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Induced dipole–induced dipole interaction: A numerical calculation

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We present the results of a numerical study of the effects of the induced dipole–induced dipole interaction on the line shape of the internal v_1 and v_3 modes of NF_3 in the plastic phase. Comparisons are made both with the experiment and with the results of a previous theoretical analysis of the effect.

INTRODUCTION

This paper stands as the direct continuation of a theoretical paper (Ref. 1) where we interpreted the unusual broadening of certain Raman lines of a plastic crystal. In fact, Ref. 1 relied on a crude approximation which could not be either avoided or justified by means of rigorous theoretical considerations. We have thus decided to test this approximation by carrying out a numerical calculation on a simple model, which will be presented in this paper after a brief summary of the main results of Ref. 1.

The Raman modes explicitly considered in Ref. 1 were the v_1 and v_3 modes of NF_3, which are very broad and have an asymmetric line shape with two unequal maxima. These characteristics are due to the strong induced dipole–induced dipole (IR–IR) interaction which exists for both modes. The line shape was, in fact, interpreted by the experimentalists[2] as the usual LO–TO, $q = 0$ splitting occurring in ordered crystals, here broadened by the orientational disorder. It was shown in Refs. 1 and 3 that, owing to the orientational disorder, the $q = 0$ selection rule which usually occurs for the Raman spectra of a crystal is no longer valid when the latter is in a plastic phase, and that all the phonons of the whole Brillouin zone contribute to the Raman spectrum (incoherent diffusion). It can then be shown that under omission of spatial orientational correlations between the crystal molecules, the spectra under study are proportional to the one phonon density of states (OPDS).

In order to calculate theoretically this OPDS for an arbitrary mode, we introduced in Ref. 1, for each molecule, a transformation from the internal vibrational normal mode under consideration, described in the molecular axes, to a suitable, threefold degenerate mode, described in the crystal axes. This method has already been used implicitly by Yvinec and Pick[3] for the interpretation of the Raman profile of the threefold degenerate v_3 mode of CF_4. In their case, since they projected a threefold degenerate mode onto another threefold degenerate mode, the method was exact, the transformation unitary, and the new dynamical variables were also a set of normal variables. For a doubly degenerate or a simple mode this is no longer true, since, for each molecule, two (respectively, one) variables are projected onto three variables, inducing one (respectively, two) relation(s) between them. The essential, abovementioned approximation proposed in Ref. 1 consisted of neglecting these relations between the new variables, i.e., in artificially increasing the number of degrees of freedom by a factor 3/2 in the case of a twofold degenerate mode and by a factor 3 in the case of a simple mode. In other words, the OPDS of these modes was by virtue of the used decoupling scheme the same as that of the threefold degenerate one. The fact that the minimum of the Raman lines of the v_1 and the v_3 mode of NF_3 is shallower than that of the line of the v_3 mode of CF_4, was interpreted as a consequence of the fact that their respective dipole moments and thus their splitting, were smaller and that, therefore, reorientational effects which broaden the line shape had a greater relative importance.

The main problem related to the results of Ref. 1, is the validity of the applied decoupling approximation. To answer it, we have constructed a model which is a simplification of the NF_3 crystal in the plastic phase. Each NF_3 molecule of this model is schematized either by one dipole or by two perpendicular dipoles, which allow to simulate once at a time, the vibrational dynamics of a strongly infrared active mode, respectively, either the simple v_1 or the doubly degenerate v_3 mode. We have calculated the OPDS for three orientational distributions in the case of the v_1 mode and for a single one in the case of the v_3 mode. The results show that the computed spectra are in much better agreement with the experimental spectra than those deduced from the crude approximation made in Ref. 1. The latter proposed that the line shape was independent of the degeneracy of the mode. Though this is a reasonable first-order approximation, the present calculation indicates that the details of this line shape depend on this degeneracy, but practically not on the molecular orientational probability. This fact suggests that there must be a better approximation than that one used in Ref. 1. The results sketched in this paragraph will be discussed in detail in Sec. III while Sec. II is devoted to a description of the constructed crystal model.

