (13) and (22) are completely general. When the inertial tensors associated with the rigid ions are isotropic, Eq. (22) reduces to the simpler form (21). When, in addition, only one molecular type has constituents undergoing substitution (but other ion types belong to the same irreducible representation), Eq. (22) reduces still further to the form (24). At this level, the inequalities (25) apply to sums over ω^2 for combined translational and rotational modes before and after substitution. For point ions, when only one ion type undergoes substitution, (but other types belong to the same representation), the inequalities (14) relate sums over ω^2 of the modes before and after isotopic replacement. Under still more restrictive assumptions, discussed in Sec. I, the simple relations (1) and (2) are recovered. Further generalizations of the inequalities (14) and (25) are possible, but will not be considered here.

To summarize, we have demonstrated that the Teller-Redlich product rule applies at arbitrary wave vector $\vec{q}$ between the frequencies of states belonging to the same irreducible representation r of the Seitz little group $G^{\vec{q}}$.[4] From our method of analysis, it also follows that the Steele-Whiffen inequalities apply at arbitrary $\vec{q}$.[5,6] In addition we obtain the sum-rule inequalities (14) and (25). Application to ammonium perchlorate, currently under active experimental investigation,[8,9] has been discussed.

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APPENDIX A

We derive inequalities between the sums of eigenvalues $\omega^2(\vec{q}r\gamma) \equiv \omega_\gamma^2$ for the case of point ions. The symmetry reduced dynamical matrix C can be written in the form

$$C = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix}, \tag{A1}$$

where the C_{ij} are themselves matrices. The index 1 is associated with the atom type t_A that undergoes isotopic substitution and the index 2 with all other atom types associated with the *same* irreducible representation r as is the type t_A. From the discussion on Sec. II of the text, it follows that

$$\tilde{C} = \begin{bmatrix} x^2 C_{11} & x C_{12} \\ x C_{21} & C_{22} \end{bmatrix}, \tag{A2}$$

where, by appropriate definition of $\tilde{M}$ vs M, one can always arrange that $x < 1$. Then

$$\sum_\gamma (\omega_\gamma^2 - \tilde{\omega}_\gamma^2) = (1 - x^2)\,\mathrm{Tr} C_{11}\ , \tag{A3}$$

where in obvious Dirac notation

$$\mathrm{Tr} C_{11} = \sum_{s_1} \sum_{\gamma\gamma'} \langle \vec{q} r\mu t_1 s_1 | \vec{q} r\mu\gamma\rangle \langle \vec{q} r\mu\gamma | C | \vec{q} r\mu\gamma'\rangle \times \langle \vec{q} r\mu\gamma' | \vec{q} r\mu t_1 s_1\rangle$$
$$= \sum_{s_1\gamma} |\langle \vec{q} r\mu t_1 s_1 | \vec{q} r\mu\gamma\rangle|^2 \omega_\gamma^2\ . \tag{A4}$$

The second equality follows from the fact that the basis $|\vec{q} r\mu\gamma\rangle$ diagonalizes the dynamical matrix [Cf. Eq. (12) and recall $j = (r\mu\gamma)$.] By completeness, for each value of γ,

$$\sum_{t_i s_i} |\langle \vec{q} r\mu t_i s_i | \vec{q} r\mu\gamma\rangle|^2 = 1\ , \tag{A5}$$

whence, for more than one atom type associated with $\vec{q} r\mu$,

$$\sum_{s_1} |\langle \vec{q} r\mu t_1 s_1 | \vec{q} r\mu\gamma\rangle|^2 < 1, \tag{A6}$$

for each γ. From Eqs. (A4) and (A6),

$$\mathrm{Tr} C_{11} < \sum_\gamma \omega_\gamma^2 . \tag{A7}$$

Substituting in Eq. (A3) and recalling that, by definition, $x^2 < 1$, we obtain

$$\sum_\gamma \tilde{\omega}_\gamma^2 > x^2 \sum_\gamma \omega_\gamma^2\ . \tag{A8}$$

Also, from Eq. (A4) it follows that $\mathrm{Tr}\, C_{11} > 0$, whence from Eq. (A3),

$$\sum_\gamma \omega_\gamma^2 > \sum_\gamma \tilde{\omega}_\gamma^2\ . \tag{A9}$$

Combining (A8) and (A9) one obtains the inequalities (14) of the text.

