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Internal mode vibrational interaction in plastic crystals: Application to the Raman spectra of strongly IR active modes

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The systematic development of the harmonic, intermolecular, internal mode interaction energy in terms of symmetry adapted Wigner functions of the molecular orientations is given for a plastic crystal. This development is used for the study of the Raman profile of a mode with a strong induced dipole-induced dipole interaction between the vibrating molecules. An approximate form of the profile is proposed, and compared with measurements made on NF_3 by Gilbert and Nectoux.

I. INTRODUCTION

Gilbert, Nectoux, and Drifford^{1,2} have reported that, in the plastic phases of NF_3 and CF_4 , some Raman active modes exhibit a very unusual asymmetric profile. These modes, namely the ν_1 and ν_3 modes of NF_3 , and the ν_3 mode of CF_4 , are strongly infrared active.

These authors interpreted this finding as the usual LO-TO($\mathbf{q} = 0$) splitting broadened by the orientational disorder present in the crystal. In a later paper,³ Yvinec and Pick carefully analyzed the case of the profile of the ν_3 mode of CF_4 . Taking into account the tetrahedral symmetry of that molecule and the threefold degeneracy of the ν_3 mode, they noticed that the induced dipole—induced dipole (ID-ID) interaction between two molecules vibrating at the ν_3 mode frequency was identical to what would have been obtained if these two molecules had their fourfold axes coinciding with those of the fcc lattice formed by their centers of mass. They thus concluded that the dynamical properties of that mode were identical to that of an ordered crystal and that the disorder could not act at this level. Analyzing the Raman detection mechanism, they were able to show that, due to the orientational disorder, the dominant scattering mechanism was a monomolecular process. The $\mathbf{q} = 0$ selection rule, valid in an ordered crystal, did not hold any longer here. What was detected was the one phonon density of states (OPDS). Computing the OPDS for a fcc lattice, they found that this OPDS had, in fact, two maxima of unequal intensity, one close to the TO($\mathbf{q} = 0$) frequency, and the other close to the LO($\mathbf{q} = 0$) one; this explained both the shape of the measured spectrum and the approximate agreement with the previously proposed origin of this profile. Nevertheless, such a technique could not be applied to the case of NF_3 , because this molecule has a C_{3v} symmetry and the ν_1 and ν_3 modes are, respectively, nondegenerate and doubly degenerate only.

The vibrational properties of those modes are thus those of a true disordered crystal and no conclusion could be drawn using the previously described analysis.

Meanwhile, after Hüller and Press,^{4,5} Yvinec and Pick⁶⁻⁸ developed a technique for expanding the properties

of a plastic crystal in terms of symmetry adapted functions of the molecular orientation. Using a complete set of Wigner functions, adapted both to the molecule and to the molecular site symmetries they were able to give close form expressions in particular for the Raman spectra of molecular internal modes and for the one particle orientational correlation function.

Using the same technique, we shall first, in this paper, express the harmonic interaction energy between two different molecules vibrating in two different modes, making use only of the symmetry properties of the crystal and of the molecular internal modes. We shall then look at the particular form of this interaction in the case of a dipole-dipole interaction. This will allow us to reproduce the exact result previously obtained for the case of the ν_3 mode of CF_4 , in a more transparent language.

We shall then show that a generalization of this result to molecules of lower symmetry is possible, if some decoupling approximation is accepted. Using this technique, we shall show that the spectral profiles of the ν_1 and the ν_3 modes of NF_3 should be identical to that of CF_4 , as they apparently are, and we shall predict a value of the “apparent LO-TO” splitting in better agreement with experiment than the one proposed by Gilbert and Nectoux.

This paper gives a report of such an analysis and is organized as follows: Section II, which heavily relies on the result of Refs. 6 and 7, hereafter referred to as I and II, is devoted to the derivation of the expression of the harmonic interaction energy in terms of symmetry adapted Wigner functions, and gives the various selection rules which allow to simplify its expression.

Section III is devoted to the study of the Raman profile of an internal mode in the case of a strong interaction energy between the vibrating molecules. After giving the general expression of this profile in terms of the appropriate vibrational Green's function, we will show why the methods currently used to approximate this Green's function are invalid in the case of a dipole-dipole interaction. We will then discuss how this difficulty was circumvented in the case of the ν_3 mode of CF_4 , and propose an approximate method for the case of a molecule

with lower symmetry. This method is finally applied to the case of NF_3 in Sec. IV. We make precise the results we obtain in this case, discuss the relationship with the previous work of Gilbert and Nectoux, and the reasons for some discrepancies between the computed OPDS and the actual profile. A final discussion of some aspects of this work is also given.

II. SYSTEMATIC DEVELOPMENT OF THE VIBRATIONAL INTERMOLECULAR INTERACTION ENERGY AND SELECTION RULES

In this section, we shall first write the expression of the vibrational intermolecular interaction energy in terms of normal vibrations.

We shall then show how the total vibrational interaction energy \mathcal{E} can be split into a sum over components, which are the two molecules interaction energy (TMIE) for two molecules L_1 and L_2 and a given normal mode j . In the second subsection, the symmetry group of the TMIE is derived for the different possible cases.

Third, we shall give a development of the energy interaction constant in terms of a symmetry adapted canonical basis and, lastly, selection rules for the development constants are deduced. These selection rules follow from the symmetry group of the TMIE.

A. Development of the interaction energy in term of vibrational normal coordinates

In the harmonic approximation, the vibrational intermolecular interaction energy of a crystal in the plastic phase can be written as:

$$\mathcal{E} = \sum_{\substack{A_1 A_2 \\ s_1 s_2 \\ L_1 L_2}} U_{s_1}^{A_1}(\Omega_{L_1}) W_{s_1 s_2}^{A_1 A_2}(\{\Omega_L\}) U_{s_2}^{A_2}(\Omega_{L_2}). \quad (2.1)$$

Here, A_1, A_2 are Cartesian coordinates in the crystal axes, L_1, L_2 label the crystal molecules, s_1, s_2 label the atoms of the molecules L_1 and L_2 , respectively, Ω_L is a shorthand notation for the three Euler angles of the molecular orientation (for the exact definition of Ω , see I), $U_s^A(\Omega_L)$ is the vibrational amplitude of the s atom of the L molecule in the direction A (the argument Ω_L does not indicate a functional dependence, but only specifies the orientation of the molecule L) and $W_{s_1 s_2}^{A_1 A_2}(\{\Omega_L\})$ is the interaction constant between the s_1 atom of the L_1 molecule vibrating in the A_1 direction, and the s_2 atom of the L_2 molecule vibrating in A_2 direction, the argument $\{\Omega_L\}$ indicating that this interaction constant depends on the orientation of all the crystal molecules.

Since this problem cannot be treated in its generality, we shall make here the crystal field approximation where the $W_{s_1 s_2}^{A_1 A_2}$ depend only on Ω_{L_1} and Ω_{L_2} :

$$W_{s_1 s_2}^{A_1 A_2}(\{\Omega_L\}) = W_{s_1 s_2}^{A_1 A_2}(\Omega_{L_1}, \Omega_{L_2}). \quad (2.2)$$

For the subsequent deduction of the symmetry properties of the interaction constant (sec. II B), it is necessary to write down this interaction energy in terms of molecular vibrational normal modes. The amplitudes U_s^A of Eq. (2.1) must therefore be transformed into normal amplitudes. This is made by successively applying two unitary transformations, which leads to the result (Appendix A)

$$\mathcal{E} = \sum_{\substack{\Lambda_1 \Lambda_2 \\ L_1 L_2}} U_{L_1}^{\Lambda_1}(\Omega_{L_1}) W_{L_1 L_2}^{\Lambda_1 \Lambda_2}(\Omega_{L_1}, \Omega_{L_2}) U_{L_2}^{\Lambda_2}(\Omega_{L_2}), \quad (2.3)$$

where Λ is a shorthand notation, introduced in I, for two indices $\Lambda = (j, N)$, j is an internal normal mode of the molecule, N labels the degenerate coordinates of the mode j and $W_{L_1 L_2}^{\Lambda_1 \Lambda_2}(\Omega_{L_1}, \Omega_{L_2})$ is the interaction constant between the Λ_1 mode of the L_1 molecule and the Λ_2 mode of the L_2 molecule.

In addition, two normal modes (j_1, N_1) and (j_2, N_2) with $j_1 \neq j_2$ only couple very little compared with the case for $j_1 = j_2$. Hence the $j_1 \neq j_2$ cross terms can be neglected and the interaction energy can be split into normal mode components

$$\mathcal{E} = \sum_{j, L_1 L_2} \mathcal{E}_{j, L_1 L_2}, \quad (2.4)$$

where

$$\mathcal{E}_{j, L_1 L_2} = \sum_{N_1 N_2} U_{L_1}^{j N_1}(\Omega_{L_1}) W_{L_1 L_2}^{j N_1 N_2}(\Omega_{L_1}, \Omega_{L_2}) U_{L_2}^{j N_2}(\Omega_{L_2}) \quad (2.5)$$

is the two molecule interaction energy (TMIE).