II. THE MODEL

The object of this section is to construct a simple model of a NF_3 crystal in its plastic phase, in view of reproducing as well as possible the OPDS of either the molecular v_1 or the molecular v_3 mode of the real crystal. For that purpose, one can make two important simplifications. The first is the molecular glass approximation, which we already used in Ref. 1 for the theoretical interpretation of the Raman spectra of the v_1 and v_3 modes of NF_3. It consists in fixing the molecular orientation of each molecule at some arbitrary instantaneous value. This is justified, since the broadening of the OPDS due to the vibrational interaction is much larger than the broad-

ening due to the molecular reorientational motion.

In order to elucidate the second simplification, we write down the pair interaction energy E of the crystal in terms of internal molecular vibrational normal coordinates, as in Ref. 1:

$$E = \sum_{\substack{jj' \\ nn' \\ LL'}} U_{n\,L}^{j*} \, W_{n\,n'\,L_{L'}}^{j\,j'} \, U_{n'\,L'}^{j'}. \tag{2.1}$$

Here,

j stands for the different internal molecular normal modes,

n labels the independent coordinates if j is a degenerate mode,

L designates the different molecules,

$U_{n\,L}^{j}$ is the (j,n) normal coordinate of the molecule L, and

$W_{n\,n'\,L_{L'}}^{j\,j'}$ the interaction constant of the (j,n) coordinate of the molecule L and the $(j'n')$ coordinate of the molecule L'.

We recall, that the interaction between a normal mode of a certain molecule and another normal mode of another molecule has a much smaller effect than the interaction between the same modes of the two molecules (Ref. 1). Therefore, we can by neglecting the $j \neq j'$ cross terms in Eq. (2.1), split the whole interaction energy E in a sum of contributions E_j:

$$E = \sum_{j} E_j, \tag{2.2}$$

where E_j is the interaction energy of the vibrational normal coordinates (j,n) of all the molecules of the crystal:

$$E_j = \tfrac{1}{2} \sum_{\substack{nn' \\ LL'}} U_{n\,L}^{j*} \, W_{n\,L\,n'\,L'}^{(j)} \, U_{n'\,L'}^{j}. \tag{2.3}$$

As we only deal with one given normal mode j, it is sufficient to model only those features of the crystal which affect the interaction energy E_j of the mode considered. Since, further, we deal with a dipole–dipole interaction, and since the electronic shells of the atoms of the NF_3 molecule are not deformed very much during the vibration, we can represent a molecule simply as a point dipole in the case of a single mode, and as two perpendicular dipoles in the case of a doubly degenerate mode (one dipole per normal coordinate). Then, the interaction constant for $L \neq L'$ is the second derivative of the dipole–dipole interaction energy with respect to the corresponding normal coordinates (for the sake of simplicity we shall suppress the subscript j in the rest of this paper):

$$W_{LL'}^{nn'} = \frac{r_{LL'}^2 \cdot (\mathbf{p}_L^n \mathbf{p}_{L'}^{n'}) - 3 \cdot (\mathbf{r}_{LL'} \cdot \mathbf{p}_L^n)(\mathbf{r}_{LL'} \cdot \mathbf{p}_{L'}^{n'})}{r_{LL'}^5}, \tag{2.4}$$

where

$$\mathbf{p}_L^n = \frac{d\,\mathbf{P}_L^n}{d U_L^n}, \tag{2.5}$$

$\mathbf{P}_L^n$ being the dipole moment corresponding to the n nor-

mal coordinate of the L molecule and $\mathbf{r}_{LL'}$, the vector joining the molecules L and L'.