APPENDIX B

We obtain inequalities in the rigid molecule approximation when the inertial ellipsoid is spherical. The appropriate generalization of Eq. (A2) is

$$\tilde{C} = \begin{bmatrix} x^2 C_{11} & xy C_{12} & x C_{13} \\ yx C_{21} & y^2 C_{22} & y C_{23} \\ x C_{31} & y C_{32} & C_{33} \end{bmatrix}\ , \tag{B1}$$

where C_{11} is a $P \times P$ matrix associated with pure translations of the molecular type t_A involved in the isotopic substitution and C_{22} is a $Q \times Q$ matrix associated with pure rotations of the same molecular type (NH_4 in the example discussed in Sec. III). C_{33} is a square matrix of dimension

$(N_r - P - Q)$ associated with the translations and the rotations of the remaining unsubstituted species (ClO_4 in the cited example). The meanings of the off-diagonal matrices are obvious from context. Then, from Eq. (B1) and Eq. (12) of the text,

$$\sum_\gamma (\omega_\gamma^2 - \tilde{\omega}_\gamma^2) = (1 - x^2)\,\mathrm{Tr}C_{11} + (1 - y^2)\,\mathrm{Tr}C_{22}. \qquad \text{(B2)}$$

Since we can always arrange the definitions of C vs $\tilde{C}$ such that $\tilde{M}_A > M_A$, it follows that $\tilde{I} \geq I$, i.e., that $1 - x^2 > 0$ and $1 - y^2 \geq 0$. Moreover, as in Appendix A, one can show that $\mathrm{Tr}C_{ii} > 0$ for $i = 1, 2, 3$, from which it follows that

$$\sum_\gamma (\omega_\gamma^2 - \tilde{\omega}_\gamma^2) > 0\,, \qquad \text{(B3)}$$

and that

$$\mathrm{Tr}C_{22} < \sum_\gamma \omega_\gamma^2 - \mathrm{Tr}C_{11}\,. \qquad \text{(B4)}$$

Substituting in Eq. (B2), we find

$$0 < \sum_\gamma (\omega_\gamma^2 - \tilde{\omega}_\gamma^2) < (1 - y^2) \sum_\gamma \omega_\gamma^2 + (y^2 - x^2)\,\mathrm{Tr}C_{11}. \qquad \text{(B5)}$$

Assume that $x^2 > y^2$ (as in our example). Then (B5) implies

$$\sum_\gamma \tilde{\omega}_\gamma^2 > y^2 \sum_\gamma \omega_\gamma^2\,. \qquad \text{(B6)}$$

Similarly, when $y^2 > x^2$, one can demonstrate that

$$\sum_\gamma \tilde{\omega}_\gamma^2 > x^2 \sum_\gamma \omega_\gamma^2. \qquad \text{(B7)}$$

The inequalities (B3), (B6), and (B7) can be restated in the form (25) given in the text.

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[13] In Ref. 1 the translations and rotations were denoted by $\chi = R$ and $\chi = \theta$, respectively. Also, the couple (t, n_t), which runs over atoms (molecules) in the unit cell, was compressed into a single index n.

[14] K. R. Rao and S. F. Trevino, J. Chem. Phys. 53, 4624 (1970).

[15] Since portions of their work are yet to be published, we do not attempt a complete analysis of their data. Nevertheless, we provide the following preliminary summary. For the A_g modes considered, Eq. (24) can be written $\prod_{\gamma=1}^{6} (\omega_D/\omega_H)_\gamma = x^2 y$. Experimentally, Rosasco and Prask find that the left-hand side reads $(1.0)(1.00)(1.02)(0.83)(0.90)(0.91) = 0.69$, whereas, since $x = 0.904$ and $y = 0.707$, the right-hand side equals 0.578. Assuming minimal mode coupling they associate the first three factors on the left with translations and rotations of the ClO_4 ions, the last two with translations of the NH_4 (ND_4) complexes, and the fourth with rotations thereof. The latter do not scale properly. The product rule informs us that even if their very plausible assumption of minimal coupling is not correct, either the harmonic approximation or the rigid-molecule approximation fails. (From their combined Raman and neutron scattering experiments, they feel reasonably confident that the modes have been properly identified. See Refs. 8 and 9.)

[16] Since $y^2 \simeq \frac{1}{2}$ for the example of deuterated ammonium perchlorate, the inequalities (25) are readily satisfied by the data of Rosasco and Prask (Ref. 8). They find $\sum_\gamma \omega_{D\gamma}^2 / \sum_\gamma \omega_{H\gamma}^2 = 0.82$, which lies between $\frac{1}{2}$ and 1. As discussed in the Introduction, when x^2 and y^2 both lie close to unity, these inequalities provide tighter constraints on the allowed assumptions.