B. The symmetry group of the TMIE

In order to express as simply as possible the interaction constant $W_{L_1 L_2}^{\Lambda_1 \Lambda_2}(\Omega_1, \Omega_2)$, it is convenient to study the transformation properties of the corresponding TMIE between two molecules labeled 1 and 2. Following I, we suppose that the molecules are invariant under a symmetry group \mathcal{M} . This group contains proper rotations r and it has been shown in I that under such an operation, the orientation Ω of the molecule is changed into $r\Omega$. Let us also recall that:

- (i) if the molecule performs a rotation r_1 around a crystal axis, its new orientation is given by $r_1\Omega$;
- (ii) if an improper rotation is noted ir_0 , where i is the inversion operation and r_0 a proper rotation, and if the molecule performs simultaneously an improper rotation ir_1 around its molecular axes and an improper rotation ir around the crystal axes, this is equivalent to a proper, thus physically possible, rotation of the molecule after which the latter has the new orientation $r\Omega r_1$. Keeping in mind that the molecules can perform only proper rotations, one finds that the TMIE $\mathcal{E}_{j,12}(\Omega_1, \Omega_2)$ must be invariant under the following symmetry operations:

- (1) Invariance under a proper rotation of the molecular symmetry group $r'_1 \in \mathcal{M}$ acting only on the molecule 1:

$$\mathcal{E}_{j,12}(\Omega_1, \Omega_2) = \mathcal{E}_{j,12}(\Omega_1 r'_1, \Omega_2). \quad (2.6a)$$

Indeed, in this transformation, the orientation of the molecule has changed with respect to the crystal axes, but this new orientation is physically indistinguishable from the first one. Nevertheless, this is not true in general for the vibrational eigenstates of the molecule which have changed with this rotation. Consequently, the normal amplitude which enters into Eq. (2.6a) is related to the original one by

$$U_1^j(\Omega_1 r'_1) = \sum_{N'} M_{\Gamma_j}^{NN'}(r'_1) U_1^j(\Omega_1), \quad (2.7)$$

where $M_{\Gamma_j}^{NN'}(r'_1)$ is the transformation matrix associated with the irreducible representation Γ_j and the operation r'_1 . [For the invariance of the TMIE $\mathcal{E}_{j,12}$, it is sufficient and necessary that after a rotation $r' \in \mathcal{M}$, the molecules have the same vibrational state as before. But the basis functions, in which this vibrational state is described, i.e., the vibrational normal modes $(j, N)_\Omega$ associated with a molecule with the orientation Ω are transformed under a rotation $r' \in \mathcal{M}$ following their irreducible representation

$$(j, N)_{\Omega r'} = \sum_{N'} M_{\Gamma_j}^{NN'}(r')(j, N')_\Omega.$$

The normal coordinate thus must transform inversely, which leads to the equality (2.7)].

(2) Invariance under a proper rotation $r'_2 \in \mathcal{M}$ acting only on the molecule 2,

$$\mathcal{E}_{j,12}(\Omega_1, \Omega_2) = \mathcal{E}_{j,12}(\Omega_1, \Omega_2 r'_2). \quad (2.6b)$$

Note that the same remark as above must be made on the vibrational amplitude.

(3) Invariance under a proper rotation $r \in S_{12}$ (where S_{12} is the subgroup of the crystal symmetry group which leaves the sites 1 and 2 individually invariant) acting simultaneously on both molecules

$$\mathcal{E}_{j,12}(\Omega_1, \Omega_2) = \mathcal{E}_{j,12}(r\Omega_1, r\Omega_2). \quad (2.8)$$

Here, the vibrational normal coordinates of the two molecules do not change, i.e. they do not keep their absolute vibrational state in the crystal lattice, but only their relative vibrational state one with respect to the other. [Since, after a rotation $r \in S_{12}$, the molecules, in their equilibrium position, cannot in general be described by the same orientation as before (since in general $r \notin \mathcal{M}$), they also cannot have the same vibrational states. But this is not necessary for the invariance of $\mathcal{E}_{j,12}$. It is sufficient that, after the transformation, they have the same relative vibrational states one with respect to the other, and that each of them has an equivalent vibrational state with respect to the crystal field. These conditions are fulfilled, if the vibrational states are "rotated" together with the molecules, i.e., if their normal amplitudes do not change:

$$U_1^j(\Omega_1) = U_1^j(r\Omega_1) \quad \text{and} \quad U_2^j(\Omega_2) = U_2^j(r\Omega_2).]$$

The symmetry operations (1), (2), and (3) form a group which can be written as the direct product $S_{12,r}\mathcal{M}_r\mathcal{M}_r$, where the indices r indicate the subgroup of all proper rotations of the corresponding symmetry group. If both

the molecular group \mathcal{M} and the site group S_{12} do not contain improper rotations or if only the molecular group does contain them, this direct product is the whole symmetry group G of the TMIE $\mathcal{E}_{j,12}$. On the contrary, if both \mathcal{M} and S_{12} contain improper rotations, we have the last kind of possible symmetry operations which leads to a new invariance of the TMIE.

(4) Invariance under the simultaneous action of the inversion rotations $ir \in S_{12}$ and $ir'_1 \in \mathcal{M}$ on the molecule 1 and of the inversion rotations $ir \in S_{12}$ and $ir'_2 \in \mathcal{M}$ on the molecule 2 (I):

$$\begin{aligned} \mathcal{E}_{j,12}(\Omega_1, \Omega_2) &= \mathcal{E}_{j,12}(ir\Omega_1 ir'_1, ir\Omega_2 ir'_2) \\ &= \mathcal{E}_{j,12}(r\Omega_1 r'_1, r\Omega_2 r'_2), \end{aligned} \quad (2.9)$$

where, again, the same remark as in I must be made.

As pointed out in I, in such a case, the group S_{12} can be written as the product of $S_{12,r}$ by the set $\{e, ir^0\}$, where ir^0 is an improper rotation of S_{12} . With a similar notation (ir^0) for \mathcal{M} , one sees that the symmetry group of the TMIE can be written as a direct product of the two elements $\{e, ir^0 ir_1^0 ir_2^0\}$ with the group $S_{12,r}\mathcal{M}_r\mathcal{M}_r$:

$$G = \{e, ir^0 ir_1^0 ir_2^0\} \times S_{12,r}\mathcal{M}_r\mathcal{M}_r. \quad (2.10)$$

The TMIE is in the unity representation of this group.

C. Development of the interaction constant in a symmetry adapted basis

Being a function of two orientations, the interaction constant $W_{L_1 L_2}^{A_1 A_2}(\Omega_{L_1}, \Omega_{L_2})$, as the self-orientational correlation function in II, can be developed on a basis of products of two symmetry adapted functions $\Delta_{l_1}^{\lambda_1 \lambda_1'}(\Omega_{L_1}) \Delta_{l_2}^{\lambda_2 \lambda_2'}(\Omega_{L_2})$. Those functions introduced in I were, in this paper, simultaneously adapted to both the molecular symmetry and the site symmetry. In the present case, the indices λ_1 and λ_2 , which take $(2l_1 + 1)$ and $(2l_2 + 1)$ values, respectively, are a shorthand notation for $\lambda_1 = (\Gamma_1, \mu_1, n_1)$ and $\lambda_2 = (\Gamma_2, \mu_2, n_2)$, where $\Gamma_1(\Gamma_2)$ indicates the irreducible representation of the group S_{12} ; (and *not* of the site symmetry S as in I), $\mu_1(\mu_2)$ labels the independent $\Gamma_1(\Gamma_2)$ subspaces for a given value of $l_1(l_2)$, and $n_1(n_2)$ numbers the one-dimensional subspaces of the multidimensional $\Gamma_1(\Gamma_2)$ representations.

Correspondingly, we have the same notations for λ'_1 and λ'_2 with respect to the molecular group \mathcal{M} . By construction (see I) each function $\Delta_i^{\lambda \lambda'}(\Omega)$ transforms under any symmetry operation of the group S_{12} as the irreducible representation Γ of S_{12} which appears in its first index and under any symmetry operation $r' \in \mathcal{M}$ as the irreducible representation Γ' of \mathcal{M} which is indicated in its second index.

The development of the interaction constant in such a basis reads, in general,

$$\begin{aligned} W_{L_1 L_2}^{A_1 A_2}(\Omega_{L_1}, \Omega_{L_2}) \\ = \sum_{\substack{l_1 l_2 \\ \lambda_1 \lambda_1' \\ \lambda_2 \lambda_2'}} C \left(\begin{matrix} A_1 A_2 \\ L_1 L_2; \end{matrix} \begin{matrix} \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ l_1 & l_2 \end{matrix} \right) \Delta_{l_1}^{\lambda_1 \lambda_1'}(\Omega_{L_1}) \Delta_{l_2}^{\lambda_2 \lambda_2'}(\Omega_{L_2}). \end{aligned} \quad (2.11)$$

D. Selection rules for the interaction constant

The TMIE (2.5) written with the development (2.11) leads to

$$\mathcal{E}_{j,12} = \sum_{\substack{N_1 N_2, l_1 l_2 \\ \lambda_1 \lambda_1', \lambda_2 \lambda_2'}} U_{N_1}^{j*}(\Omega_1) U_{N_2}^j(\Omega_2) \times C \left(\begin{matrix} j & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ 1 & l_1 & l_2 \end{matrix} \right) \Delta_{l_1}^{\lambda_1 \lambda_1'}(\Omega_1) \Delta_{l_2}^{\lambda_2 \lambda_2'}(\Omega_2). \quad (2.12)$$

We can easily find out which coefficients $C \left(\begin{matrix} j & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ 1 & l_1 & l_2 \end{matrix} \right)$ appear in Eq. (2.12) if we recall that, as noticed at the end of Sec. II B, Eq. (2.12) is in the unity representation of G , with the rules given by Eqs. (2.7)–(2.10). We must first recall that, as explained in I, for any point group \mathcal{P} containing improper rotations, there exist two one dimensional representations of \mathcal{P} which induce the unity representation of \mathcal{P}_r , the subgroup of proper rotations of \mathcal{P} . One, Γ_{0+} is the unity representation of \mathcal{P} , the second, Γ_{0-} has the character 1 for all the proper rotations, and -1 for all the improper ones.