For the $L = L'$ term of the interaction constant, we have

$$W_{LL}^{nn'} = \omega_0^2 \delta_{nn'}, \tag{2.6}$$

where ω_0 is the unperturbed frequency of the corresponding normal mode. So, inserting Eqs. (2.4) and (2.6) into Eq. (2.3) and taking into account the kinetic energy term $1/2(\dot{U}_L^n)^2$ per normal coordinate, the Lagrangian of our model reads

$$L = \tfrac{1}{2} \sum_{n,L} (\dot{U}_L^n)^2 - \tfrac{1}{2} \sum_{\substack{nn' \\ LL'}} U_L^{n*} W_{LL'}^{nn'} U_{L'}^{n'}, \tag{2.7}$$

from which the dynamical equations follow immediately as

$$\ddot{U}_L^n = - \sum_{n'L'} W_{LL'}^{nn'} U_{L'}^{n'}$$

$$= -\omega_0^2 U_L^n$$

$$- \sum_{L' \neq L} \sum_{n'} \frac{r_{LL'}^2 \cdot (\mathbf{p}_L^n \mathbf{p}_{L'}^{n'} - 3 \cdot (\mathbf{r}_{LL} \cdot \mathbf{p}_L^n)(\mathbf{r}_{LL'} \cdot \mathbf{p}_{L'}^{n'})}{r_{LL'}^5} \cdot U_{L'}^{n'}. \tag{2.8}$$

These represent the equations of motion of a system of identical, coupled harmonic oscillators.

The principal characteristics of plastic crystals are related to their orientational disorder which we want to model as close as possible to reality. If one neglects any orientational correlation (which are of little importance, because of the existence of a long-range interaction), the orientational disorder can be completely described by an appropriate probability density function (PDF) which may be developed onto a basis of symmetry adapted rotator functions,[4] which are the so-called modified Wigner functions $\Delta_l^{\lambda\lambda'}(\Omega)$:

$$P(\Omega) = \sum_{l\lambda\lambda'} A_l^{\lambda\lambda'} \cdot \Delta_l^{\lambda\lambda'}(\Omega). \tag{2.9}$$

These functions have been introduced by Press and Hüller (Ref. 4) and by Yvinec and Pick (Ref. 5). Here, we only repeat those properties, which are of interest in our case. First, we may remark that since either a dipole or the normal to a dipole plane is a one-dimensional object, the orientation of which can be described by the two spherical angles (Θ,ϕ), the harmonic rotator functions $\Delta_l^{\lambda\lambda'}(\Omega)$ in Eq. (2.9) reduce immediately to surface harmonics $S_l^\lambda(\Theta,\phi)$ adapted to the symmetry of the molecular site:

$$P(\Omega) = \sum_{l\lambda} A_l^\lambda \cdot S_l^\lambda(\Theta,\phi), \tag{2.10}$$

where λ is a composite index which contains, *inter alia*, the name of a representation of the symmetry group of the molecular site. One can then show that nonzero coefficients A_l^λ can only arise, if the corresponding surface harmonics are in the identity representation of this site symmetry group.

Now, in its plastic phase, NF_3 is a cubic crystal, the site symmetry group of which is O_h. For such a group, in the lowest orders, there arises one coefficient at a time for $l = 0$, 4, and 6. We will here limit ourselves to the $l = 0$ and the $l = 4$ terms. Then, the development, now written in Cartesian coordinates of the unity vector $\hat{\mathbf{r}} = (x, y, z)$, becomes

explicitly

$$P(\hat{r}) = \frac{1}{4\pi} + A_4(x^4 + y^4 + z_4 - 0.6), \qquad (2.11)$$

where A_0 ($= 1/4\pi$) is fixed by the normalization condition $\int P(\Omega)d\Omega = 1$ and where the range of values of A_4 is limited by the condition that the PDF must not be negative.

In the present calculation, the orientations of the dipoles (or of the normal to the dipole plane) were, for each case, chosen to be a random distribution compatible with Eq. (2.11) for a given value of A_4. This was achieved by generating this distribution by a Markovian process described in Ref. 6. In the case of the v_1 mode, three different calculations were performed, choosing A_4 to be either 0, or to have the maximum value compatible with $P(\hat{r}) > 0(A_4 = 15/16\pi)$, or its minimum value compatible with the same condition $(A_4 = -5/8\pi)$. The second case corresponds to a distribution with pronounced maxima pointing in the directions of the fourfold axes, while the last one corresponds to maxima pointing along the eight threefold axes. For the v_3 mode, we only treated the case where the normal to the dipole planes pointed in the directions of the threefold axes.