Furthermore, it has been shown in II that, for such groups, for each representation Γ_1 there exists one and only one representation $\Gamma_{1-} = \Gamma_{0-}\Gamma_1$ such that $\Gamma_1^* \Gamma_{1-}$ induces Γ_{0-} .

Let us now discuss first the case for which \mathcal{M} and S_{12} do not contain any improper rotation, i.e. $\mathcal{M} = \mathcal{M}_r$ and $S_{12} = S_{12,r}$. We have thus, for the symmetry group of the TMIE

$$S_{12,r} \mathcal{M}_r \mathcal{M}_r = S_{12} \mathcal{M} \mathcal{M}.$$

The product $S_{12} \mathcal{M} \mathcal{M}$ is a direct product of three independent groups. Thus, its representations are the product of the representations of these groups and we shall label its representations by giving in order the representation of $S_{12}(\Gamma)$, $\mathcal{M}^{(1)}(\Gamma^1)$, and $\mathcal{M}^{(2)}(\Gamma^2)$. In this notation, the unity representation of $S_{12} \mathcal{M}^{(1)} \mathcal{M}^{(2)}$ is written $\Gamma_0 \Gamma_0^1 \Gamma_0^2$.

Now, the first factor of Eq. (2.12) $\left[U_{N_1}^j(\Omega_1) \right]$ in the representation $\Gamma_0 \Gamma_j^1 \Gamma_0^2$ and the second in the representation $\Gamma_0 \Gamma_0^1 \Gamma_j^{2*}$ together give the representation $\Gamma_0 \Gamma_j^1 \Gamma_j^{2*}$. Furthermore, the product of basis functions $\Delta_{l_1}^{\lambda_1 \lambda_1'}(\Omega_1) \Delta_{l_2}^{\lambda_2 \lambda_2'}(\Omega_2)$ is in the representation $(\Gamma^* \Gamma_2) \Gamma_1^* \Gamma_2^2$; hence, the product of these representations is

$$(\Gamma^* \Gamma_2)(\Gamma_j^1 \Gamma_1^{1*})(\Gamma_j^{2*} \Gamma_2^2). \quad (2.13)$$

{We remark that there are two different products of representations. First, we have the product of two representations of the same group as, i.e., inside the parentheses of the expression (2.13); in this case, the product of two irreducible representations is in general not an irreducible representation of the group. And secondly, there are the products of representations which are associated with the direct product of different groups and are indicated as the products of parentheses in Eq. (2.13). In this case, the product of two irreducible representations is an irreducible representation of the group product. When those two types of product appear together [as it is the case in Eq. (2.13)] in order to avoid ambiguity, we always put paren-

theses around the product belonging to the same group.} Equation (2.13) must be in the unity representation of G which means that $(\Gamma^* \Gamma_2)$ must contain the unity representation Γ_0 of S_{12} , $\Gamma_j^1 \Gamma_1^{1*}$ that of $\mathcal{M}^{(1)}$ and $\Gamma_j^{2*} \Gamma_2^2$ that of $\mathcal{M}^{(2)}$. We thus find the following selection rule:

$$\Gamma_1 = \Gamma_2; \quad \Gamma_1' = \Gamma_j; \quad \Gamma_2' = \Gamma_j \quad (2.14)$$

so that the development constants $C \left(\begin{matrix} \Lambda_1 \Lambda_2 & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ L_1 L_2 & l_1 & l_2 \end{matrix} \right)$ reduce to

$$C \left(\begin{matrix} \Lambda_1 \Lambda_2 & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ L_1 L_2 & l_1 & l_2 \end{matrix} \right) = C \left[\begin{matrix} j & \Gamma_1 & \mu_1 \mu_1' & \mu_2 \mu_2' \\ L_1 L_2 & l_1 & l_1 & l_2 \end{matrix} \right] \delta_{N_1 n_1'} \delta_{N_2 n_2'} \delta_{n_1 n_2}. \quad (2.15)$$

If, now, the molecular group \mathcal{M} contains improper rotations, but the group S_{12} still does not, we have for the TMIE symmetry group

$$G = S_{12} \mathcal{M}_r \mathcal{M}_r.$$

There are four irreducible representations of the group $S_{12} \mathcal{M} \mathcal{M}$, which induce the unity representation of G , namely the representations $\Gamma_0 \Gamma_0^1 \Gamma_0^2$, $\Gamma_0 \Gamma_0^1 \Gamma_0^{2-}$, $\Gamma_0 \Gamma_0^1 \Gamma_0^{2+}$ and $\Gamma_0 \Gamma_0^1 \Gamma_0^{2-}$.

Therefore, using Eq. (2.13), four coefficient series are found with the selection rules

$$\begin{aligned} (1) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_j, \quad \Gamma_2' = \Gamma_j, \\ (2) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_{j-}, \quad \Gamma_2' = \Gamma_{j-}, \\ (3) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_j, \quad \Gamma_2' = \Gamma_{j-}, \\ (4) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_{j-}, \quad \Gamma_2' = \Gamma_j, \end{aligned} \quad (2.16)$$

$$C \left(\begin{matrix} \Lambda_1 \Lambda_2 & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ L_1 L_2 & l_1 & l_2 \end{matrix} \right) = C^{(i)} \left[\begin{matrix} j & \Gamma_1 & \mu_1 \mu_1' & \mu_2 \mu_2' \\ L_1 L_2 & l_1 & l_1 & l_2 \end{matrix} \right] \delta_{N_1 n_1'} \delta_{N_2 n_2'} \delta_{n_1 n_2}$$

with $i = 1, 2, 3, 4$.

Lastly, let us consider the case where both groups S_{12} and \mathcal{M} contain improper rotations. As mentioned in Eq. (2.10) the operations of G now contain the proper rotations of S_{12} and both molecular groups, and the improper rotations of all these three groups simultaneously. But for an improper rotation, Γ_{0-} has the character -1 . Thus the product representing the unity representation of G , which has the character 1 for all the operations of G , must contain an even number of Γ_{0-} representations. In other words, only the four representations $\Gamma_0 \Gamma_0^1 \Gamma_0^2$, $\Gamma_0 \Gamma_0^1 \Gamma_0^{2-}$, $\Gamma_0 \Gamma_0^1 \Gamma_0^{2+}$, and $\Gamma_0 \Gamma_0^1 \Gamma_0^{2-}$ of $S_{12} \mathcal{M} \mathcal{M}$ induce the unity representation of G . Consequently, again using (2.13), one easily obtains the following selection rules:

$$\begin{aligned} (1) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_j, \quad \Gamma_2' = \Gamma_j, \\ (2) \quad & \Gamma_1 = \Gamma_2, \quad \Gamma_1' = \Gamma_{j-}, \quad \Gamma_2' = \Gamma_{j-}, \\ (3) \quad & \Gamma_1 = \Gamma_{2-}, \quad \Gamma_1' = \Gamma_j, \quad \Gamma_2' = \Gamma_{j-}, \\ (4) \quad & \Gamma_1 = \Gamma_{2-}, \quad \Gamma_1' = \Gamma_{j-}, \quad \Gamma_2' = \Gamma_j, \end{aligned} \quad (2.17)$$

$$C \left(\begin{matrix} \Lambda_1 \Lambda_2 & \lambda_1 \lambda_1' & \lambda_2 \lambda_2' \\ L_1 L_2 & l_1 & l_2 \end{matrix} \right) = C^{(i)} \left[\begin{matrix} j & \Gamma_1 & \mu_1 \mu_1' & \mu_2 \mu_2' \\ L_1 L_2 & l_1 & l_1 & l_2 \end{matrix} \right] \delta_{N_1 n_1'} \delta_{N_2 n_2'} \delta_{n_1 n_2}, \quad \text{with } i = 1, 2, 3, 4.$$

Table I shows the first coefficients arising in the development for some selected cases.

E. Remarks

(i) If \mathcal{M} is a centered group and if the mode j is Raman active, the representation Γ_j is a representation Γ_g and the representation Γ_{j-} is a representation Γ_u . Γ_g is only included in a given l subspace for l even and Γ_u only for l odd. Therefore the possibility (1) of the selection rules (1.17) arises if, and only if l_1 and l_2 are both even, the possibility (2) arises, if and only if l_1 and l_2 are both odd and the possibilities (3) and (4) arise, if and only if l_1 and l_2 have different parity.

(ii) The subgroup S_{12} of the site group S cannot be a centered group, since the inversion i does not let the molecules 1 and 2 individually invariant.

III. APPROXIMATE CALCULATION OF THE RAMAN SPECTRUM OF A MODE WITH DIPOLE-DIPOLE INTERACTION

In this section, we shall first recall the formal expression for the Raman profile of an internal mode in the case where the decoupling approximation between the molecular reorientations and the internal vibrational Green's function is possible. We then discuss how this Green's function is generally computed and why such a method is unapplicable in the case of an ID-ID interaction. Using the expression for this interaction obtained with the method of Sec. II, we show how, in the case of a molecule with cubic symmetry, a change of dynamical variables allows for an easy computation of this Green's function. We finally consider the case of a molecule with lower symmetry and prove that the same result for the dynamical matrix as above can be obtained; nevertheless, in this last case, the dynamical variables are coupled, and we finally use, in order to obtain the Raman profile, a decoupling technique, the validity of which is discussed.

A. Raman intensity in molecular crystals

As has been shown in Ref. 8 the crystal symmetry adapted components of the Raman spectrum for the normal mode j can be written as

$$R_{j,l_1 l_2}^{\lambda_1 \lambda_2} = \frac{k_d^4}{2\pi} TF_\omega \left\langle \sum_{\substack{N'_1 N'_2 \\ L_1 L_2}} \epsilon_{L_1} \left[\begin{matrix} N'_1 \\ j \\ l_1 \end{matrix} \right]_{\lambda_1} (0) U_{L_1}^{j*}(\Omega_{L_1}, 0) \right. \\ \left. \times U_{L_2}^j(\Omega_{L_2}, t) \epsilon_{L_2} \left[\begin{matrix} N'_2 \\ j \\ l_2 \end{matrix} \right]_{\lambda_2} (t) \right\rangle, \quad (3.1)$$

where $\epsilon_L \left[\begin{matrix} N' \\ j \\ l \end{matrix} \right]_{\lambda} (t) \equiv \left[\partial \epsilon_L \left(\begin{matrix} \lambda \\ l \end{matrix} \right) (t) / \partial U_N^j(\Omega_L, t) \right]$ is the crystal

irreducible (l, λ) component of the (j, N') Raman tensor of the molecule L at time t when this molecule has the orientation $\Omega(t)$, $\epsilon_L \left(\begin{matrix} \lambda \\ l \end{matrix} \right)$ being the crystal irreducible (l, λ)

component of the polarizability of this molecule.

Here, contrary to Sec. II, λ_1 and λ_2 refer to the irreducible representations of the site group (and *not* of the group $S_{L_1 L_2}$). As a Raman tensor is a symmetric second rank tensor, l takes the values 0 and 2 only. Finally, the mean value appearing in Eq. (3.1) is taken over all the orientations Ω .

The transformation of the crystal irreducible components of the individual Raman tensor into their molecular irreducible components leads to

$$\epsilon_L \left[\begin{matrix} N' \\ j \\ l \end{matrix} \right]_{\lambda} (t) = \epsilon_{jl}^{N'X}(\{\Omega_L, t\}) \Delta_l^{\lambda X}[\Omega_L(t)] \quad (3.2)$$

where $\epsilon_{jl}^{N'X}$ does not depend specifically on L , but is, in principle, a function of the orientations of all the molecules. Let us simplify this expression by making the usual Kastler-Rousset approximation, which postulates that $\epsilon_{jl}^{N'X}$ has definite components which do not depend on $\{\Omega_L, t\}$; then Eq. (3.1) reads

TABLE I. Number of the first development constants of the interaction energy for the first values of l_1 and l_2 and the following molecular symmetries: (A) molecular symmetry group $\mathcal{M} = T_d$, normal mode representation $\Gamma_j = F_2$; (B) $\mathcal{M} = C_{3v}$, $\Gamma_j = E$; (C) $\mathcal{M} = C_{3v}$, $\Gamma_j = A_1$.

j :	(A) $\Gamma_j = F_2$		(B) $\Gamma_j = E$		(C) $\Gamma_j = A_1$	
$S_{12} \mathcal{M}$:	$C_{4v} T_d T_d$	$C_{3v} T_d T_d$	$C_{4v} C_{3v} C_{3v}$	$C_{3v} C_{3v} C_{3v}$	$C_{4v} C_{3v} C_{3v}$	$C_{3v} C_{3v} C_{3v}$
$l_1 = 1$	$C^1(A_1)$	$C^1(A_1)$	$C^1(A_1)$	$C^1(A_1)$	$C^1(A_1)$	$C^1(A_1)$
$l_2 = 1$	$C^1(E)$	$C^1(E)$	$C^1(E)$	$C^1(E)$	$C^1(E)$	$C^1(E)$
$l_1 = 1$	$C^1(A_1)$	$C^1(A_1)$	$2C^1(A_1)$	$2C^1(A_1)$	$C^1(A_1)$	$C^1(A_1)$
$l_2 = 2$	$C^1(E)$	$2C^1(E)$	$2C^1(E)$	$4C^1(E)$	$C^1(E)$	$2C^1(E)$
$l_1 = 1$	$C^1(A_1)$	$2C^1(A_1)$	$2C^1(A_1)$	$4C^1(A_1)$	$2C^1(A_1)$	$4C^1(A_1)$
$l_2 = 3$	$2C^1(E)$	$2C^1(E)$	$4C^1(E)$	$4C^1(E)$	$4C^1(E)$	$4C^1(E)$
	$2C^3(E)$	$C^3(A_1)$		$2C^3(A_1)$	$2C^3(E)$	$C^3(A_1)$
		$2C^3(E)$				$2C^3(E)$
$l_1 = 2$	$C^1(A_1)$	$C^1(A_1)$	$4C^1(A_1)$		$C^1(A_1)$	$C^1(A_1)$
$l_2 = 2$	$C^1(B_1)$	$4C^1(E)$	$4C^1(B_2)$	$4C^1(A_1)$	$C^1(B_1)$	$C^1(B_1)$
	$C^1(B_2)$		$4C^1(E)$	$16C^1(E)$	$C^1(B_2)$	$4C^1(E)$
	$C^1(E)$		$4C^3(B_1)$		$C^1(E)$	

$$R_{j,l_1 l_2}^{\lambda_1 \lambda_2} = \frac{k_d^4}{2\pi} \sum_{\substack{N_1 \lambda_1 \\ N_2 \lambda_2}} \epsilon_{j l_1}^{N_1 \lambda_1} \epsilon_{j l_2}^{N_2 \lambda_2} T F_{\omega} \\ \times \left\langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}(0)) [U_{N_1}^{j*}(\Omega_{L_1}, 0) U_{N_2}^j(\Omega_{L_2}, t) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}(t))] \right\rangle. \quad (3.3)$$

In (3.3), Ω_{L_1} and Ω_{L_2} depend, in principle, on time. Nevertheless, when the coupling between the internal vibrations produces a broadening much larger than the rotational effects, the latter can be neglected; this means that, in such a case, the time dependence of the orientation can be omitted in Eq. (3.3). This is usually referred to as the molecular glass approximation, which we shall make in the rest of this paper.

Finally, the usual approximation, which we shall not retain in Secs. III C and III D of this chapter, is the so-called decoupling approximation which postulates that

$$T F_{\omega} \left\langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) U_{N_1}^{j*}(\Omega_{L_1}, 0) U_{N_2}^j(\Omega_{L_2}, t) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \right\rangle \\ = \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \rangle \\ \times T F_{\omega} \left\langle U_{N_1}^{j*}(\Omega_{L_1}, 0) U_{N_2}^j(\Omega_{L_2}, t) \right\rangle. \quad (3.4)$$

Before proceeding further, let us discuss our inability to use this last expression in the case of an ID-ID interaction.

B. The ordinary approximation methods and their failure in the case of a dipole-dipole interaction

In order to treat Eq. (3.4) one must be able, at least, to have a proper evaluation of the two correlation functions it contains. We wish simply to show, in this subsection, why the ordinary perturbation methods, currently used in similar problems, fail to provide a correct answer in the present case.

As in the case of ID-ID interaction, the contribution of the first neighbors to the interaction energy is not the dominant part, one can, at the same level of approximation as the one leading to Eq. (3.4), decompose its first term for $L_1 \neq L_2$ into a product of mean values

$$\langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \rangle = \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \rangle \langle \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \rangle. \quad (3.5)$$

In the case of a cubic crystal, when the probability distribution function of the molecular orientation $P_0(\Omega)$ is expanded on symmetry adapted Wigner functions, the lowest l values are equal to 0 and 4. Now, in Eq. (3.5), l_1 and l_2 are equal to 0 and 2, and to 2 only if j is not in the molecular identity representation. Thus, except if both l values can be taken equal to zero, the right-hand side of Eq. (3.5) is equal to zero; nevertheless, even in the absence of any orientational correlation, Eq. (2.5) is not valid when $L_1 = L_2$, in which case the left-hand side always has a nonzero value related to the $l_1 = l_2 = 2$ term. We can thus conclude that, for a vibration j not in the identity representation of the molecular group, the only contribution to Eq. (3.4) stems from the $L_1 = L_2$ term, and that, even for a vibration in the identity representation, this term contributes to the line shape.

We shall thus, now, concentrate on this term in our discussion.