The eigenvalues of our model system were computed by diagonalizing the dynamical matrix $W_{LL'}^{nn'}$, of Eq. (2.8), the dimension of which is equal to the number of degrees of freedom of the system. The maximum size of this matrix depends on the memory size and the computing speed of the used computer. We have chosen a size of $5 \times 5 \times 5$ cubic unit cells, the centers of charge of the molecules forming an fcc Bravais lattice, (which is the most probable for the NF_3 crystal in its plastic phase, even if a bcc Bravais lattice cannot be excluded with absolute certainty) with Born–van Karman boundary conditions. Thus, the system has 500 degrees of freedom for the v_1 and 1000 degrees of freedom for the v_3 mode, which was about the limit of what can be solved in this way.

The numerical calculations were performed on a CRAY I computer with 1 Mwords central memory. For the matrix diagonalization, we have used the Eispack subroutines, in detail the Householder transformation, to transform the original, symmetric matrix to tridiagonal form with subsequent complete diagonalization by the use of the QR algorithm (Ref. 7). The original matrix is well conditioned and we had no problems with the numerical precision. As a test, with a completely ordered system, the degenerate eigenvalues were found to be equal up to the tenth decimal. In fact the output of the computation was an OPDS. As long as the induced dipole–induced dipole interaction (2.4) is a perturbation with respect to the intramolecular term (2.6), the *relative* width of the OPDS which can be deduced from Eq. (2.8) depends only on $p^2/(d^3\omega_0^2)$ where d is the length of the fcc lattice unit cell. In the present calculation we thus used arbitrary values ($\omega_0 = 2\pi$, $p = 1$, and $d = 2$) which ensured the perturbation approximation to be valid. The comparison with experiment was then made by first fixing ω_0, and then using the gas phase value of p, and the value of d obtained from density measurements.
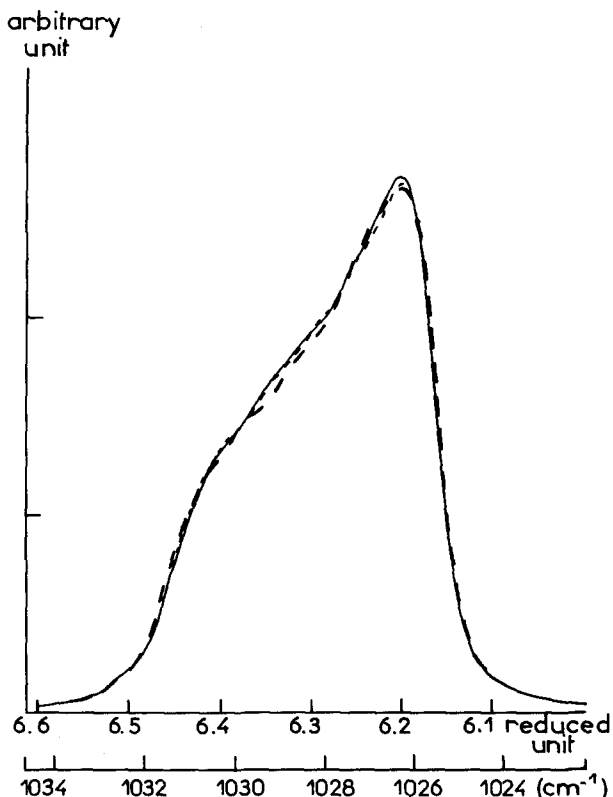