From the very definition of the harmonic interaction energy (2.5) one has

$$T F_{\omega} \left\langle U_{N_1}^{j*}(\Omega_{L_1}, 0) U_{N_2}^j(\Omega_{L_2}, t) \right\rangle = \langle g_{L_1 L_2}^{N_1 N_2}(\omega) \rangle \\ = \left\langle \frac{1}{(\omega^2 - \omega_0^2) \delta_{L_1 L_2} \delta_{N_1 N_2} - W_{L_1 L_2}^{N_1 N_2}(\Omega_{L_1}, \Omega_{L_2})} \right\rangle \quad (3.6)$$

and we are interested here in the $L_1 = L_2$ terms of the above Green's function. In the case of a dipole-dipole interaction, using the results of Sec. II, we find that the development of $W_{L_1 L_2}^{N_1 N_2}(\Omega_{L_1}, \Omega_{L_2})$ takes the very simple form (see Appendix B)

$$W_{L_1 L_2}^{N_1 N_2}(\Omega_{L_1}, \Omega_{L_2}) \\ = \frac{\mathbf{r}_{L_1 L_2}^2 (\mathbf{P}_{N_1}^j \cdot \mathbf{P}_{N_2}^j) - 3(\mathbf{r}_{L_1 L_2} \cdot \mathbf{P}_{N_1}^j)(\mathbf{r}_{L_1 L_2} \cdot \mathbf{P}_{N_2}^j)}{r_{L_1 L_2}^5} \\ = \sum_{\substack{\lambda_1 \Gamma_1 \mu_1 \\ \lambda_2 \Gamma_2 \mu_2}} C \left(\begin{matrix} j \\ N_1 N_2 \end{matrix}; \begin{matrix} \Gamma_1 \\ \lambda_1 \mu_1 \end{matrix}; \begin{matrix} \Gamma_2 \\ \lambda_2 \mu_2 \end{matrix} \right) \Delta_{\lambda_1 \mu_1}^{\Gamma_1}(\Omega_{L_1}) \Delta_{\lambda_2 \mu_2}^{\Gamma_2}(\Omega_{L_2}) \quad (3.7)$$

with the development constant

$$C \left(\begin{matrix} j \\ N_1 N_2 \end{matrix}; \begin{matrix} \Gamma_1 \\ \lambda_1 \mu_1 \end{matrix}; \begin{matrix} \Gamma_2 \\ \lambda_2 \mu_2 \end{matrix} \right) = \frac{P_j^2}{r_{L_1 L_2}^3} \{ \delta_{\lambda_1 \lambda_2} - 4\pi S_{1\lambda_1}(\hat{\mathbf{r}}) S_{1\lambda_2}(\hat{\mathbf{r}}) \} \\ \equiv C_D \left(\begin{matrix} j \\ L_1 L_2; \lambda_1 \lambda_2 \end{matrix} \right). \quad (3.8)$$

In this expression, $\mathbf{r}_{L_1 L_2} = \mathbf{r}_{L_2} - \mathbf{r}_{L_1}$ indicates the vector which points from the site L_1 to the site L_2 , $\mathbf{P}_{N'}^j$ is the dipole moment of the (j, N') molecular vibration mode, $P_j = |\mathbf{P}_{N'}^j| = |\mathbf{P}_{N_2}^j|$, \mathbf{r} is a unit vector which points in the direction of $\mathbf{r}_{L_1 L_2}$, λ_1 and λ_2 , which are composite indices $\lambda_1 = (\Gamma_1 \mu_1 n_1)$ and $\lambda_2 = (\Gamma_2 \mu_2 n_2)$ refer to irreducible representations of the site symmetry group, and $S_{l\lambda}(\hat{\mathbf{r}})$ is the surface harmonic with $l = 1$ relative to this group.

The very unpleasant feature of Eq. (3.8) is its long range $1/r^3$ dependence. The only known theoretical methods to approximate the Green's function (3.6) are the possible variations on the "locator" developments.⁹ In these methods, one considers $1/(\omega^2 - \omega_{jL}^2)$ (where ω_{jL} is the bare mode frequency at site L) as the principal term of the denominator, and the various W as perturbations. As $\omega_{jL}^2 \equiv \omega_0^2$ does not depend either on L , or on N , the perturbation series is not convergent; one normally proceeds by first resumming some of the diagrams of this series by singling out some "proper parts" of this development. This leads to

$$\langle g_{L L}^{N_1 N_2}(\omega) \rangle = \left\langle \frac{1}{\omega^2 - \omega_0^2 - P_{L L}^{N_1 N_2}(\omega)} \right\rangle, \quad (3.9)$$

where $P_{L L}^{N_1 N_2}(\omega)$ is the sum of all the diagrams which do not contain L .

The usual approximation for treating Eq. (3.9) consists in considering only the first few terms of $P_{L L}^{N_1 N_2}(\omega)$.

Then, by construction, this method leads to a symmetrical line shape; unsymmetrical line shapes are obtained only when the proper diagrams are summed up to infinity, and the simplest method for so doing is the coherent potential approximation (CPA). Unfortunately, this method is presently restricted to the case where $W_{L_1 L_2}^{N_1 N_2}$ is a short range interaction, which is not the case here.

In the case of a dipole-dipole interaction, the experimental spectra^{1,2} are, in fact, unsymmetrical, and the theoretical discussion made in the case of tetrahedral molecules³ has shown that this asymmetry was basically related to the long range aspect of the dipole-dipole interaction. As the locator perturbation method can be of no use in the present case, we shall need to take another approach that we shall discuss now.

C. The projection method—Change of dynamical variables

The starting point of the present analysis is the study of the line shape of the ν_3 mode for a CX₄ molecule with tetrahedral symmetry. The Raman spectrum of this mode has been previously analyzed³ by Yvinec and Pick. In their paper, they implicitly used a projection of the dynamical variables described in the molecular axes, onto dynamical variables described in the crystal axes. In fact, since for the description of a threefold degenerate mode, one can choose any set of three orthogonal axes, the three orthogonal crystal axes choice was made as a starting point. Therefore, the dynamical properties of this threefold degenerate mode was that of an ordered crystal, for which the dynamical matrix could be factored out in $N \times 3 \times 3$ matrices, each value of N representing a wave vector \mathbf{q} of the reciprocal space. Thus, one can write down directly the Green's function (3.6) under the form

$$TF_{\omega} \left\langle U_{N_1}^{j*}(0) U_{N_2}^j(t) \right\rangle = \sum_{\mathbf{q}, k} e_{\mathbf{q}}^{k, N_1} e_{\mathbf{q}}^{k, N_2} (n_{\mathbf{q}} + 1) \delta(\omega_{\mathbf{q}, k} - \omega), \quad (3.10)$$

where k is a branch index for phonons propagating with wave vector \mathbf{q} , and $e_{\mathbf{q}}^{k, N}$ the corresponding eigenvector.

Owing to the cubic symmetry (O_h) of the crystal, we have further

$$\begin{aligned} \sum_{\mathbf{q}, k} e_{\mathbf{q}}^{k, N_1} e_{\mathbf{q}}^{k, N_2} \delta(\omega_{\mathbf{q}, k} - \omega) \\ = \frac{1}{3} \delta_{N_1 N_2} \sum_{\mathbf{q}, k} \delta(\omega_{\mathbf{q}, k} - \omega) = \frac{1}{3} \delta_{N_1 N_2} g(\omega), \end{aligned} \quad (3.11)$$

where $g(\omega)$ is the one phonon density of states (OPDS).

Inserting Eqs. (3.10) and (3.11) into Eq. (3.1) leads immediately to

$$R_{\nu_3, l_1 l_2}^{\lambda_1 \lambda_2} = \frac{k_d^4}{2\pi} \sum_{\substack{L_1 \lambda_1 N_1 \\ L_2 \lambda_2 N_2}} \epsilon_{\nu_3 l_1}^{N_1 \lambda_1} \epsilon_{\nu_3 l_2}^{N_2 \lambda_2} \times TF_{\omega} \left\langle \Delta_{l_1}^{\lambda_1 \lambda_1}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_1 \lambda_1}(\Omega_{L_1}) b_{L_1}^{\lambda_1}(0) b_{L_2}^{\lambda_2}(t) \Delta_{l_2}^{\lambda_2 \lambda_2}(\Omega_{L_2}) \Delta_{l_2}^{\lambda_2 \lambda_2}(\Omega_{L_2}) \right\rangle, \quad (3.17)$$

where $\lambda_i' = (F_2, N_i')$.

Making again a decoupling between the Wigner functions and the vibrational variables, one gets

$$R_{\nu_3, l_1 l_2}^{\lambda_1 \lambda_2} \simeq \frac{n+1}{3} \sum_{L N'} \left\langle \epsilon_L^{N' \lambda_1} \left[\epsilon_L^{N' \lambda_2} \right] (\Omega_L) \epsilon_L^{N' \lambda_2} \left[\epsilon_L^{N' \lambda_1} \right] (\Omega_L) \right\rangle g(\omega). \quad (3.12)$$

The mean value on the Raman tensors does not depend on k or \mathbf{q} . Therefore the Raman profile is proportional to the OPDS for the two polarizations ($\lambda_1 = E_g$ and $\lambda_1 = F_{2g}$) for which Eq. (3.12) is different from zero.

The preceding result can be reexpressed in our formalism. Following Eq. (3.7), the interaction energy for the ν_3 mode, with the self-term included, is

$$\begin{aligned} \mathcal{E}_{\nu_3} = \sum_{\substack{L_1 \lambda_1 N_1 \\ L_2 \lambda_2 N_2}} U_{L_1}^{N_1}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_1 \lambda_1}(\Omega_{L_1}) C_D \left(\begin{matrix} \nu_3 \\ L_1 L_2, \lambda_1 \lambda_2 \end{matrix} \right) \\ \times \Delta_{l_1}^{\lambda_1 \lambda_1}(\Omega_{L_2}) U_{L_2}^{N_2}(\Omega_{L_2}) + \sum_{L N'} \omega_{\nu_3}^2 |U_L^{N'}(\Omega_L)|^2. \end{aligned} \quad (3.13)$$

For each value of L , in the first term of the right-hand side of this equation, we can clearly use, instead of the three dynamical variables $U_L^{N'}(\Omega_L)$, the three new variables

$$b_L^{\lambda} = \sum_{N'} U_L^{N'}(\Omega_L) \Delta_{l_1}^{\lambda F_2}(\Omega_L). \quad (3.14a)$$

(where we have made use of the fact that the ν_3 mode is in the F_2 representation of the T_d molecular group).

Now, as for any molecular symmetry,

$$\sum_{\Lambda} \Delta_{l_1}^{\Lambda F_2}(\Omega) \Delta_{l_1}^{\Lambda F_2}(\Omega) = \delta_{\Gamma \Gamma} \delta_{N' N''} \quad (3.15a)$$

and conversely,

$$\sum_{\Gamma' N'} \Delta_{l_1}^{\Gamma' F_2}(\Omega) \Delta_{l_1}^{\Lambda_2 \Gamma'}(\Omega) = \delta_{\Lambda_1 \Lambda_2} \quad (3.15b)$$

one can invert (3.14a) to obtain

$$U_L^{N'}(\Omega) = \sum_{\Lambda} b_L^{\Lambda} \Delta_{l_1}^{\Lambda F_2}(\Omega). \quad (3.14b)$$

Inserting Eq. (3.14b) into the second term of the right-hand side of (3.13), noting that a unique F_2 representation spans the $l = 1$ subspace, and using Eq. (3.15b), this finally yields

$$\mathcal{E}_{\nu_3} = \sum_{\substack{L_1 \lambda_1 \\ L_2 \lambda_2}} b_{L_1}^{\lambda_1} \tilde{W}_{L_1 L_2}^{\lambda_1 \lambda_2} b_{L_2}^{\lambda_2} + \sum_{L \Lambda} \omega_{\nu_3}^2 |b_L^{\Lambda}|^2. \quad (3.16)$$

The new interaction constant $\tilde{W}_{L_1 L_2}^{\lambda_1 \lambda_2} = C_D \left(\begin{matrix} \nu_3 \\ L_1 L_2, \lambda_1 \lambda_2 \end{matrix} \right)$

no longer depends on the molecular orientations and is simply the dipole-dipole interaction between the crystal fixed dynamical variables used in Ref. 3. Similarly, according to Eq. (3.3) and with the transformation (3.14b), the Raman spectrum is given by

$$TF_{\omega} \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_1^*}(\Omega_{L_1}) b_{L_1}^{\lambda_1^*}(0) b_{L_2}^{\lambda_2^*}(t) \Delta_{l_2}^{\lambda_2^*}(\Omega_{L_2}) \Delta_{l_2}^{\lambda_2}(\Omega_{L_2}) \rangle$$

$$= \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_1^*}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \rangle \times TF_{\omega} \langle b_{L_1}^{\lambda_1^*}(0) b_{L_2}^{\lambda_2^*}(t) \rangle. \quad (3.18)$$

As mentioned above [Eq. (3.5)], l_1 and l_2 are equal to 2 for the ν_3 mode. With the approximation of a complete disorder (no orientational correlation), one shows, in the same manner as for Eq. (3.5), that the first mean value of Eq. (3.18) is zero for $L_1 \neq L_2$. As Eq. (3.16) is identical to the interaction energy between the crystal fixed threefold degenerate dipoles considered in Ref. 3, one immediately gets, as above [see Eq. (3.11)],

$$TF_{\omega} \langle b_L^{\lambda_1^*}(0) b_L^{\lambda_2^*}(t) \rangle = g_L^{\lambda_1 \lambda_2}(\omega) = \frac{1}{3} \delta_{\lambda_1 \lambda_2} g(\omega). \quad (3.19)$$

Inserting this result into Eq. (3.18), summing over Λ , and using Eq. (3.15a), one has

$$\sum_{\substack{L_1 \Lambda_1 \\ L_2 \Lambda_2}} \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_1^*}(\Omega_{L_1}) \Delta_{l_1}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_{L_2}) \rangle g(\omega) \delta_{\Lambda_1 \Lambda_2} \delta_{L_1 L_2} = \sum_L \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_L) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_L) \rangle \delta_{\lambda_1 \lambda_2} g(\omega) \quad (3.20)$$

with $\lambda_1'' = (F_2, N_1')$ and $\lambda_2'' = (F_2, N_2')$.

Using Eq. (3.20), Eq. (3.17) finally reduces to

$$R_{\nu_3, l_1 l_2} = \mathcal{N} \frac{k_d^4}{2\pi} \sum_{\substack{N' \\ \lambda_1 \lambda_2}} \epsilon_{\nu_3 l_1}^{N' \lambda_1} \epsilon_{\nu_3 l_2}^{N' \lambda_2} \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_L) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_L) \rangle g(\omega)$$

$$= \mathcal{N} \frac{k_d^4}{2\pi} \sum_{\substack{N' \\ \lambda_1 \lambda_2}} \mathcal{E}_{\nu_3} \left(\begin{smallmatrix} \mu'_1 \\ l_1 \end{smallmatrix} \right) \mathcal{E}_{\nu_3} \left(\begin{smallmatrix} \mu'_2 \\ l_2 \end{smallmatrix} \right) \delta_{\Gamma_1 \Gamma_2'} \delta_{\Gamma_1 \Gamma_2} \delta_{N' n_1'} \delta_{N' n_2'} \langle \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_L) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_L) \rangle g(\omega), \quad (3.21)$$

where \mathcal{N} is the total number of molecules. We have explicitly taken into account (cf. II) that the molecular irreducible components of the Raman tensor for the mode j can be written as

$$\epsilon_{jl}^{N' N} = \epsilon_j \left(\begin{smallmatrix} \mu' \\ l \end{smallmatrix} \right) \delta_{N' N} \quad [\lambda' = (\Gamma_j, \mu', n')]$$

(note that, as we are dealing with a ν_3 mode of a molecule with T_d symmetry $l = 2$, $\Gamma_j = F_2$, in which case the index μ' takes only the value $\mu' = 1$).

D. The projection method for arbitrary modes

From the physical point of view, the transformation (3.14) simply represents the projection of the three independent, degenerate, infrared active molecular variables onto the corresponding variables in the cubic crystal axes. From a mathematical standpoint, this method can be viewed as a canonical transform from a set of three independent variables into a set of three other independent variables, the important advantage being that, in the new basis, the interaction energy does not depend any longer on the orientation of the molecules. Nevertheless, formally the use of Eq. (3.14a) has no reason to be limited to threefold degenerate modes and we shall here, in order to take a specific example, apply the same method to a doubly degenerate E mode, both Raman and IR active, of a molecule with a unique three- or fourfold degenerate

axis, keeping in mind that the interaction between the various molecules is an ID-ID interaction.

Exactly as in Eq. (3.14a), one can define the three new variables

$$b_L^{AE} = \sum_{N'=1}^2 U_N^E(\Omega_L) \Delta_1^{AE}(\Omega_L), \quad (3.22)$$

where Λ stands for the threefold degenerate F_{1u} representation contained in the $l = 1$ manifold, for a cubic crystal, and (E, N') is the doubly degenerate representation of the molecular group contained in the same $l = 1$ manifold. There is, in addition, a third, one-dimensional representation A_1 contained in $l = 1$, and the three b_L^{AE} , which are not independent, are related by

$$\sum_{\Lambda} b_L^{AE} \Delta_1^{A1}(\Omega_L)$$

$$= \sum_{\substack{N'=2 \\ \Lambda, N'=1}} U_N^E(\Omega_L) \Delta_1^{AE}(\Omega_L) \Delta_1^{A1}(\Omega_L) = 0, \quad (3.23)$$

a result based on Eq. (3.15a). Nevertheless, Eq. (3.22) can still be inverted through the relation

$$U_N^E(\Omega_L) = \sum_{\Lambda} b_L^{AE} \Delta_1^{AE*}(\Omega_L). \quad (3.24)$$

Let us now show that, using Eqs. (3.22) and (3.24), we obtain the same expression for the vibrational energy as in Eq. (3.16); indeed

$$\mathcal{E}_E = \sum_{\substack{L_1 \Lambda_1 N_1' \\ L_2 \Lambda_2 N_2'}} U_{N_1'}^E(\Omega_{L_1}) \Delta_1^{A_1 E*}(\Omega_{L_1}) C \left(\begin{smallmatrix} j \\ L_1 L_2; \Lambda_1 \Lambda_2 \end{smallmatrix} \right) \Delta_1^{A_2 E}(\Omega_{L_2}) U_{N_2'}^E(\Omega_{L_2}) + \sum_{LN'} \omega_E^2 \left| U_N^E(\Omega_L) \right|^2$$

$$= \sum_{\substack{L_1 \Lambda_1 \\ L_2 \Lambda_2}} b_{L_1}^{A_1 E*} \tilde{W}_{L_1 L_2} b_{L_2}^{A_2 E} + \sum_{\substack{LN' \\ \Lambda_1 \Lambda_2}} \omega_E^2 b_{L_1}^{A_1 E*} \Delta_1^{A_1 E*}(\Omega_L) \Delta_1^{A_2 E}(\Omega_L) b_{L_2}^{A_2 E}. \quad (3.25)$$

The second term of the right-hand side of Eq. (3.25) can be transformed into

$$\sum_{\substack{\lambda \\ A_1 A_2}} \omega_E^2 b_{L_1}^{A_1 E*} \Delta_1^{A_1 \lambda*}(\Omega_L) \Delta_1^{A_2 \lambda}(\Omega_L) b_{L_2}^{A_2 E} \quad (3.26)$$

[where λ stands for both (E, N) and A_1], if one notes that, due to Eq. (3.23), all the terms which differ from one expression to the other are identical to zero. Finally using Eq. (3.15b) one obtains

$$\mathcal{G}_E = \sum_{\substack{L_1 A_1 \\ L_2 A_2}} b_{L_1}^{A_1 E*} \tilde{W}_{L_1 L_2}^{A_1 A_2} b_{L_2}^{A_2 E} + \sum_{L A} \omega_E^2 |b_L^{A E}|^2 \quad (3.27)$$

which is indeed, formally identical to Eq. (3.16).