FIG. 1. Calculated OPDS of the simple mode (v_1 mode of NF_3). The different lines correspond to different orientational distribution functions. (a) ⋯: Complete disorder. (b) ---: Maxima of the PDF parallel to the fourfold crystal axes. (c)—: Maxima of the PDF parallel to the threefold crystal axes.
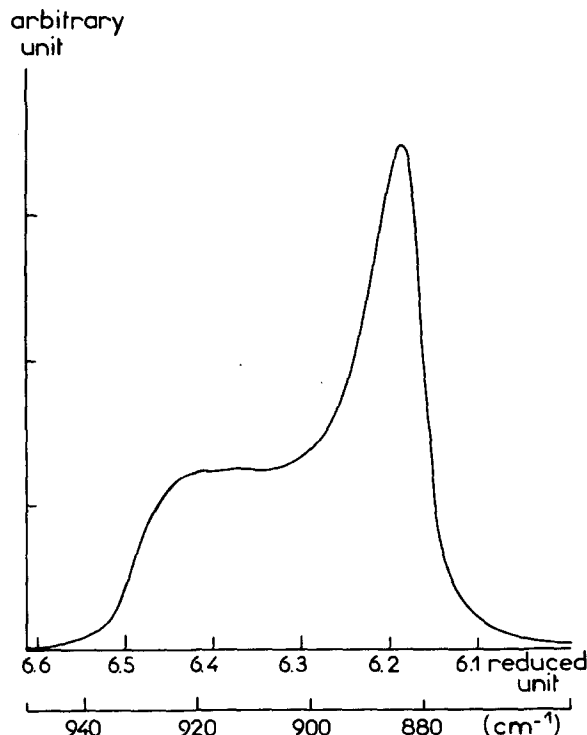

FIG. 2. Calculated OPDS of the doubly degenerate mode (v_3 mode of NF_3).

TABLE I. Comparison of measured and calculated width of the v_1 and v_3 line of NF_3. The last column gives the distance between the two maxima if the OPDS is computed with the value of the dipole moment given in Ref. 8.

Normal mode	Degeneracy	Width of the different spectra in cm^{-1}			
		Measured in Ref. 2	Calculated in Ref. 2	Calculated in Ref. 1	Calculated in this paper
v_1	1	6	3.85	9.25	4.0
v_3	2	46	52	62.5	40

III. DISCUSSION OF THE RESULTS

The decoupling approximation of Ref. 1 would be completely justified, if the shape of the calculated OPDS would not depend on the degeneracy of the treated mode and if the width of the OPDS would be in agreement with experiment. In fact, the results obtained in our calculation are much less simple to interpret. They are shown in Figs. 1 and 2, after convolution with an appropriate Lorentzian with HWHM of 0.5 cm^{-1} for the v_1 mode and of 2.5 cm^{-1} for the v_3 mode. These HWHM were chosen in order to give a good agreement with the experimental line shape; they have various origins, such as rotational contribution, intraanharmonic effects, etc., and have no reasons to be the same for the two modes.

Let us first discuss the relationship between our results and the experimental ones (Ref. 2). In the one-dimensional case (v_1 mode) the calculated OPDS (Fig. 1) reproduces very well the measured line shape up to a scaling factor: if we use the reported value[8] for the induced dipole moment, the distance between the two maxima is about 30% too small (Table I). (Even if a real high frequency maximum cannot be defined properly, for sake of comparison, we speak about a distance between maxima as in Ref. 2.) It seems that there are two possible explanations for this discrepancy: either additional effects which are not included in our model are responsible for the larger width of the measured spectra or, what is more likely since the shape of the measured and the calculated spectra are in so good agreement, this reported value of the induced dipole moment of the v_1 mode of NF_3 is too low (Fig. 3).

The situation in the two-dimensional case is quite different: the width of the spectrum is in good agreement with experiment (Table I), but the line shape is somewhat different: between the high frequency and the low frequency maximum, there appears in the experiment (Fig. 4) a small, poorly defined additional peak, not reproduced by our calculation. The origin of this additional line is not clear. It is presumably related to hot band effects (such as $v_3 + v_2 - v_2$) as Gilbert et al. reported the same effects on the v_4 line, for instance. Nevertheless, no precise assignment can be made, because there exists a negative frequency shift of 8 cm^{-1} of the bare frequency ω_0 with respect to its free molecule value. [For the zero frequency ω_0, the condition $\int \omega \rho(\omega + \omega_0)d\omega = 0$ with the OPDS $\rho(\omega)$ must be fulfilled.] As all the pertinent data on these anharmonic effects are related to the free molecule, there exists no possibility of properly describing such effects in the plastic phase.

Let us now proceed to the comparison of the results of this paper with the theoretical predictions of Ref. 1, where we postulated that neither the shape nor the width of the OPDS would depend on the degeneracy of the treated mode. Comparing the different results (before convolution, Table II), we can conclude that though there is a slight decrease of the width with smaller degeneracy, the maximum width of the OPDS calculated here and in Ref. 1 are in rather good agreement. As far as shape is concerned, the agreement is not as good (Figs. 1, 2, and 5), and the evaluation of the line shape with decreasing degeneracy can be described as follows.

In the three-dimensional case, the area under the low frequency part is the double of the area under the high frequency part. Simultaneously, the distance from the low frequency maximum to the unperturbed frequency ω_0 is half the distance from the high frequency maximum to ω_0, and therefore the "center of mass" of the OPDS does not change. (This follows directly from the fact, that the ID–ID interac-
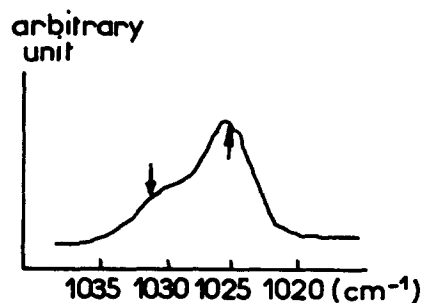
arbitrary
unit

1035 1030 1025 1020 (cm^{-1})

FIG. 3. Raman line shape of the v_1 mode of NF_3 in the plastic phase. (Reproduced from Ref. 2.)

arbitrary
unit

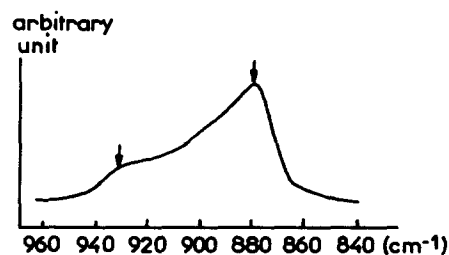960 940 920 900 880 860 840 (cm^{-1})

FIG. 4. Raman line shape of the v_3 mode of NF_3 in the plastic phase. (Reproduced from Ref. 2.)

TABLE II. Comparison of the width of the calculated OPDS for different modes.

Degeneracy of the mode	Width in reduced units	Theoretical width as calculated in Ref. 1
3	0.50	0.5
2	0.45	0.5
1	0.37	0.5

tion does not change the trace of the dynamical matrix.) When the degeneracy diminishes, the width of the OPDS decreases only a little, but the minimum between the two maxima becomes shallower and shallower so that, finally, in the nondegenerate case, one cannot speak any longer about two maxima at all. Simultaneously, the ratio between the low frequency area and the high frequency area changes also: it is 1/3:2/3 for a threefold degenerate mode, 0.6:0.4 for a doubly degenerate mode and approximately 0.5:0.5 for a simple mode.

A qualitative explanation of this behavior goes as follows: in a cubic crystal, a threefold degenerate, strongly infrared active internal mode has the same vibrational dynamics in the plastic phase as in the ordered phase (Ref. 3). The corresponding crystal normal modes are thus optical phonons, which are either quasilongitudinal or quasitransverse. Since the frequency of a longitudinal phonon is higher than or equal to the frequency of a transverse phonon, there arises a pronounced minimum in the OPDS. Furthermore, since there are twice as many TO phonons than LO phonons, the ratio of the corresponding areas must be 2:1.