We must now emphasize that this simple form of the interaction energy is only valid because of the relation (3.23), i.e., because the three variables b^{AE} are not independent. Our present approximation, nevertheless, consists in treating Eq. (3.27) as if these variables were independent. With this important approximation, which can be seen as a decoupling technique, we obtain an interaction energy which no longer depends on the molecular orientations and which then gives a Green's function for the b_L^{AE} variables identical to the one we have discussed above.

Finally, one can still use Eq. (3.24) in order to express Eq. (3.3) in the same way as this was done for Eq. (3.17), leading exactly to the same expression (3.17). We thus conclude that the approximation which consists in considering the three variables b_L^{AE} as independent rather than linked by Eq. (3.23) leads exactly to the same spectral profile for the E mode as the one which was obtained for the ν_3 mode of a CX_4 molecule. The same technique can be used for an A_1 mode, both Raman and IR active, for a molecule, say, with the same symmetry group. One has just to invert the A_1 and (E, N) subscripts, in the previous derivation, the only difference being that now Eq. (3.23) contains two relations between the three $b_L^{A_1}$ variables. If, again, these three variables are decoupled, i.e., if one forgets about these two Eq. (3.23) relations, one obtains the same form for the Green's function, and for the Raman profile, as for a triply degenerate mode. Before applying the preceding results to the ν_1 and the ν_3 modes of NF_3 , let us just point out that this decoupling technique is not new in the framework of disordered crystals. It has, e.g., been successfully applied in the case of mixed alkali halide crystals in order to explain the two-mode behavior which appears in some cases in the Raman spectra.^{10,11} Though this method is basically incorrect (as it multiplies by 3/2 or 3 the number of dynamical variables of the problem), we are here only interested in the Raman profile, i.e., the OPDS, and one can expect that, as in the case cited above, the shape of this OPDS is not largely affected by this artificial increase in the number of variables.

IV. EXPLICIT DISCUSSION OF THE CASE OF NF_3 AND FINAL REMARKS

(1) As can be seen in Fig. 1, which is reproduced from Ref. 1, the ν_1 and ν_3 spectral profiles of NF_3 are very similar, and also similar to that of the ν_3 line of CF_4

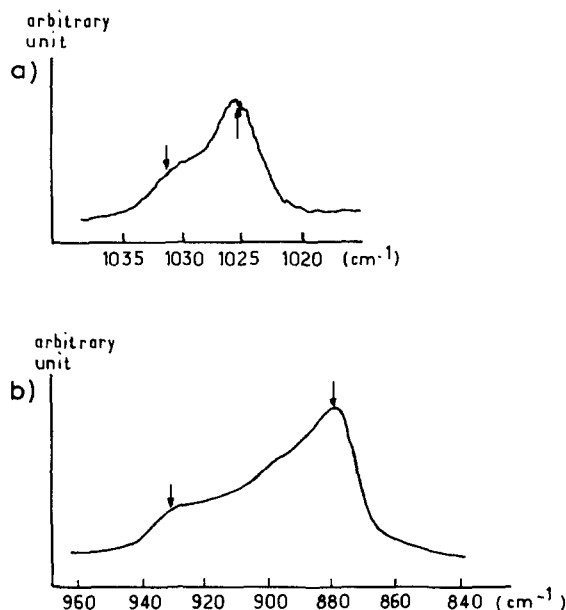


FIG. 1. Raman spectra of NF_3 (a) Profile of the ν_1 line in the ODIC phase at 60 K. (b) Profile of the ν_3 line in the ODIC phase at 62 K (reproduced from Ref. 1).

(Fig. 2). The Yvinec-Pick analysis³ of the latter case showed (a) that this profile was essentially similar to the OPDS obtained with a triply degenerate mode for a fcc Bravais lattice, with an ID-ID interaction and (b) that the apparent "LO-TO" splitting between the two maxima, which have unequal intensities, was approximately 0.8 times the actual LO-TO splitting between the $q = 0$ modes.

In the case of the ν_1 and ν_3 modes of NF_3 , this $q = 0$ (LO-TO) splitting was obtained by Nectoux and Gilbert in the following way: they used an exact formula due to Haas and Hornig,¹² valid for cubic crystals, and related this splitting to the value of the refractive index and to the dipole derivative $\partial P/\partial Q$ (where Q is the normal coordinate of the mode) as obtained from IR absorption in the gas phase. Nevertheless, as the ν_1 and ν_3 modes are not triply degenerate, they multiplied this value by $g/3$ where g is the degeneracy of the considered mode.

Our approximation consists in treating the dynamics of these modes as if they were really triply degenerate. Consequently, and using the result mentioned in (b), the experimental LO-TO "splitting" seen in Raman experiment should actually be approximately $0.8 \times 3/g$ times

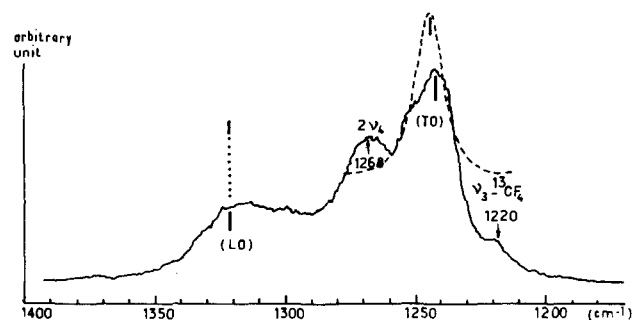


FIG. 2. Raman spectra of the ν_3 mode of CF_4 in the ODIC phase (reproduced from Ref. 2).

TABLE II. Comparison of the "splitting" of the Raman spectra of NF_3 normal modes at (A) measured values, (B) theoretical values calculated by Gilbert, Nectoux and Drifford (Ref. 1), (C) theoretical values calculated in this paper.

Normal mode	Degeneracy	Symmetry group	"Splitting" $\nu_{\max 1} - \nu_{\max 2} \text{ (cm}^{-1}\text{)}$		
			(A) Measured at 62 K	(B) Calculated in Ref. 1	(C) Calculated in this paper
ν_3	2	E	50, 8	52	62, 5
ν_1	1	A	6, 5	3, 85	9, 25

the value computed by Gilbert and Nectoux. Those results are reported in Table II, which shows that our prediction for the ν_1 splitting is larger than the experimental value and not smaller as in Ref. 1. This is more satisfactory, because the effect of our approximation is to artificially increase this splitting, which is what appears in the comparison between theory and experiment. On the contrary, too small a splitting, as proposed by the previous theory, cannot be accounted for.

(2) The comparison of the two spectra of Fig. 1 with Fig. 2 which shows the profile of the ν_3 line of CF_4 , and with Fig. 3 giving the computed OPDS, shows that the smaller is the distance between the two maxima, the shallower is the minimum between these maxima. This result is not surprising as we have, throughout this paper, made the molecular glass approximation. This means that we have neglected any rotational effect; in the lowest order approximation, the latter effect manifests itself as a convolution of the OPDS with the appropriate rotational function, thus as a broadening of the measured spectrum. This broadening will have a relatively more important effect on the profile of the narrower ν_1 mode of NF_3 than on the corresponding ν_3 mode.

(3) The relative intensities are still given by Eq. (3.21), where the $\epsilon_j(\nu_i)$ are now relative to the ν_1 mode (of A_1 symmetry) and the ν_3 mode (of E symmetry), and where $\langle \Delta_{l_1}^{\lambda_1 \lambda_1'}(\Omega) \Delta_{l_2}^{\lambda_2 \lambda_2'}(\Omega) \rangle$ has to be computed with the orientational probability function $P_0(\Omega)$ appropriate for a molecule with C_{3v} symmetry located on a cubic site. This calculation has been done independently by us and by Sauvajol¹³ in his study of the Raman spectrum of cyanoadamantane. For the sake of completeness, the results

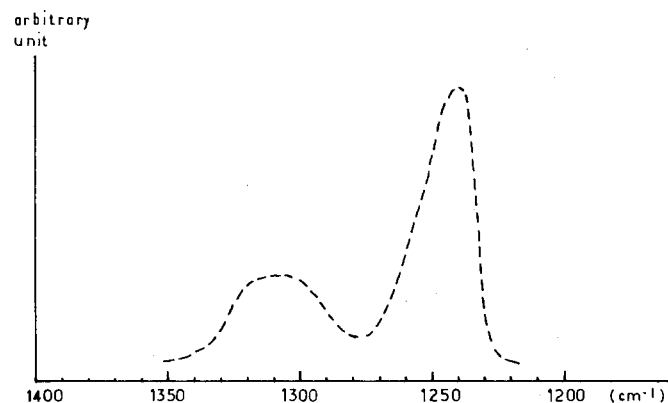


FIG. 3. Calculated OPDS for the ν_3 mode of CF_4 in the ODIC phase (reproduced from Ref. 3).

of this analysis are summarized in Table III. They show that, as expected, the ν_3 mode appears only in the E_g and the F_{2g} spectra, while the ν_1 mode appears in the three independent A_{1g} , E_g , and F_{2g} ones. Furthermore, the relative intensity depends on $P_0(\Omega)$, and Table III shows that one coefficient, A_{41} , of the development of $P_0(\Omega)$ in symmetrized Wigner functions can be measured by comparing the intensity of the E_g and the F_{2g} spectra of the ν_1 mode.

(4) The proposed method for discussing the Raman profile of the ν_1 and ν_3 modes of NF_3 is based on the decoupling approximation of the end of Sec. III. The validity of this approximation needs clearly to be checked by further calculations. This is the subject of a subsequent work which we are presently starting. Nevertheless, the usual Green's function method discussed in Sec. III B can be used in the case of short range forces, i.e., for non-IR active modes and short range forces of the atom-atom potential type. For typical plastic crystals such as neopentane or adamantane, this Green's function method can give an estimate for the vibrational contribution to the measured profile. Further work is also planned in this direction.

APPENDIX A

In order to transform the intermolecular interaction energy (2.1) in terms of monomolecular normal modes, two transformations must be done in turn. The first one transforms the vibrational amplitudes, described in the

TABLE III. Explicit formulas of the intensity of the Raman spectra of modes with A_1 and E symmetry, respectively, in a crystal with cubic symmetry (O_h), in terms of the molecular irreducible Raman tensors and of the coefficients of the pdf. Here the following notations are used: $B(\omega) = k_j^2 N [\sum_{qk} \delta(\omega - \omega_{qk})]$; $\epsilon_\mu = \epsilon_\mu(\nu_{\mu=2})$; $\epsilon'_\mu = \epsilon_{A_1}(l')$; $b = 21^{-1/2}$; $c = (\frac{2}{3})^{1/2}$. The first development constants of the pdf are $A_0 = A_0^{A_1 \nu_1}$; $A_1 = A_1^{A_1 \nu_1}$; $A_2 = A_2^{A_1 \nu_1}$. In the case of (A) A_1 symmetry, one obtains three independent spectra, R^{A_1} , R^{E_g} , and $R^{F_{2g}}$, while in the case of (B) E symmetry, there are only two independent spectra, R^{E_g} and $R^{F_{2g}}$.

(A) $j = A_1$

$$R^{A_1}(\omega) = 4\pi B(\omega) A_0 \epsilon_0^2$$

$$R^{E_g}(\omega) = \frac{4}{3} \pi B(\omega) [A_0 + b A_{41}] \epsilon_2^2$$

$$R^{F_{2g}}(\omega) = \frac{4}{3} \pi B(\omega) [A_0 - \frac{2}{3} b A_{41}] \epsilon_2^2$$

(B) $j = E$

$$R^{E_g}(\omega) = \frac{8}{3} \pi B(\omega) \{ (\epsilon_1^2 + \epsilon_2^2) A_0 + \frac{1}{6} b (-4\epsilon_1^2 + \epsilon_2^2) A_{41} + \frac{1}{3} c \epsilon_1 \epsilon_2 A_{42} \}$$

$$R^{F_{2g}}(\omega) = \frac{8}{3} \pi B(\omega) \{ (\epsilon_1^2 + \epsilon_2^2) A_0 - \frac{1}{6} b (-4\epsilon_1^2 + \epsilon_2^2) A_{41} - \frac{2}{3} c \epsilon_1 \epsilon_2 A_{42} \}$$

crystal axes, into those described in the molecular axes, and is just a simple three dimensional rotation (we suppress the index L which labels the different molecules, when we deal only with a single molecule)

$$U_S^A(\Omega) = T^{A\alpha}(\Omega)U_S^\alpha(\Omega), \quad (A1)$$

where $T^{A\alpha}(\Omega)$ is the transformation matrix and α is a direction in the molecular system.

The second transformation is that from these vibrational amplitudes to the vibrational normal modes of an individual, isolated molecule. We have the transformation equation

$$U_S^\alpha(\Omega) = \omega_S^{\alpha\Lambda} U^\Lambda(\Omega) \equiv \omega_{SN}^{\alpha j} U_N^j(\Omega), \quad (A2)$$

where the square matrix $\bar{\omega}$ is a unitary matrix, the elements of which are the projections of the normal mode Λ of the isolated molecule on $U_S^\alpha(\Omega)$.

Together, we finally have the following transformation for the normal amplitudes:

$$U_S^A(\Omega) = T^{A\alpha}(\Omega)\omega_S^{\alpha\Lambda} U^\Lambda(\Omega) \quad (A3)$$

and consequently, in this new basis, the interaction constant is written:

$$W_{12}^{A_1 A_2}(\Omega_1, \Omega_2) = \omega_{S_1}^{\alpha_1 \Lambda_1} T^{A_1 \alpha_1}(\Omega_1) W_{S_1 S_2}^{A_1 A_2}(\Omega_1, \Omega_2) \times T^{A_2 \alpha_2}(\Omega_2) \omega_{S_2}^{\alpha_2 \Lambda_2}. \quad (A4)$$

APPENDIX B: DEVELOPMENT OF THE ID-ID INTERACTION IN A SYMMETRY ADAPTED BASIS

The usual formula for the dipole-dipole interaction constant between molecules 1 and 2 is

$$W_{12}^{A_1 A_2}(\Omega_1, \Omega_2) = \frac{r_{12}^2 [\mathbf{P}^{A_1} \cdot \mathbf{P}^{A_2}] - 3[\mathbf{r}_{12} \cdot \mathbf{P}^{A_1}][\mathbf{r}_{12} \cdot \mathbf{P}^{A_2}]}{r_{12}^5}, \quad (B1)$$

where $\mathbf{P}^{A_i} = (\partial \mathbf{P}_i / \partial U_i^{A_i})$ is the derivative of the dipole moment with respect to the A_i -normal coordinate of the molecule i and \mathbf{r}_{12} is the distance between molecules 1 and 2.

In order to develop the interaction energy in a basis of functions $\Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_1) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_2)$, we make the following remarks:

(i) Molecular symmetry adapted harmonics $\mathcal{M}_{\Lambda}(\hat{\mathbf{r}})$ and site symmetry adapted harmonics $S_{\Lambda}(\hat{\mathbf{r}})$ (which are both surface harmonics derived and classified by Cracknell and Bradley¹⁴ transform one into the other through formulas derived from the usual Wigner matrices.

$$\mathcal{M}_{\Lambda}(\hat{\mathbf{r}}) = \Delta_l^{\lambda \lambda^*}(\Omega) S_{\Lambda}(\hat{\mathbf{r}}) \quad (B2a)$$

and

$$S_{\Lambda}(\hat{\mathbf{r}}) = \Delta_l^{\lambda \lambda^*}(\Omega) \mathcal{M}_{\Lambda}(\hat{\mathbf{r}}), \quad (B2b)$$

where $\hat{\mathbf{r}}$ describes a unit vector pointing in a given direction in the molecular system and $\hat{\mathbf{r}}$ describes the same unit vector, as seen in the site system.

(ii) An arbitrary vector \mathbf{x} can be expressed by its $l = 1$ symmetry adapted components which are given by

$$x_{\lambda} = \frac{4\pi}{3} |\mathbf{x}| \cdot S_{1\lambda}(\hat{\mathbf{x}}) \quad (B3)$$

or

$$x'_{\lambda} = \frac{4\pi}{3} |\mathbf{x}| \cdot \mathcal{M}_{1\lambda}(\hat{\mathbf{x}}). \quad (B4)$$

Let us use here the site symmetry adapted components of the following vectors:

$$(\mathbf{r}_{12})_{\lambda} = \frac{4\pi}{3} r_{12} \cdot S_{1\lambda}(\hat{\mathbf{r}}_{12}), \quad (B5)$$

$$(\mathbf{P}^A)_{\lambda} = \frac{4\pi}{3} P^A \cdot S_{1\lambda}(\hat{\mathbf{P}}^A) \quad (B6)$$

as well as their molecular symmetry adapted components.

(iii) We are here interested in the ID-ID interaction between two molecules vibrating in the same mode. For that particular mode, the molecular axes can always be chosen in such a way that the direction of one of them coincides with the induced dipole, if the mode is not degenerate, and their directions coincide with that of the induced dipoles, if the mode is degenerate (cf. the case of an E mode for a molecule with C_{4v} symmetry). With such a choice of molecular axes, if the internal mode is labeled by $\Lambda \equiv (j, N)$, we have the relation

$$\mathcal{M}_{1\lambda}(\hat{\mathbf{P}}^A) = \sqrt{\frac{3}{4\pi}} \delta_{\Lambda\Lambda'}. \quad (B7)$$

[It is possible that the representation is complex (cf. the case of an E mode for a molecule with C_{3v} symmetry). Nevertheless, in such a case the two complex conjugate representations correspond to the same eigenfrequency of the molecule; they can always be combined into a real twofold degenerate representation, physically irreducible, and for which Eq. (B7) still holds.]

With the remarks, the development of the dipole-dipole interaction energy follows immediately. Inserting Eqs. (B5) and (B6) into Eq. (B1) and applying Eqs. (B2) and (B7) leads to

$$W_{12}^{A_1 A_2}(\Omega_1, \Omega_2) = \frac{P^{A_1} P^{A_2}}{r_{12}^3} \sum_{\substack{\lambda_1 \lambda_2 \\ \lambda_1' \lambda_2'}} \{ \delta_{\lambda_1 \lambda_2} - 4\pi S_{1\lambda_1}^*(\hat{\mathbf{r}}) S_{1\lambda_2}(\hat{\mathbf{r}}) \} \times \delta_{\lambda_1 A_1} \delta_{\lambda_2 A_2} \Delta_{l_1}^{\lambda_1 \lambda_1^*}(\Omega_1) \Delta_{l_2}^{\lambda_2 \lambda_2^*}(\Omega_2). \quad (B8)$$

Comparison with Eq. (2.11) and identification of the particular terms finally gives Eqs. (3.7) and (3.8).

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