Now, in the two-dimensional case, one can still define one transverse phonon for each wave vector q, but the other phonon is neither longitudinal nor transverse. This fact reflects itself in the shape of the OPDS, since the low frequency part has still a high maximum, while the maximum of the high frequency part becomes a broad shoulder. In the nondegenerate case, finally, there are in general neither LO nor TO phonons. Correspondingly, the minimum has completely disappeared, while it still remains an unsymmetric line shape.

Finally, we note that we cannot find any dependency of the OPDS on the PDF of the crystal. But there is a great difference between the shape of the OPDS of a plastic crystal (Fig. 1) and that of an ordered one (cf. Fig. 6) where we have shown the same OPDS for the case where all the dipoles would be aligned along the x axis. (The site symmetry remains fcc. Though this is not a physically possible but a theoretically constructed case, it reveals clearly the influence of orientational disorder on the OPDS.) The shape of the OPDS is thus a definite characteristic of the absence of orientational correlation between the dipoles, but is not sensitive to the distribution of the molecular orientations in the crystal.

The approximation proposed in Ref. 1 could not be expected to give a density of states in complete agreement with that of a model crystal with an uncorrelated orientational disorder. We have shown in this paper that this approximation yields results which are not too far from those obtained with an exact calculation starting from the same hypotheses. It is thus a valuable first step in constructing an exact theory of the actual line shape, and the lack of sensitivity of the OPDS to the details of the PDF is, in this respect, a reward-
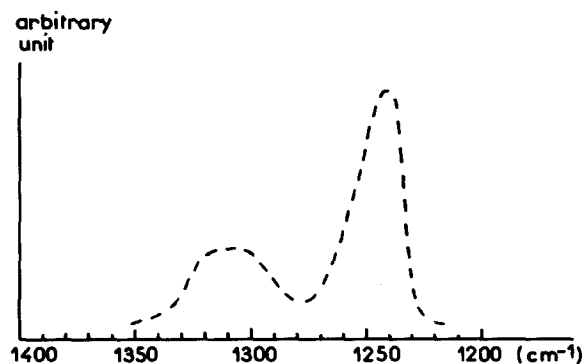

FIG. 5. Calculated OPDS of the threefold degenerate mode (ν_3 mode of CF_4). (Reproduced from Ref. 3.)
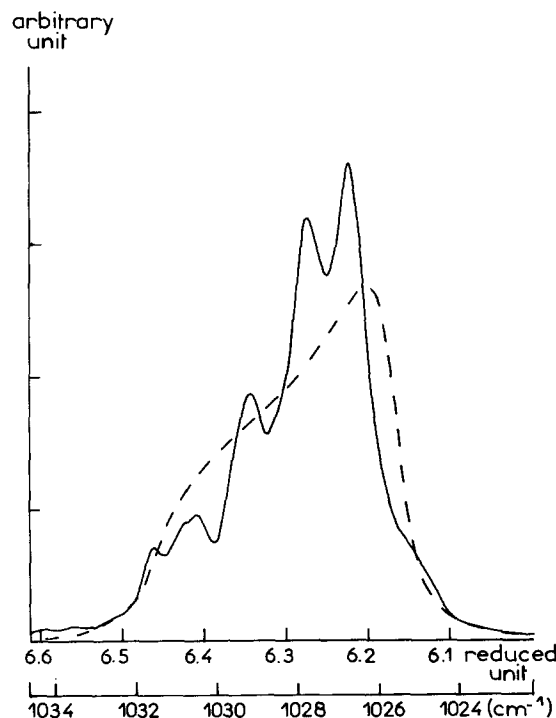

FIG. 6. OPDS of the simple mode in the case of a completely ordered crystal (all the dipoles point in the direction of the crystal x axis). The dotted line is an average of the three cases shown in Fig. 1.

ing result; it suggests that any method which would take, even partially, into account the relationship between dependent variables which have been taken in Ref. 1 to be independent, would improve upon our first theoretical results. Research along these lines is presently in progress.

ACKNOWLEDGMENT

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